ESR 1: Control of Hydrates

Mid-Term Project Review Meeting
Accademia delle Scienze dell'Istituto di Bologna
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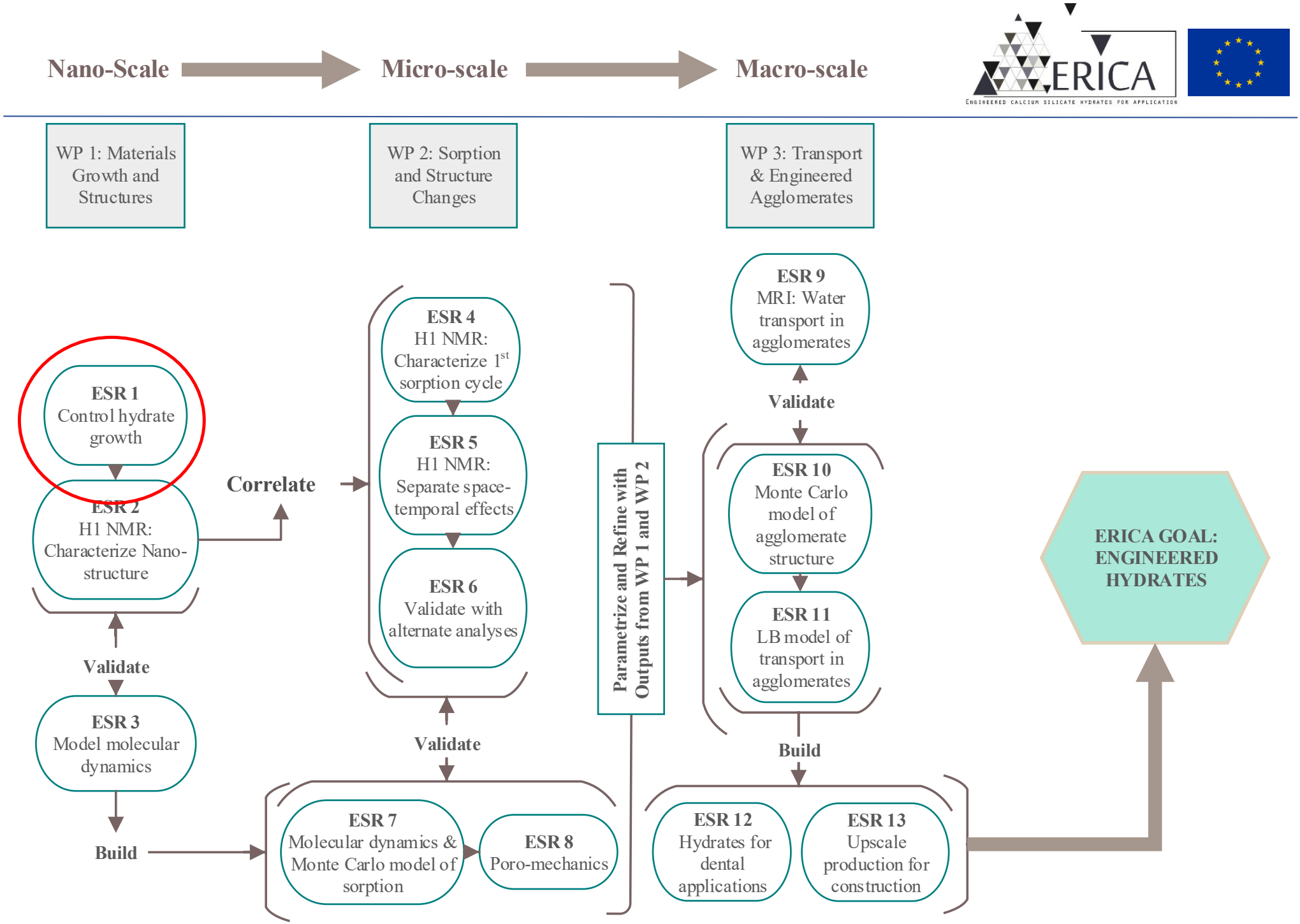
Swiss Federal Institute of Technology (EPFL)


Nano-Scale
Micro-scale
Macro-scale
WP 1: Materials Growth and Structures
WP 2: Sorption and Structure Changes
WP 3: Transport & Engineered Agglomerates
ESR 1 Control hydrate growth
ESR 2 H1 NMR: Characterize Nano-structure
Validate
ESR 3 Model molecular dynamics
Build
Correlate
ESR 4 H1 NMR: Characterize 1st sorption cycle
ESR 5 H1 NMR: Separate space-temporal effects
ESR 6 Validate with alternate analyses
Validate
ESR 7 Molecular dynamics & Monte Carlo model of sorption
ESR 8 Poro-mechanics
Parametrize and Refine with Outputs from WP 1 and WP 2
ESR 9 MRI: Water transport in agglomerates
Validate
ESR 10 Monte Carlo model of agglomerate structure
ESR 11 LB model of transport in agglomerates
Build
ESR 12 Hydrates for dental applications
ESR 13 Upscale production for construction
ERICA GOAL: ENGINEERED HYDRATES

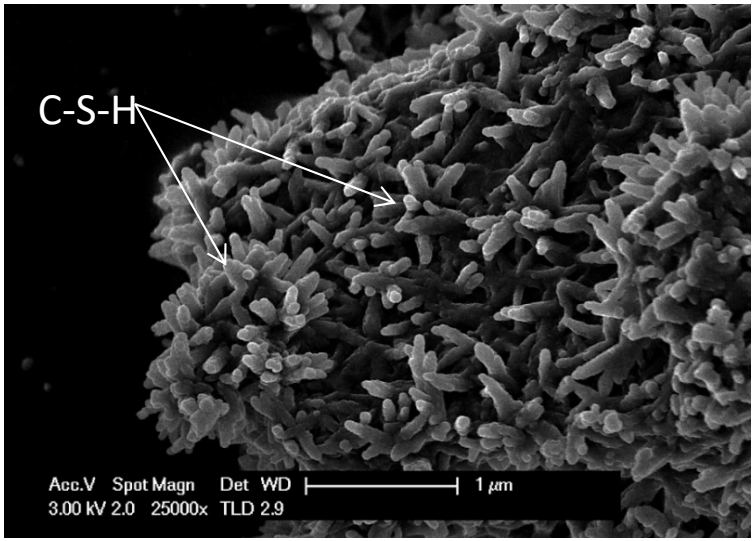
Introduction
What is C-S-H?

- **Cement is a very complex system! It can be composed of 8-10 phases.**

Impure Alite + water → **C-S-H** + portlandite + heat

$$C_3S + H \rightarrow \boldsymbol{C\text{—}S\text{—}H} + CH \quad \Delta H = 502\ kJ/kg$$

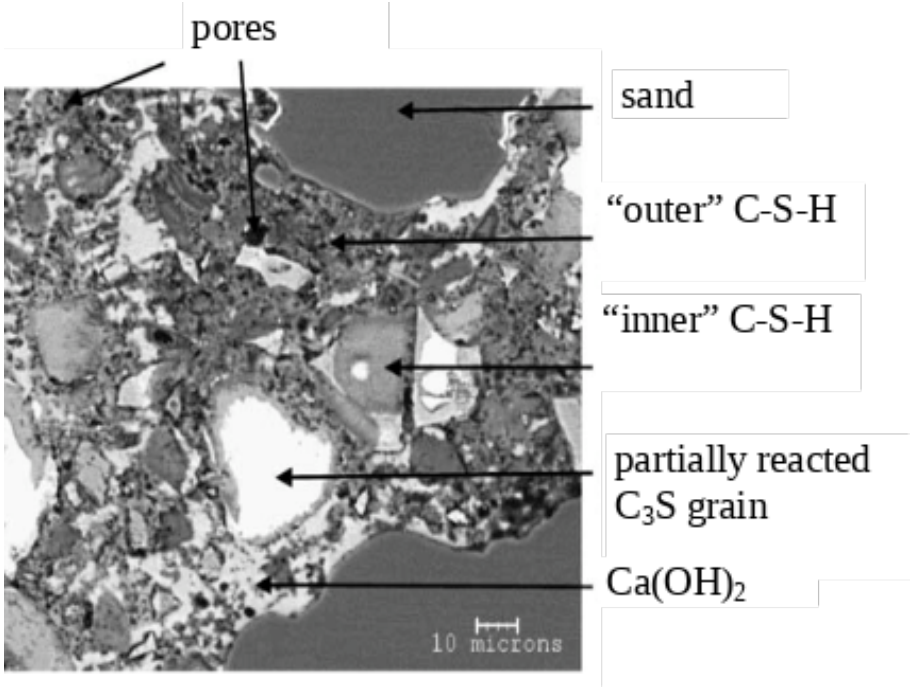
- C-S-H composes **50-60%** of hardened cement paste by volume
- Study of calcium silicate hydrate (C-S-H) gives information on growth mechanism of main hydration phase



**SEM - Ca_3SiO_5 hydration stopped at 6h*

Mohamed, Master Thesis, 2014

- C-S-H has a variable stoichiometry
  - Variable water content
  - Ca:Si ratio varies from 1.2 to 2.1
  - Portland cement shows Ca:Si molar ratios near 1.75, but C-S-H is not uniform

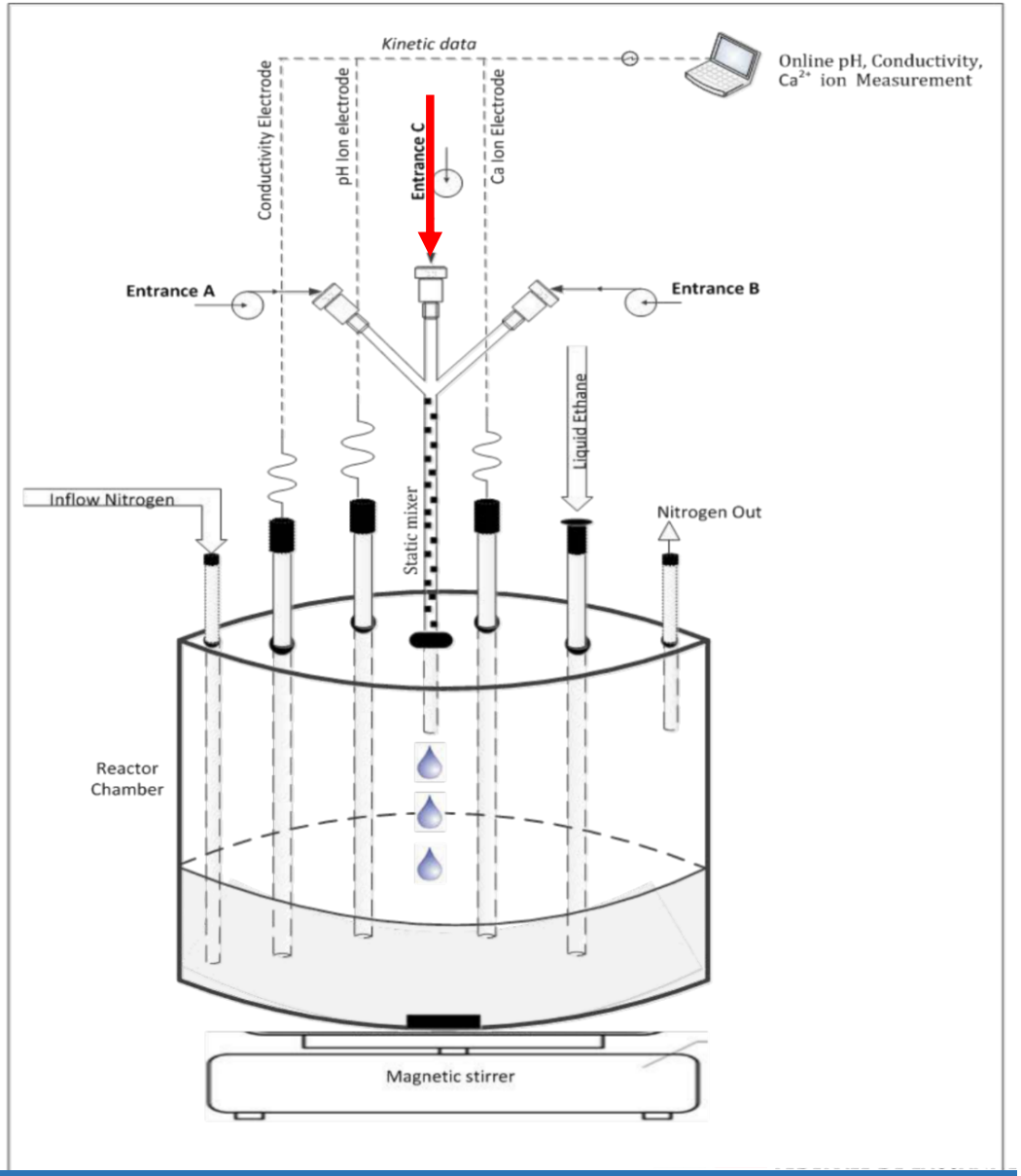


C-S-H in cement is difficult to characterize experimentally.

Synthetic C-S-H

Synthetic C-S-H: Dropwise Method

- Precipitation by adding **calcium nitrate** (100-200 mL) at (2mL/min) to
- **sodium silicate** (100-200 mL)
- Controlled N2 atmosphere
  - pH regulator added
  - System purged 30 mins with N_2 before synthesis
  - 1 liter reactor
- High mixing maintained
- Kinetics & pH by *in-situ* monitoring

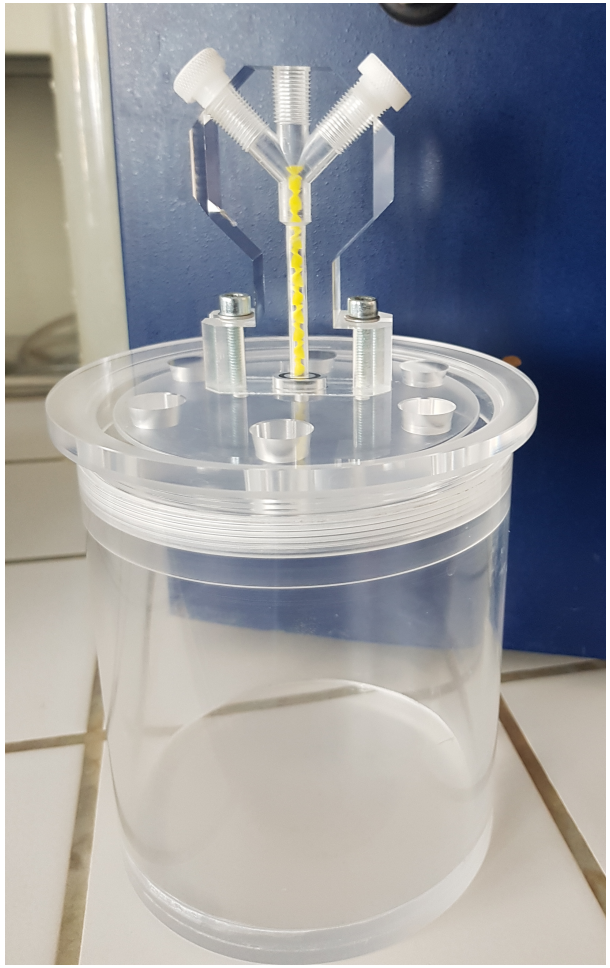


J. Phys. Chem. C, 17188-17196, 2017

Synthetic C-S-H: Post-Synthesis

- Washed with 50/50 pure water & ethanol
- Collected as damp cake
- 24 hours in -80 ℃ freezer
- 24 hours in freeze dryer

- Characterized by XRD, TGA, ICP-OES, TEM, and SEM



- *A. Kumar et al. 2017 ,"The Atomic-level structure of cementitious calcium silicate hydrate" J. Phys Chem C. (2017) 17188-17196*

Synthetic C-S-H: Conditions

Thermodynamic modelling (GEMS)*

Predictions for precipitation conditions

- Temperature range: 19-20 °C

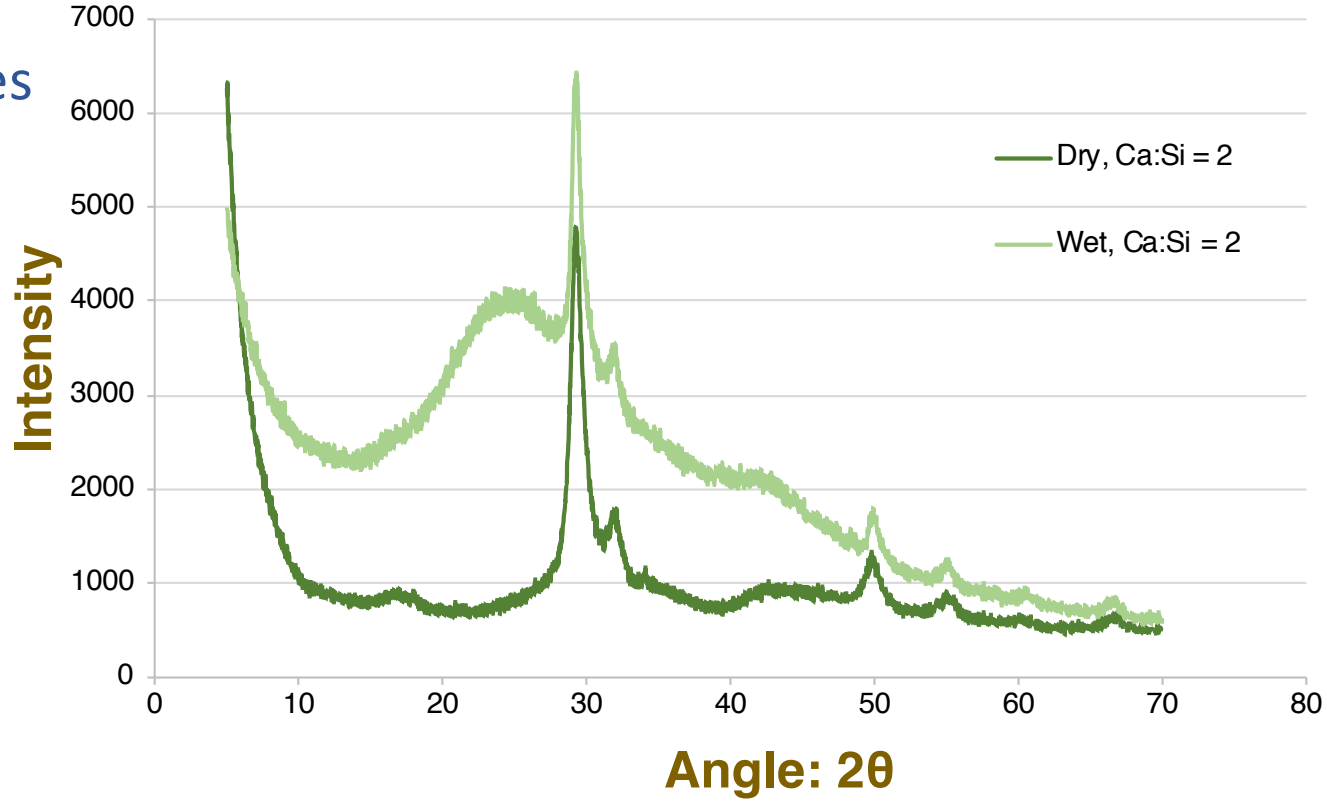
Ca:Si	10 M NaOH (GEMS)	pH (GEMS)
1	75 µL	11.4
1.25	675 µL	11.9
1.5	1.675 mL	12.5
1.75	3.475 mL	12.9
2	10 mL	13.5

**For 200 mL total volume*

- *Gibbs Energy Minimisation Software, D. Kulik, CCR, 41 (2011) 477–495*

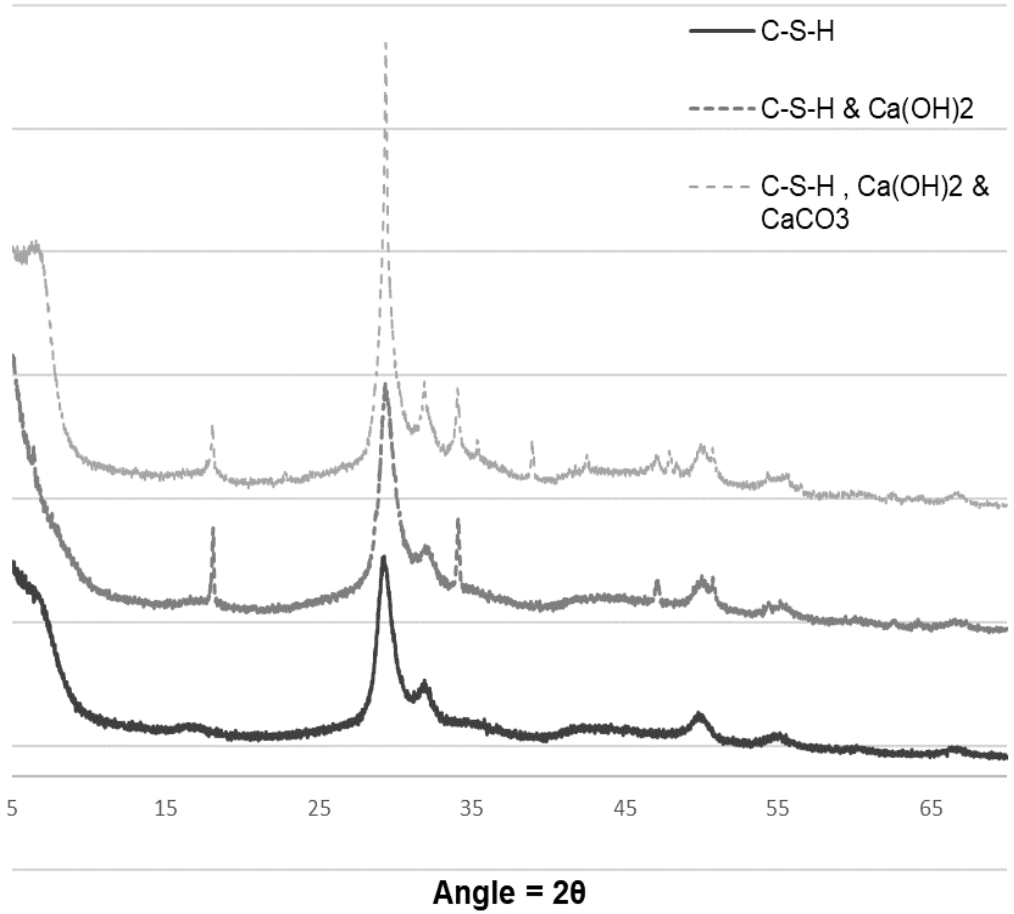
Results

80% of 70 samples showed no impurities in synthesis



Wet and dry XRD diffractogram of Ca:Si = 2 synthetic C-S-H displaying intrinsic peaks

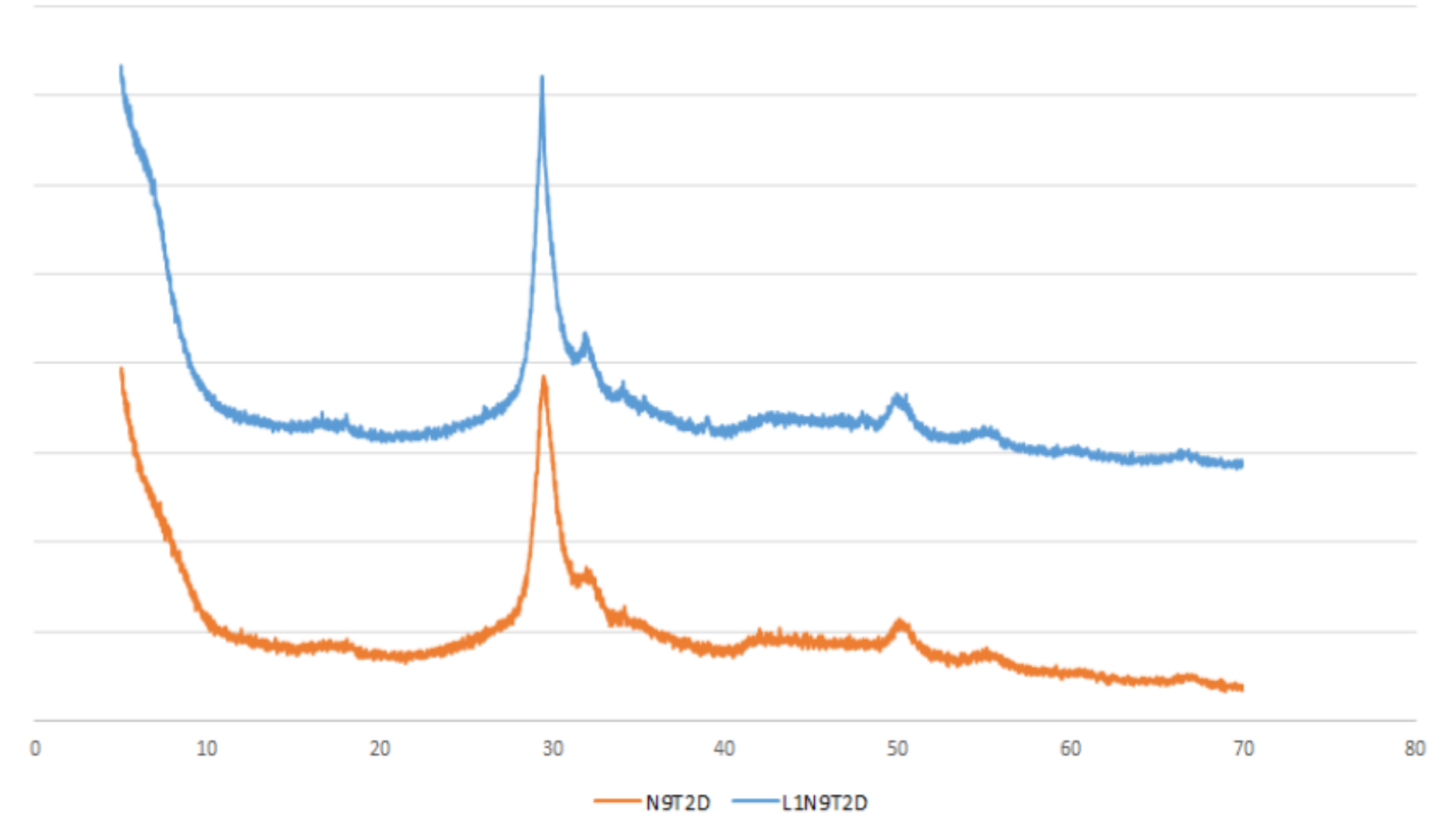
- There are many parameters to control in fine particle nucleation
  - Temperature & pH
  - Mixing speeds
  - Vacuum filtration
  - Drying
  - Storage
  - Etc.



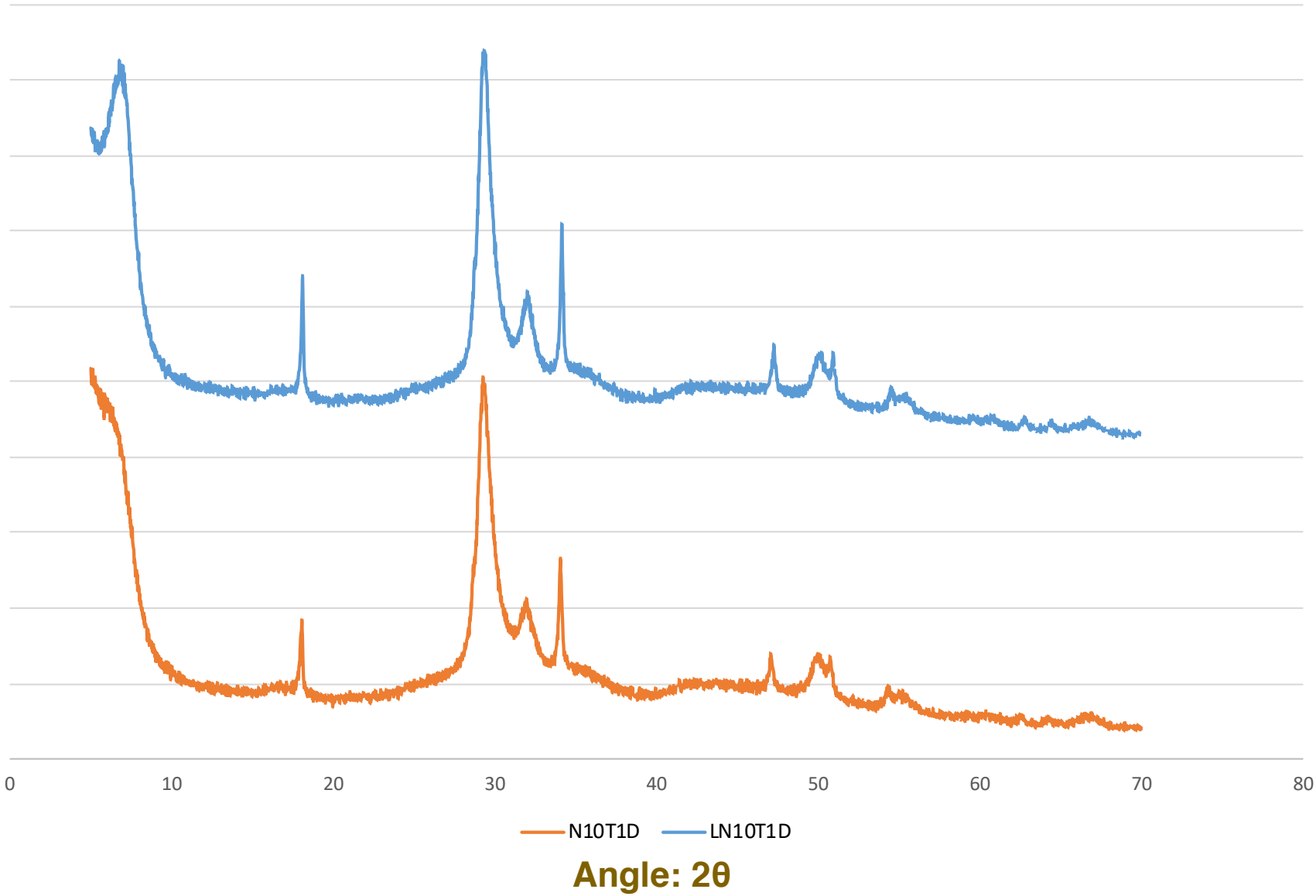
- 3 separate samples
- Dropwise method
- Ca:Si = 1.87
- Formation of $Ca(OH)_2$ and $CaCO_3$ in filtration & drying processes

XRD Diffractogram comparison of dry, pure C-S-H and impure C-S-H with the presence of Ca(OH)2 and CaCO3, Ca:Si = 1.87

Longevity Studies

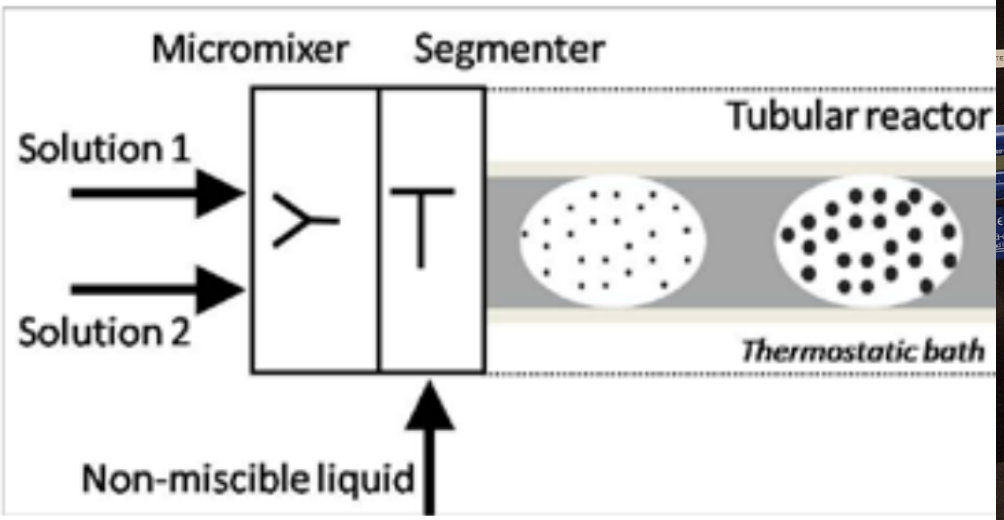


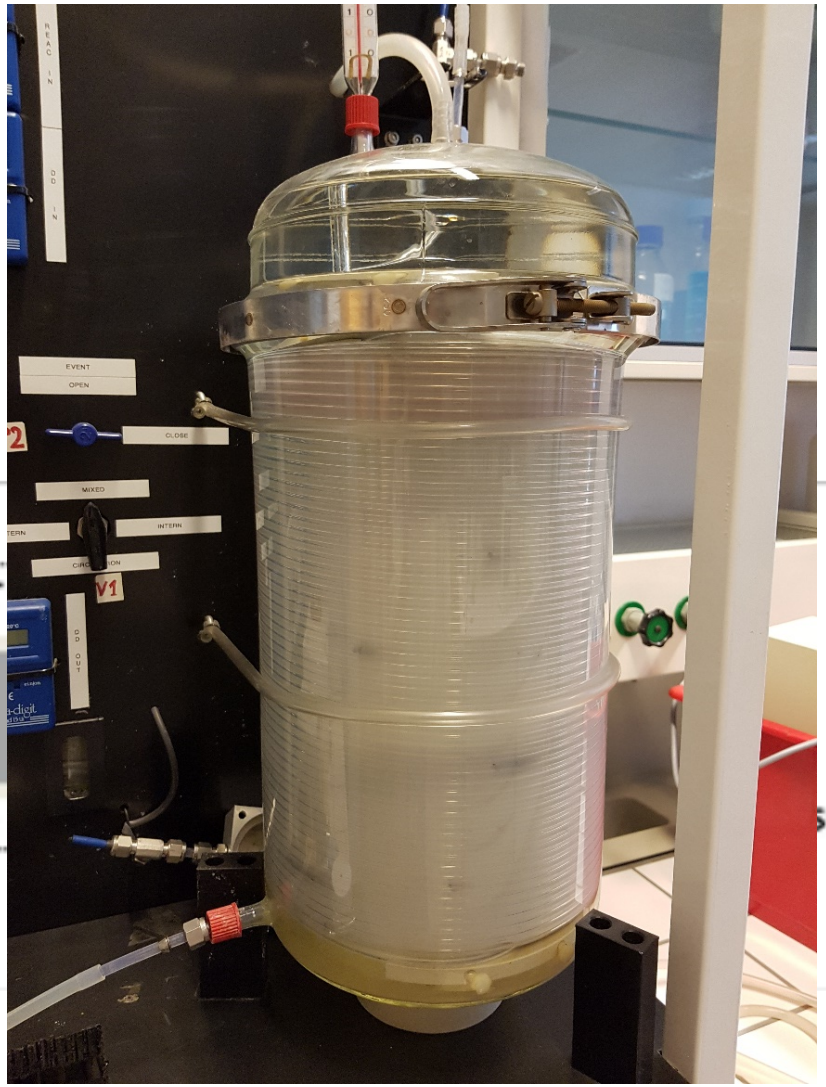
Longevity Studies (cont.)



Scaling Up:
Segmented Flow Tubular Reactor (SFTR)

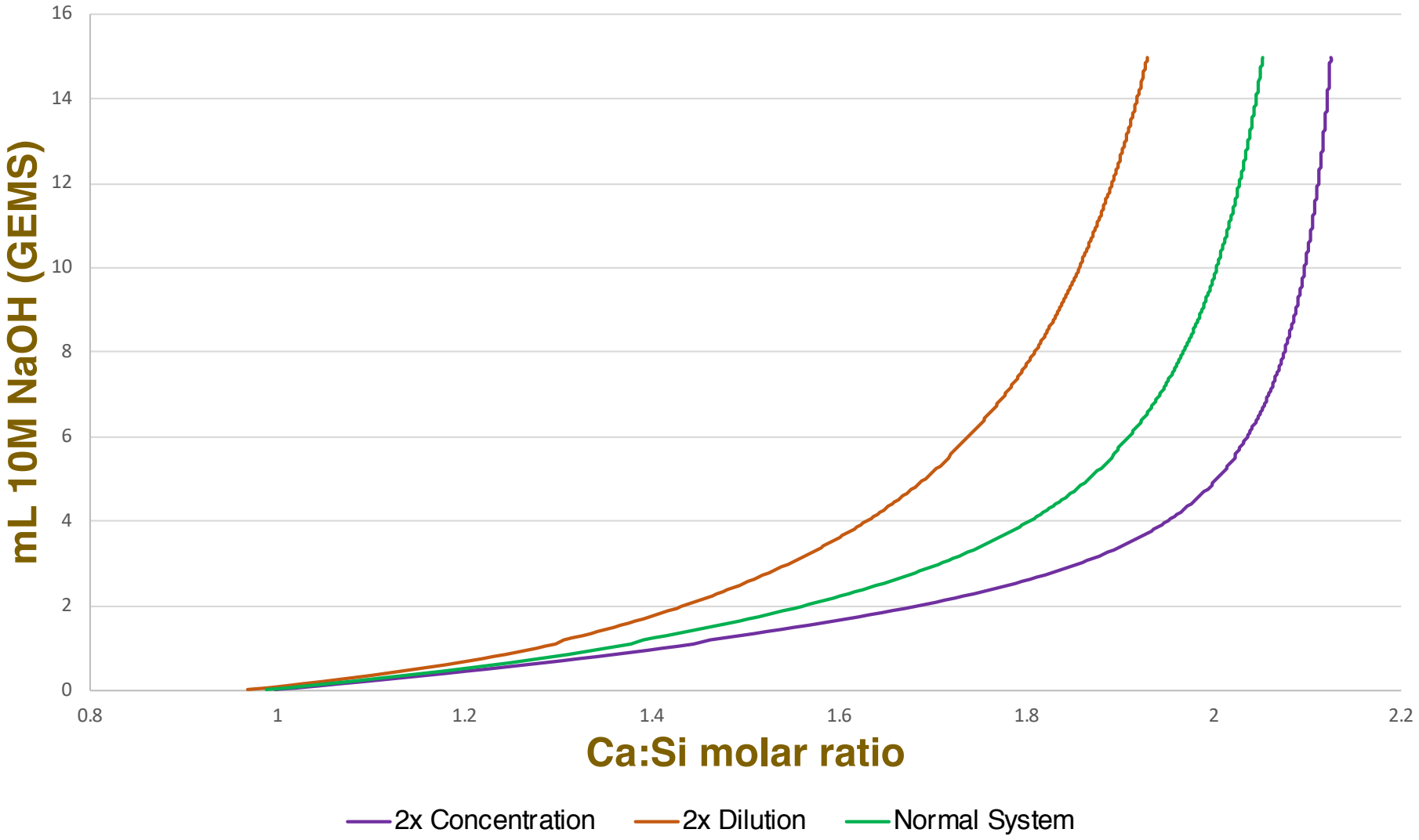
- Scaling up
  - Continuous production
  - Homogeneous batches
  - Temperature control
  - 100g in 3hrs





Processing and Application of Ceramics, 107-114, 2010

Effect of Diluted System



Effect of Diluted System

- 10 M NaOH
- 0.1 M Silicate solution

Calcium solution (M)	Ca:Si	pH (GEMS)	pH (observed)
0.19	1.73	13.36	13.39
0.21	1.82	13.33	13.37
0.25	1.93	13.31	13.35
0.3	2	13.30	13.34

Summary

- Successful production of pure CSH in batch reactor and SFTR reactor
  - Drying & storage methods to be further defined
  - Methods to use XRD to quantify impurities in tandem with TGA in process
- Thermodynamic & kinetic modelling work to begin in October

ESRs who want samples, let me know in advance!

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Future Work

Methods

C-S-H Systems

	Thermodynamic & Kinetic Modelling	Scaling up	Substrate study	Proton NMR
Pure, single-phase C-S-H		X	X	X
C-S-H + sulfates	X		X	X
C-S-H + aluminates	X		X	X

Secondements

- Learn and perform characterization of hydrate shrinkage in industrial environment
  - Location: HTC
  - Start: February 2020 (project month 28)
  - Duration: 3 months
- Carry out NMR on synthetic C-S-H
  - Location: Usurrey
  - Start: End of 2019 (to be determined)
  - Duration: 1 month

Outreach Activity

- St. Philip's School & Community Center
  - Dallas, TX United States

- Science Day Workshop:
  - Earthquakes, buildings, and sustainability outreach

Thank you!

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