Characterization of water sorption cycle in hydrates of controlled oxide composition

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Outline

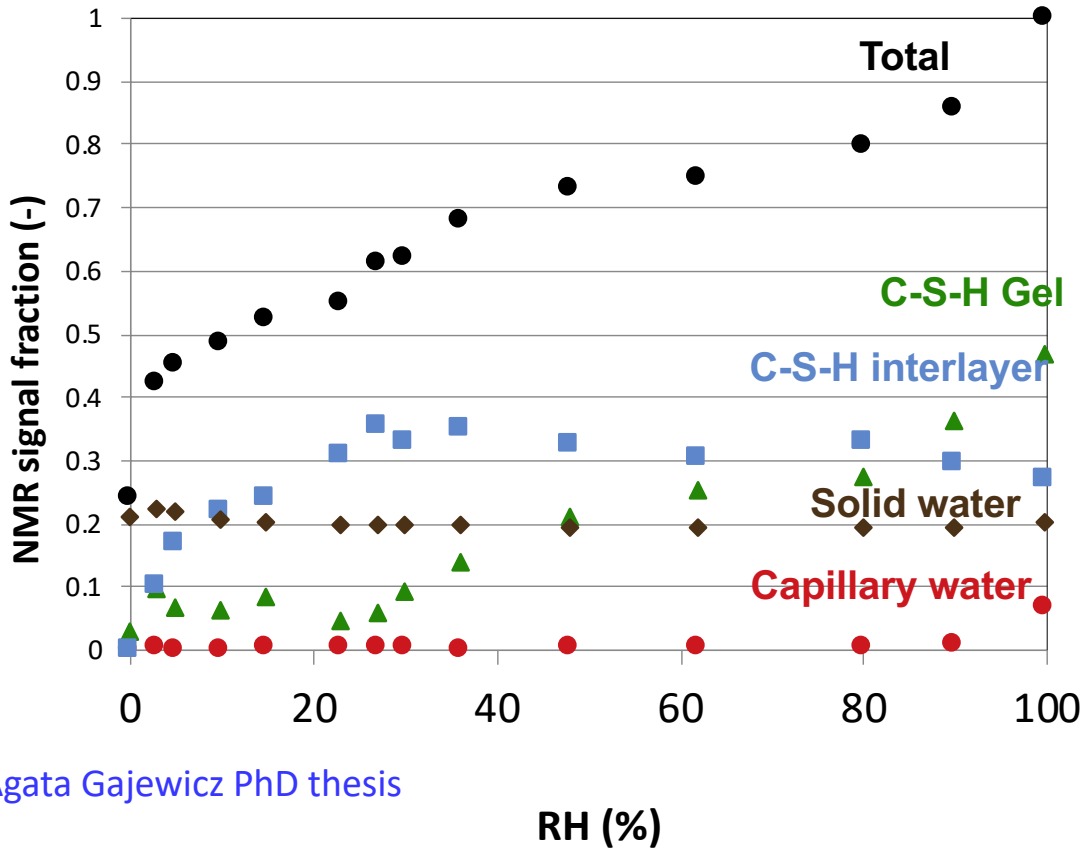
- Motivation and objective of the work
- Sample synthesis and characterization
- Investigating the moisture response of hydrates
- Conclusion
- Future plans

Objective of the work: Continued

- Cyclic changes of water content in cementitious materials are responsible for several physical and chemical degradation processes.
- Moisture movement due to capillary suction, condensation, gradient of density of water vapor, among others.
- Durability assessment requires characterization of its sorption (drying/re-wetting) cycles.

C-S-H governs most of the moisture movement!

^{1}H NMR relaxometry based desorption isotherm (drying cycle)



Courtesy: Agata Gajewicz PhD thesis

Isolate the response of C-S-H to moisture changes from other parts of system and account for microstructural and dimensional changes

Open questions/Knowledge gaps

- ✓ Does the first drying cycle introduce irreversible microstructural change?
- ✓ Reversibility depends on?
  - Time
  - Speed of drying
  - Extent of drying
- ✓ What is the influence of C-S-H morphology curing temperature and density on sorption isotherm and reversibility?

Maximizing the content of C-S-H in the hydrated product

White clinker

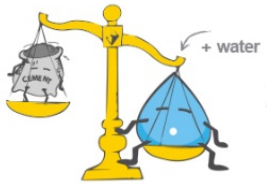
AALBORG WHITE® 10% by wt.

Microsilica

Hemihydrate (optimized)

Elkem

d50~ 0.478 µm

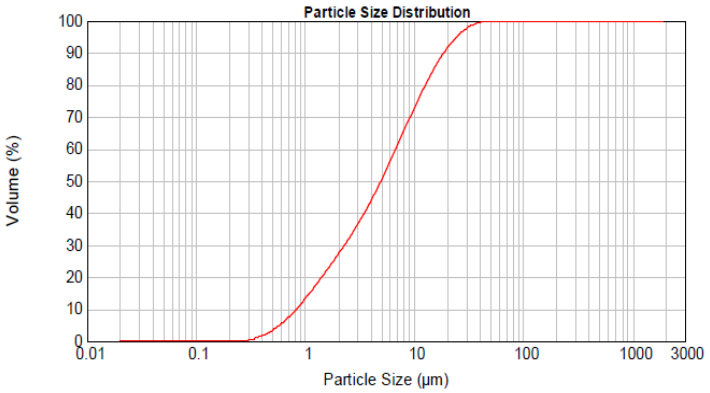


= 0.7

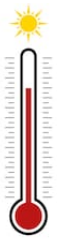
Ground

d50~ 5 µm

Protocol optimized at EPFL During two months secondment period



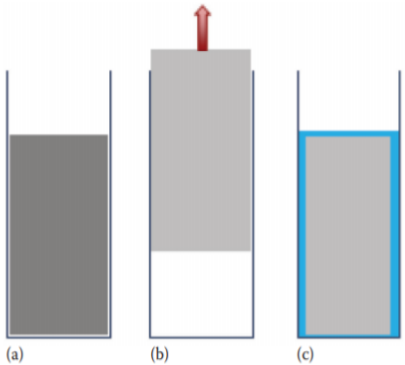
5 °C  20 °C

40 °C  60 °C

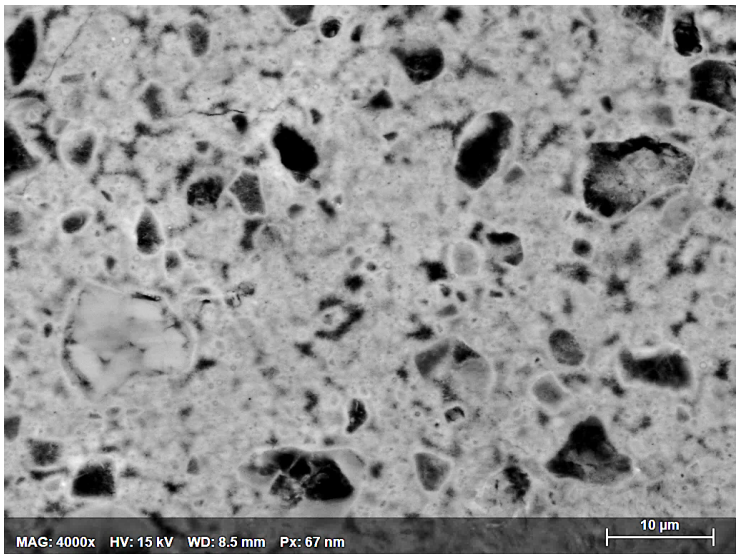
d50 ~ 5 µm d90 ~ 18 µm

Pozzolanic silica facilitates in consumption of portlandite!

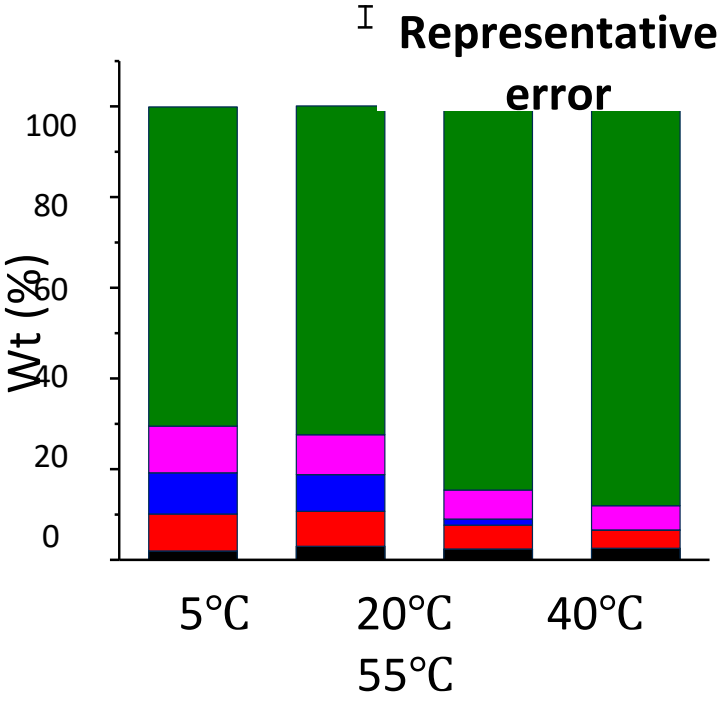
Synthesis of sample with C-S-H dominated phase



Cured under water



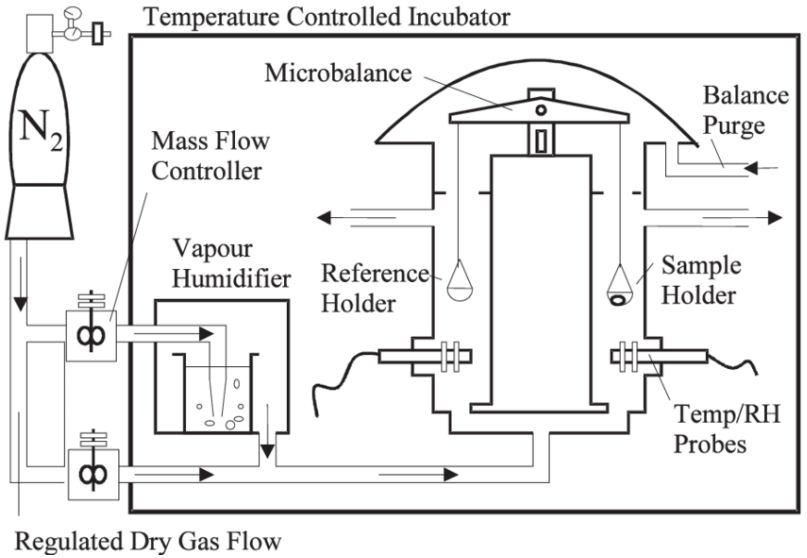
SEM image of a sample cured at 55°C for 90 days



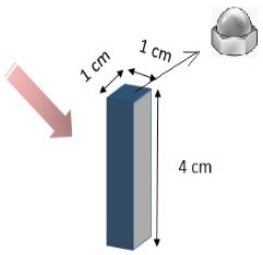
Phase assemblage XRD–Rietveld and TGA measurements

Potential tools to investigate the moisture sorption response of C-S-H

Long-term moisture sorption setup

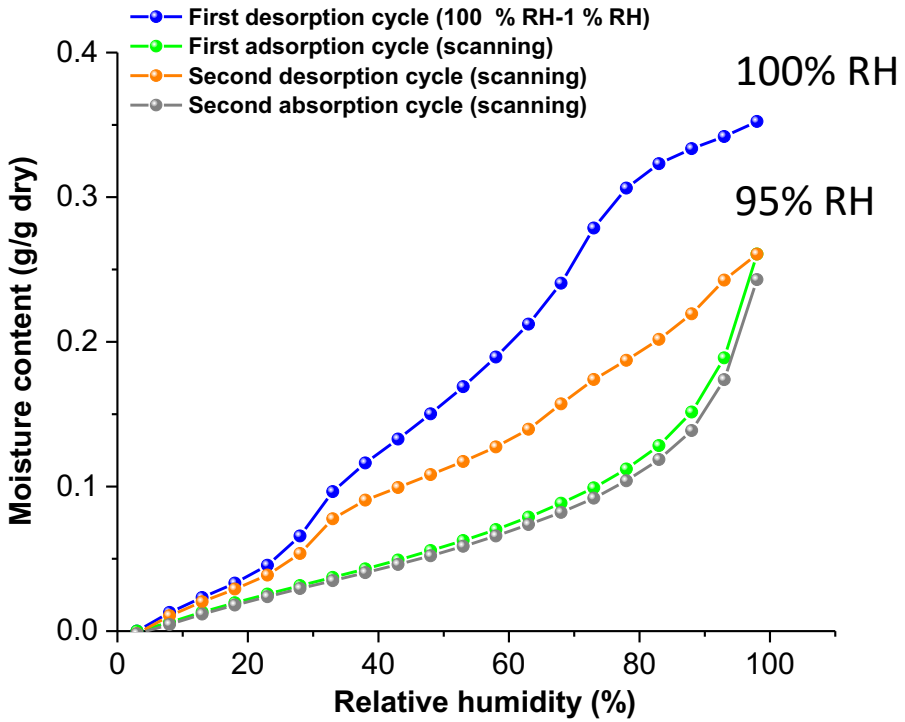


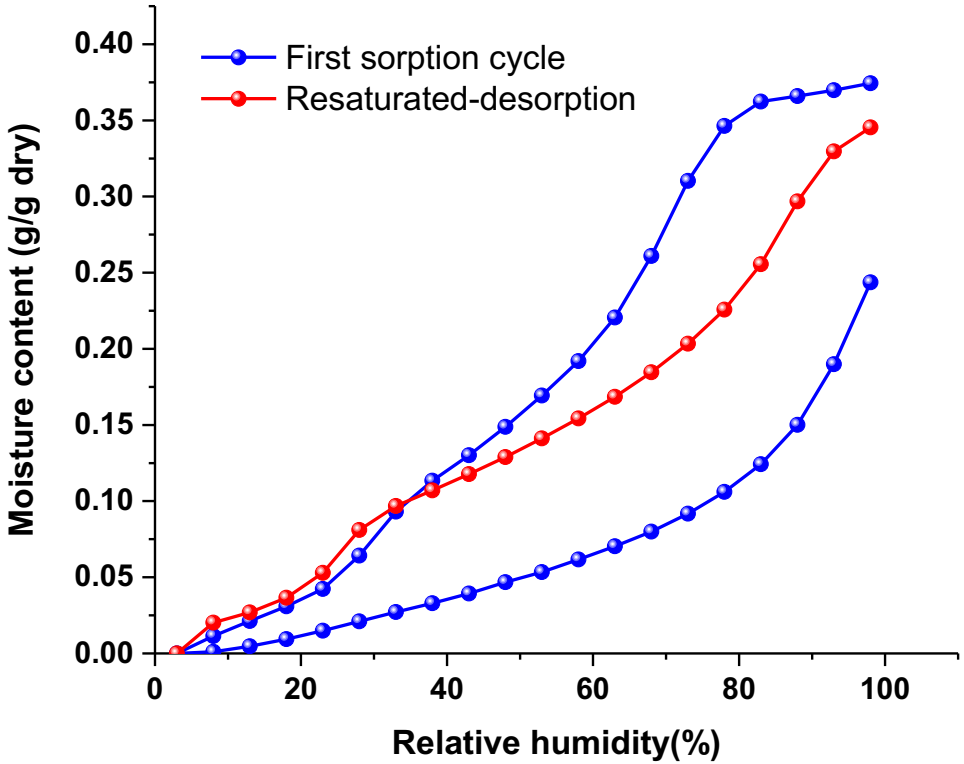
Short-term moisture sorption setup



Length change measurement setup

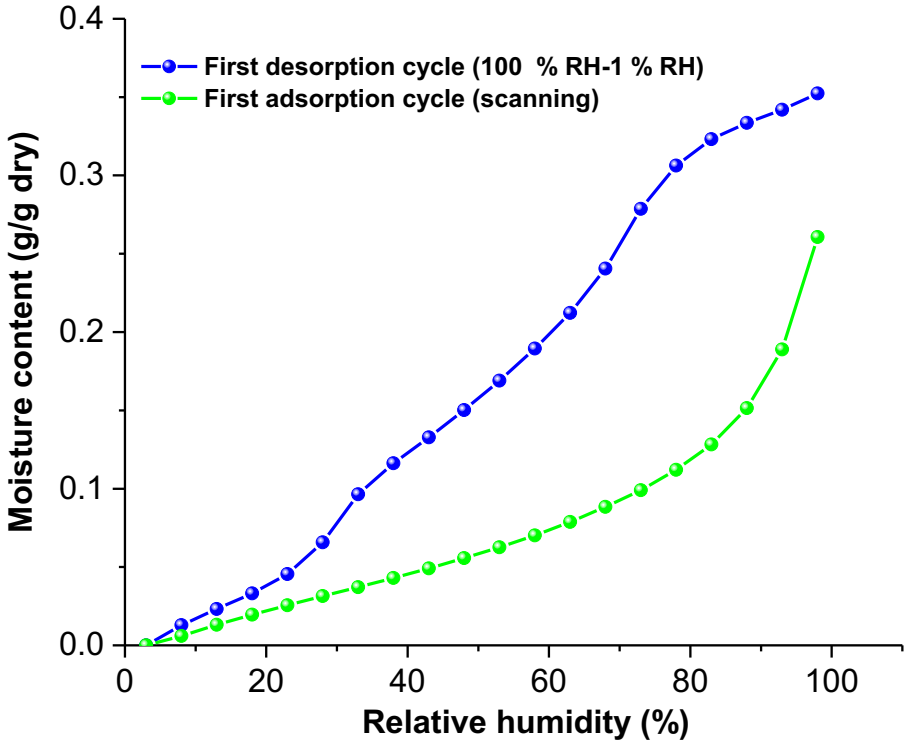
On second desorption cycle: Reversibility and irreversibility



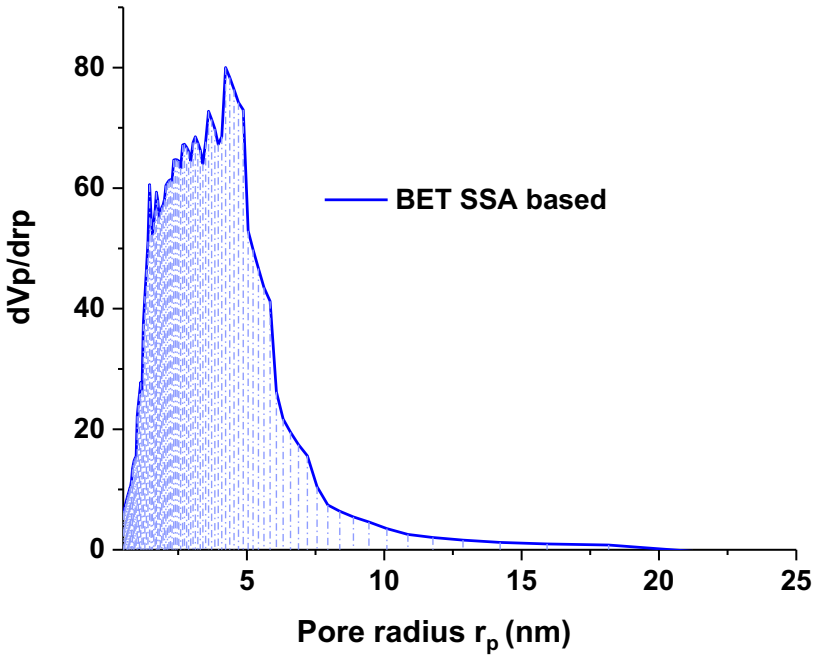


Re-saturated in distilled water for 1 day

Employing kelvin eqaution based BJH method to calculate pore size distribution



Barrett, Joyner and Halenda pore size distribution using desorption branch



20 degree celcius, wet curing 90 days

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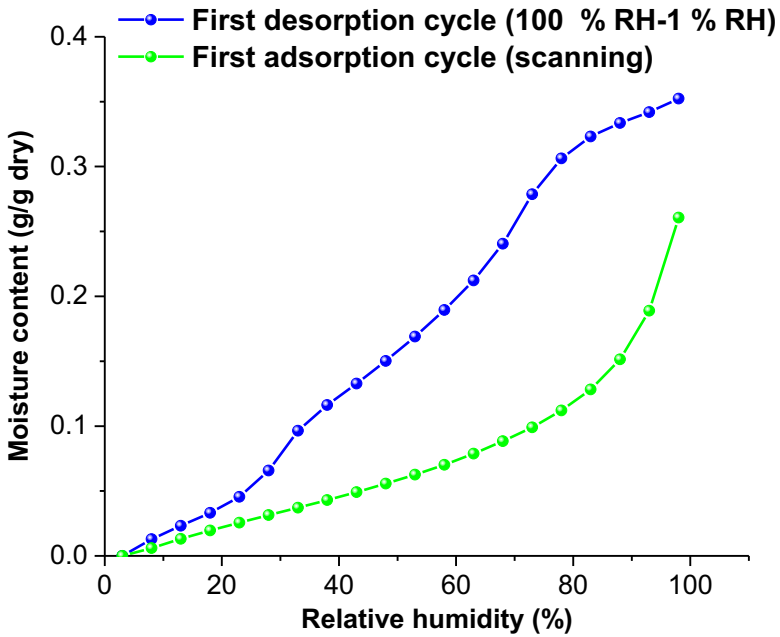
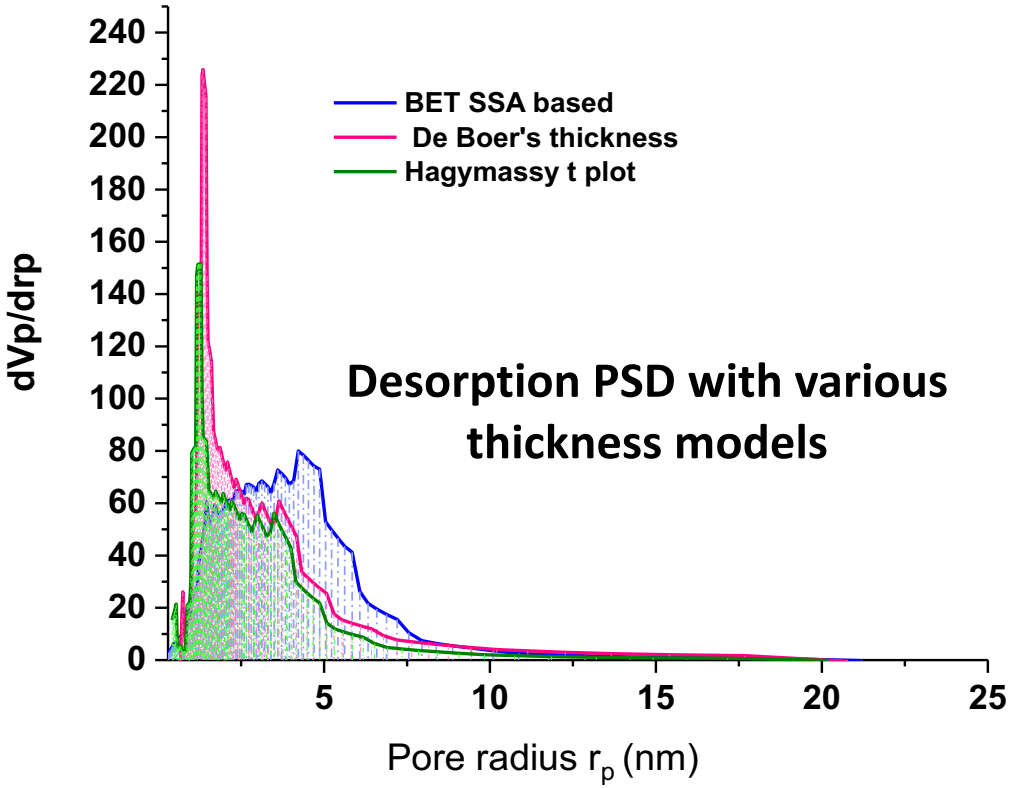
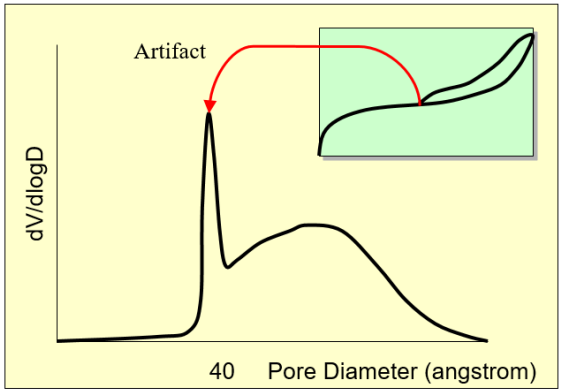
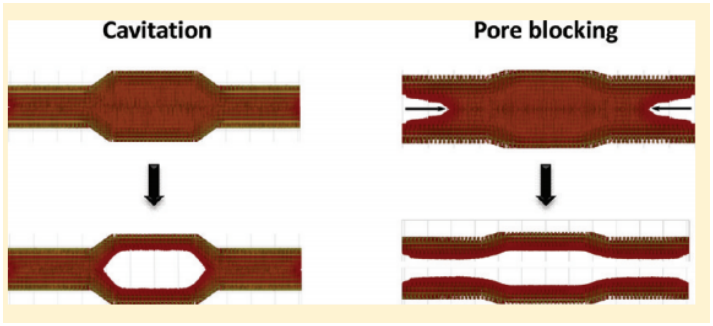




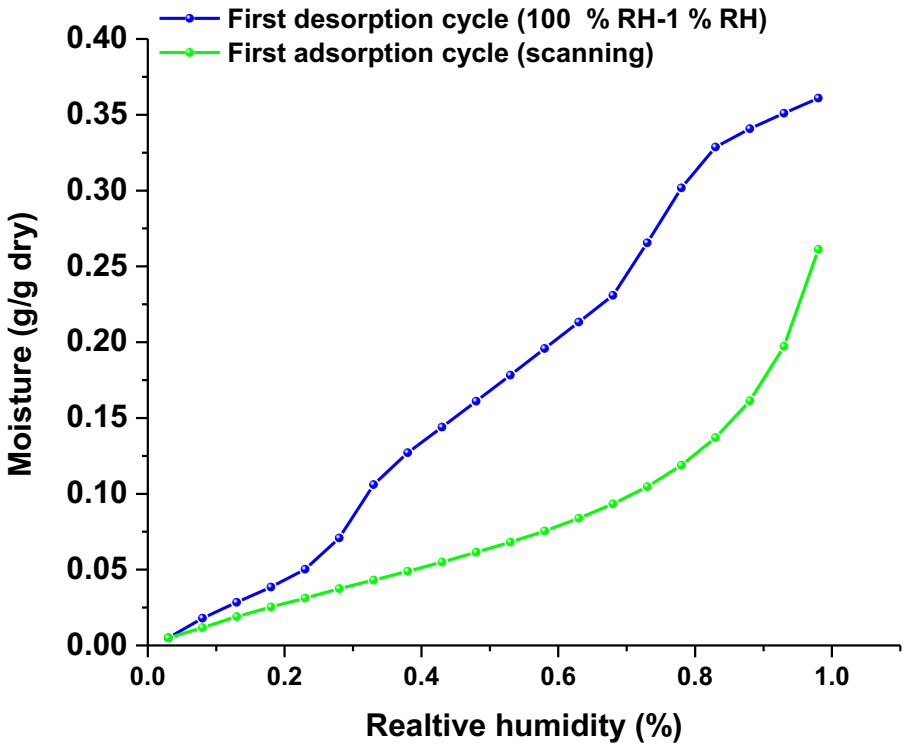
Tensile strength effect



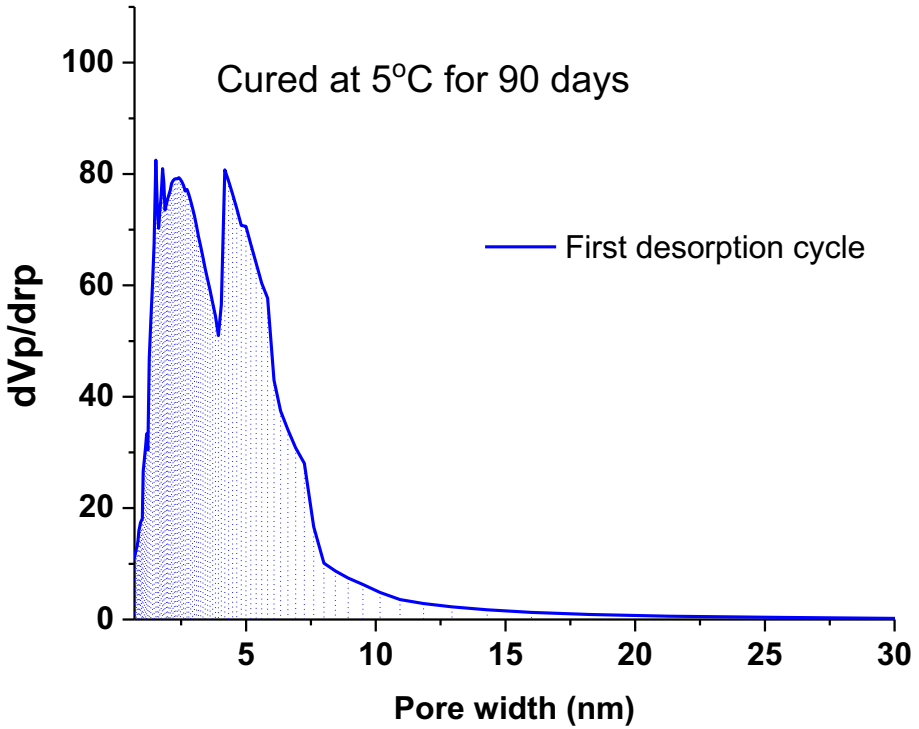


- **There exists a mechanical stability limit below which a macroscopic meniscus cannot exist anymore and which leads to a spontaneous evaporation of the pore liquid.**
- This forced closure of the hysteresis leads to an artificial step in the desorption isotherm .Pore size distribution artifact at ca. 3.4 nm
- When the neck size is larger, the menisci recede in the necks, leaving the fluid in the larger pore stretched but intact called as pore blocking
- There is no clear distinct boundary between pore blocking and cavitation but rather a gradual transition between them.
- This is due to the competition between the removal of adsorbate from the receding menisci (pore blocking) and the tension in the stretched fluid in the cavity (cavitation) as the pressure is decreased.

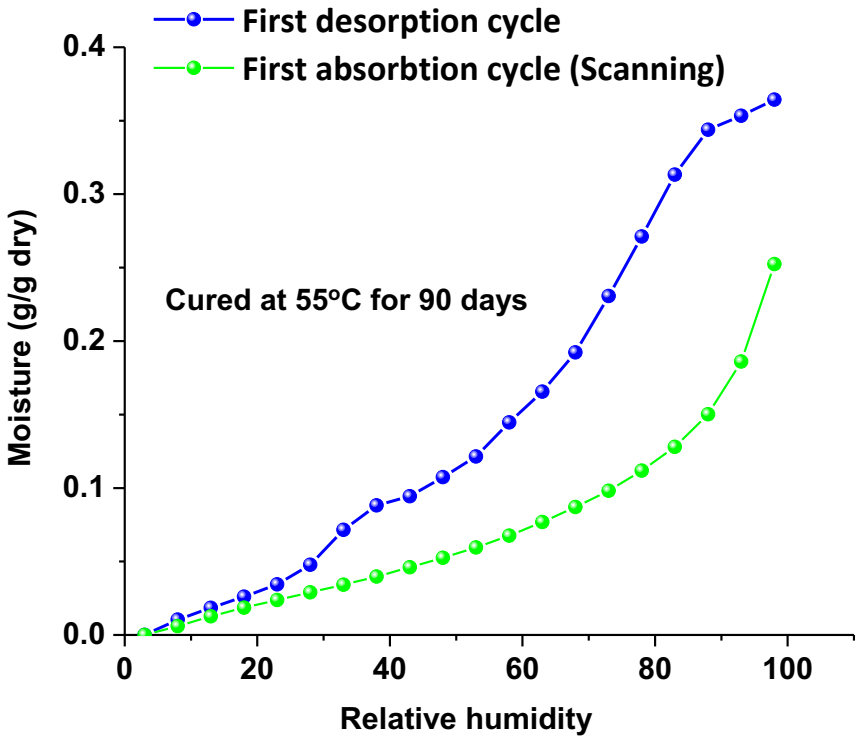
5 degree celcius, wet curing 90 days



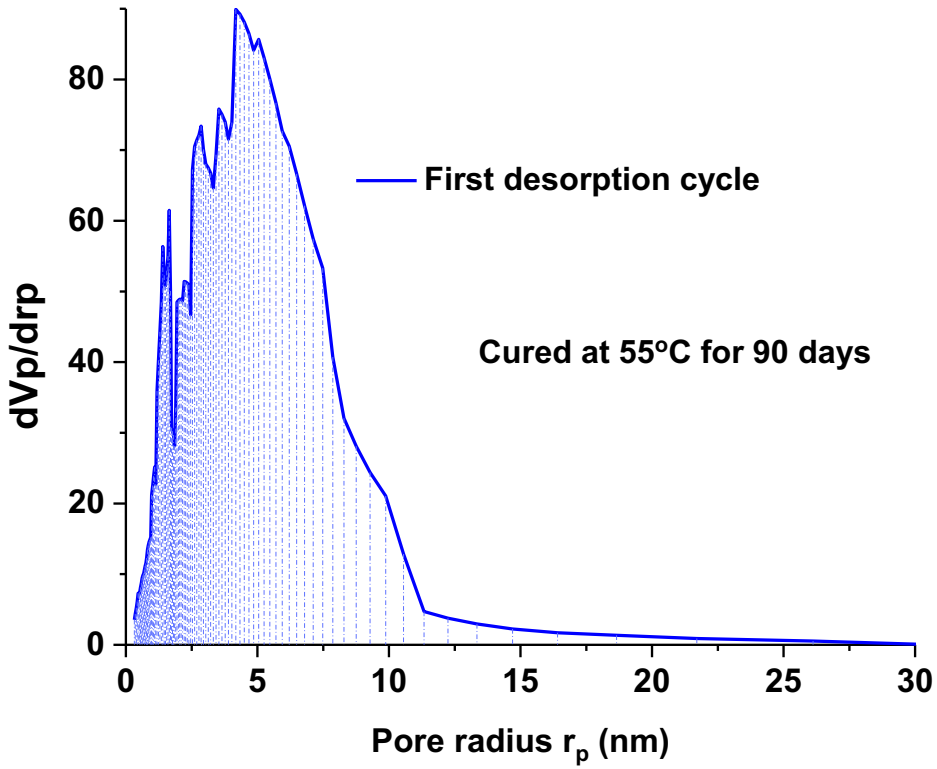
BJH pore size distribution



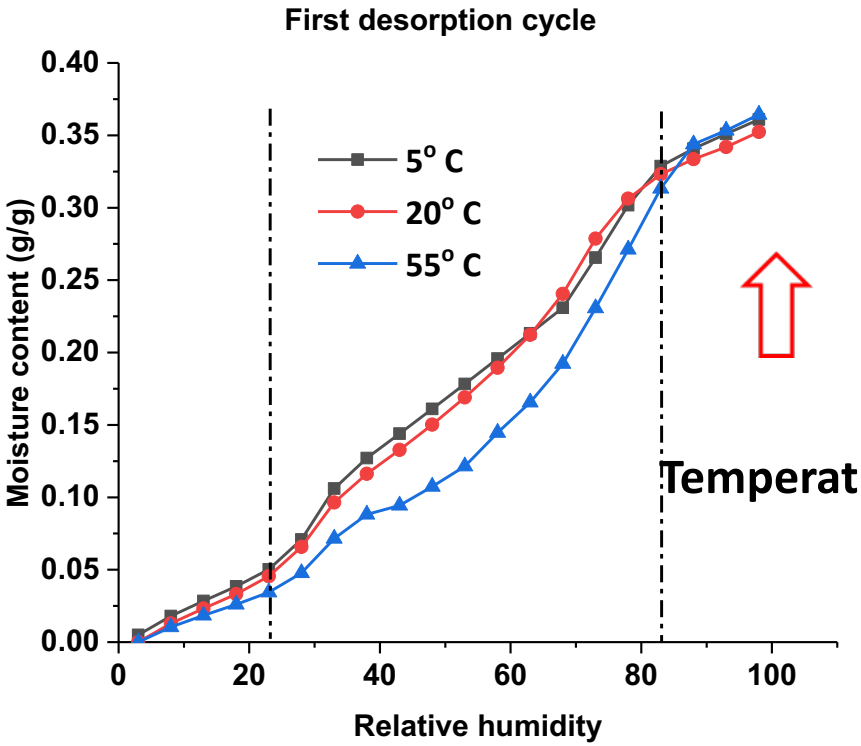
55 degree celcius, wet curing 90 days



BJH pore size distribution

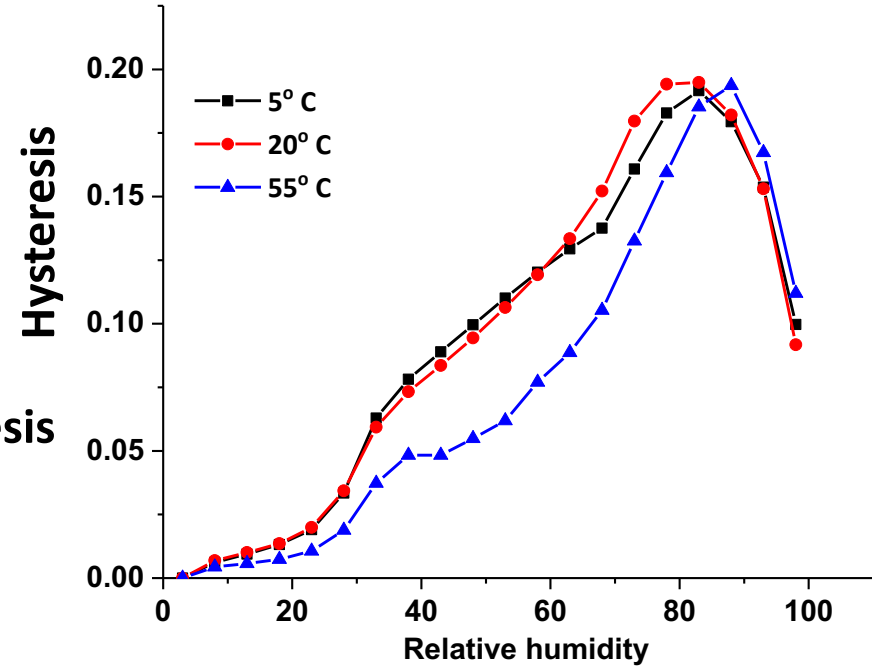


Hysteresis and curing temperature



Temperature

Hysteresis



- Hysteresis reduces but not owing to the temperature dependent properties of water/more active sites since the isotherm temperature was fixed at 20 degree celcius.
- Perhaps depends more on Ca/Si ratio or porosity .

Conclusion

- Accurately determine the statistical thickness, especially below monolayer capacity to implement kelvin equation based model properly.

- Transition point from hygroscopic into over-hygroscopic water content that occurs between 94%RH and 99%RH. Below this point, adsorption and capillary condensation occur in micro- and mesopores, above 95%RH, condensation in presumed in macropores.

- Macropore condensation takes place in static tests and hence a full saturation of pore structure. This can easily result in differences in mass content at 100% RH more than 10%.

- **It is therefore advisable to start desorption from a completely saturated substrate (bulk condensation, submersion in water) , in order to determine the true boundary desorption isotherm and hence the extent of hysteresis loop .**

Future plans

- Using semi empercal /thermodynamics based models to assimilate the sorption behaviour of C-S-H.
- Analysing the goodness of fit attained from various models. (ongoing)
- Analyis of the samples synthesized by other techniques : belite hydration and synthestic CSH. (on going)
- Curing the samples for ^{1}H NMR measurements. (ongoing)

Future plans

Secondments at EPFL

April -May 2018 (2 months) : To determine the protocol for synthesizing samples with C-S-H as the dominating phase.

March 2020 (tentative): Investigation of the desorption cycle for samples cured at different temperatures with NMR.

April-June 2021: Wrapping up experiments

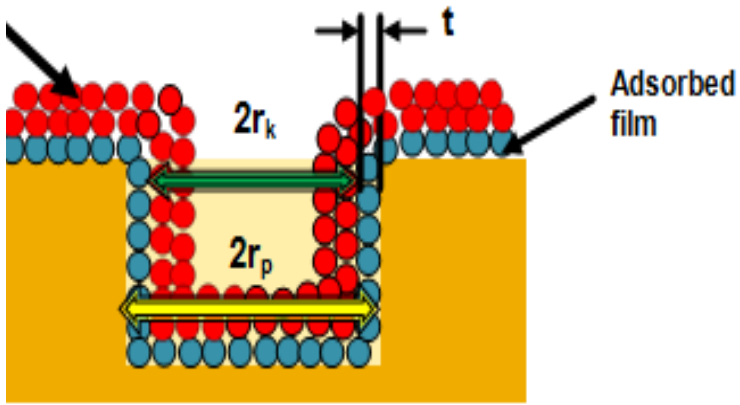
Outreach activity

to make an animated video on this project in which I will provide an overview of the fundamentals pertaining to this research project. Thereafter, it will be uploaded to social media platforms such as Youtube and Linkedin where it can garner high visibility.

Thank you for your attention!

Questions

yner and Halenda (BJH) method for pore size distribution: The choice of thickness calculation



n radius is not the actual pore radius since
adsorption has already occurred on the
wall prior to condensation leaving a
al core of radius r_k.

ersely an adsorbed film remains on the
when evaporation of the center core
place.

Various methods exist of calculation of thickness a
of relative pressure for calculating the pore size dis

De Boer`s $t_a = 0.1\sqrt{\frac{13.99}{0.034-0.4343.ln\frac{p}{p_o}}}$

Halsey $t = 3{,}54\left[\frac{5}{\ln\left(\frac{P_0}{P}\right)}\right]^{1/3}$

Hagymassy t plot

Based on BET surface area