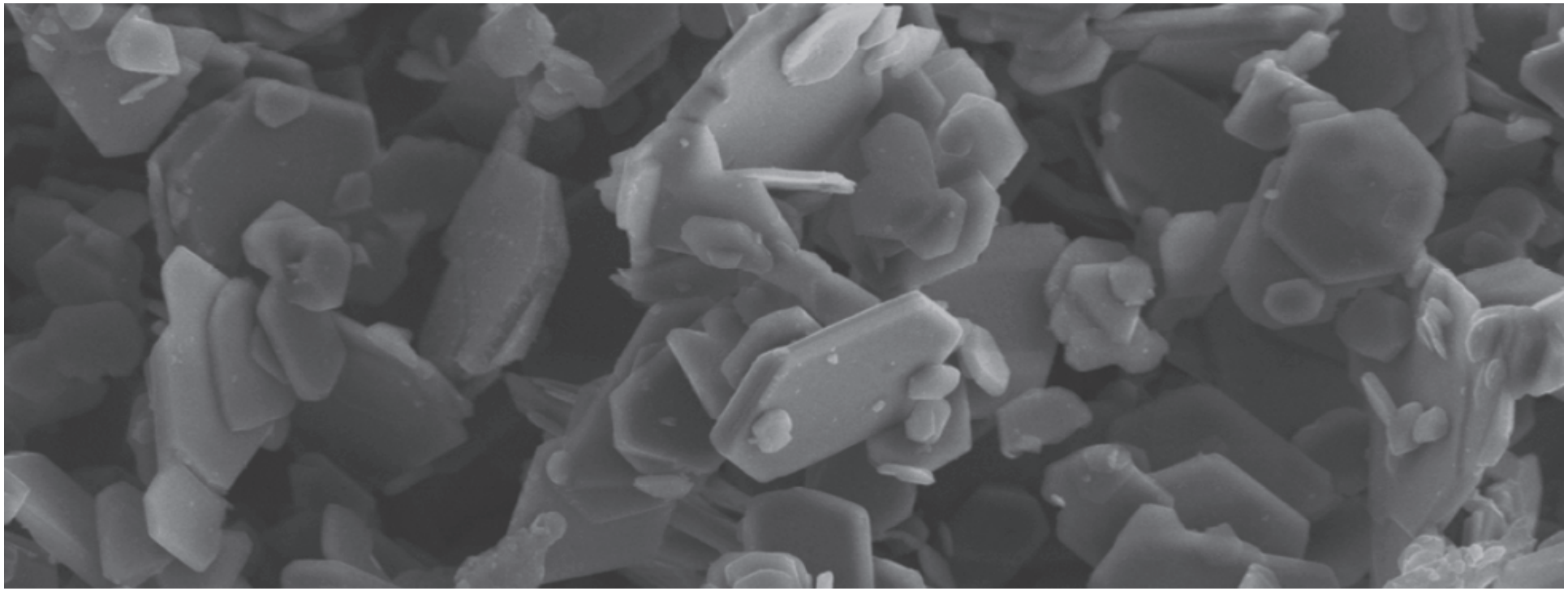


Studies of cement hydrates by application of sorption calorimetry

4th European Cement Calorimetry Conference

Dresden – Germany

Luis Baquerizo

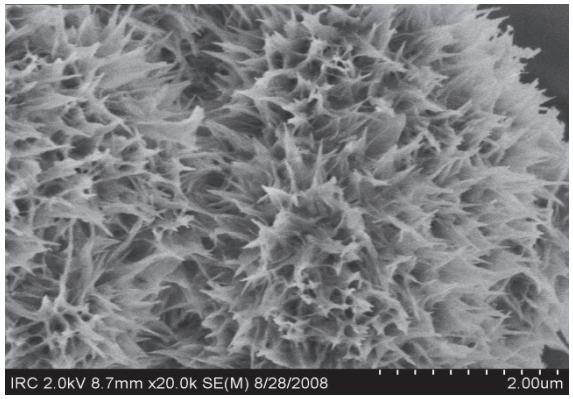
LafargeHolcim Research Center

LafargeHolcim

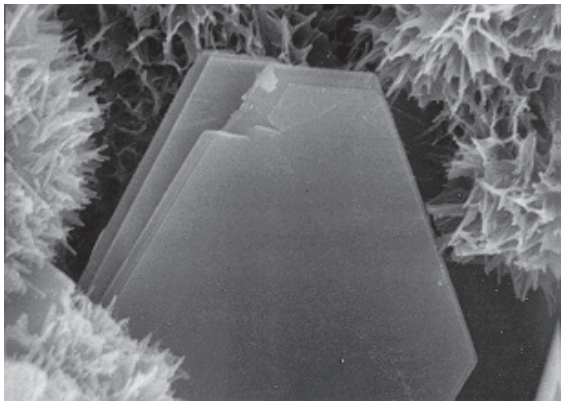
Stability of cement hydrates

- Cement paste is composed of different hydration phases. The main cement hydrates are:

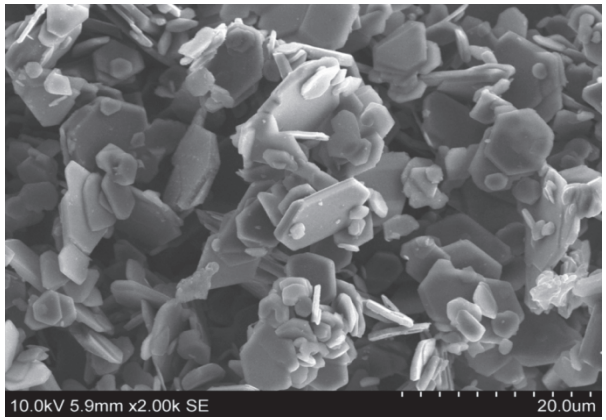
C-S-H*
(50-60% by volume), amorphous, varying water content, sensitive to RH.

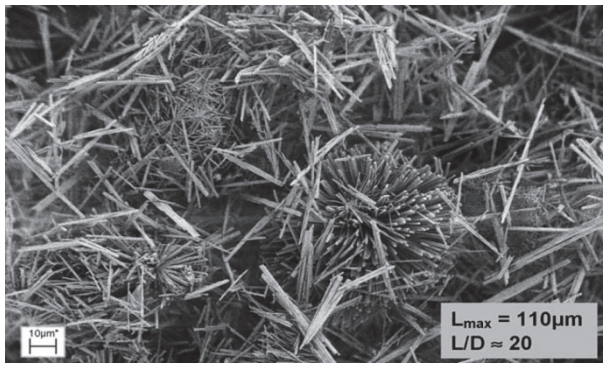


CH*
(15-25% by volume), crystalline, water content doesn't change.



AFm – AFt phases**
(15-20% by volume), crystalline, sensitive to changing RH.



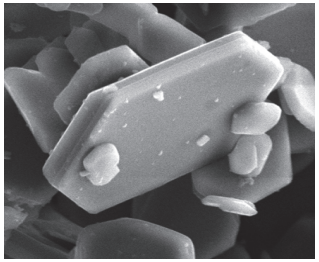


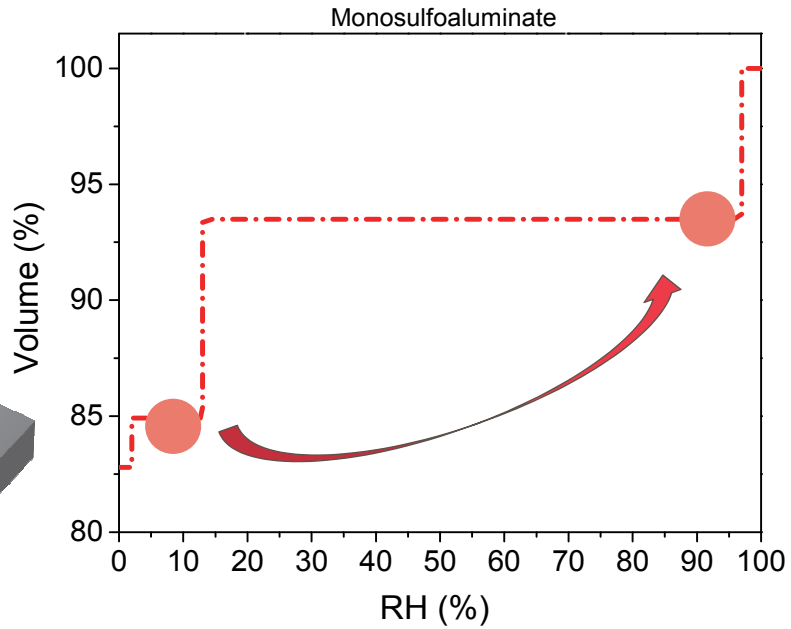
* *http://www.cementlab.com/cement-art.htm*

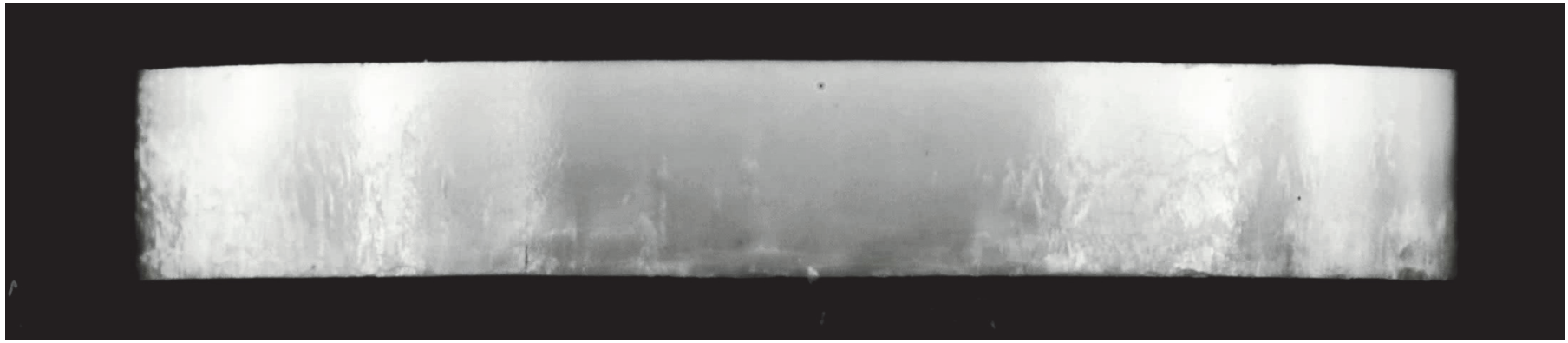
** *Goetz-Neunhoeffer, F., Neubauer, J., Schwesig, P., Cem. Concr. Res. 36, 2006, 65-70*

Stability of cement hydrates

Monosulfoaluminate



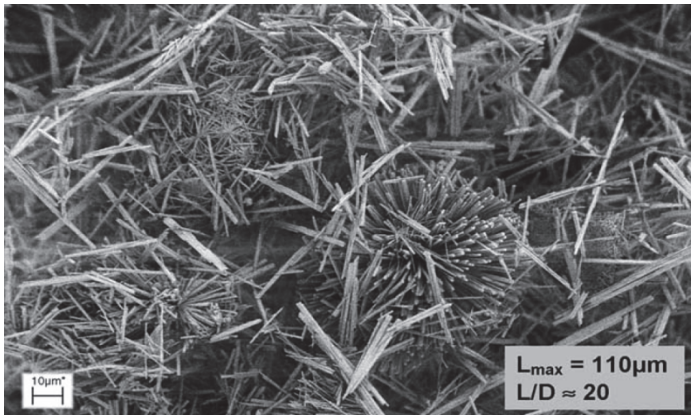


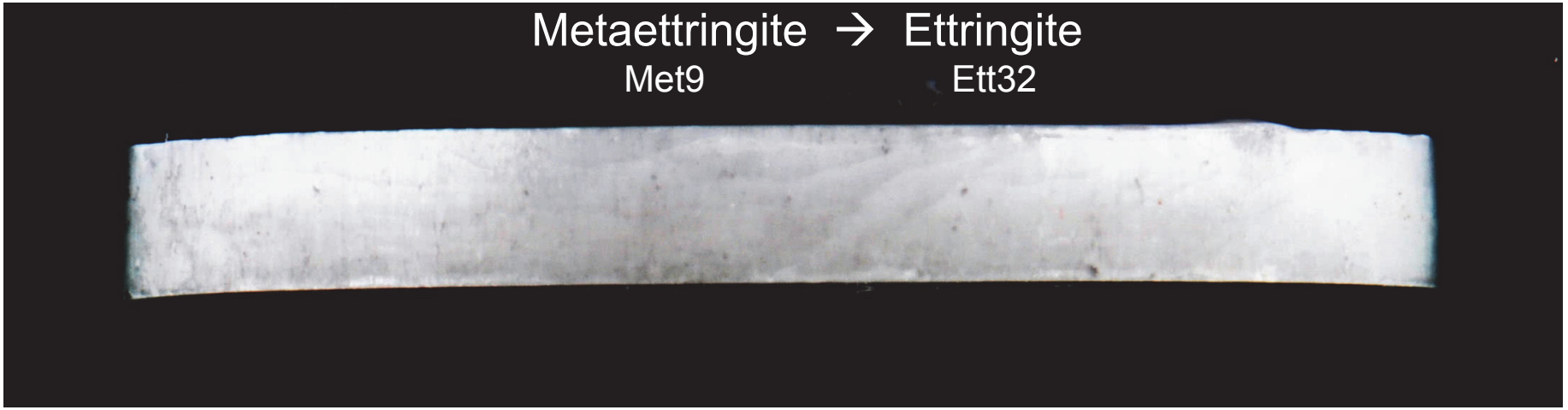


Stability of cement hydrates

Ettringite

- Ettringite is an important hydration product in Portland based systems and the main one in CSA and CAC blended with sulfates
- It is known to decompose at high temperatures into an amorphous product called metaettringite
  - **How stable is ettringite?**

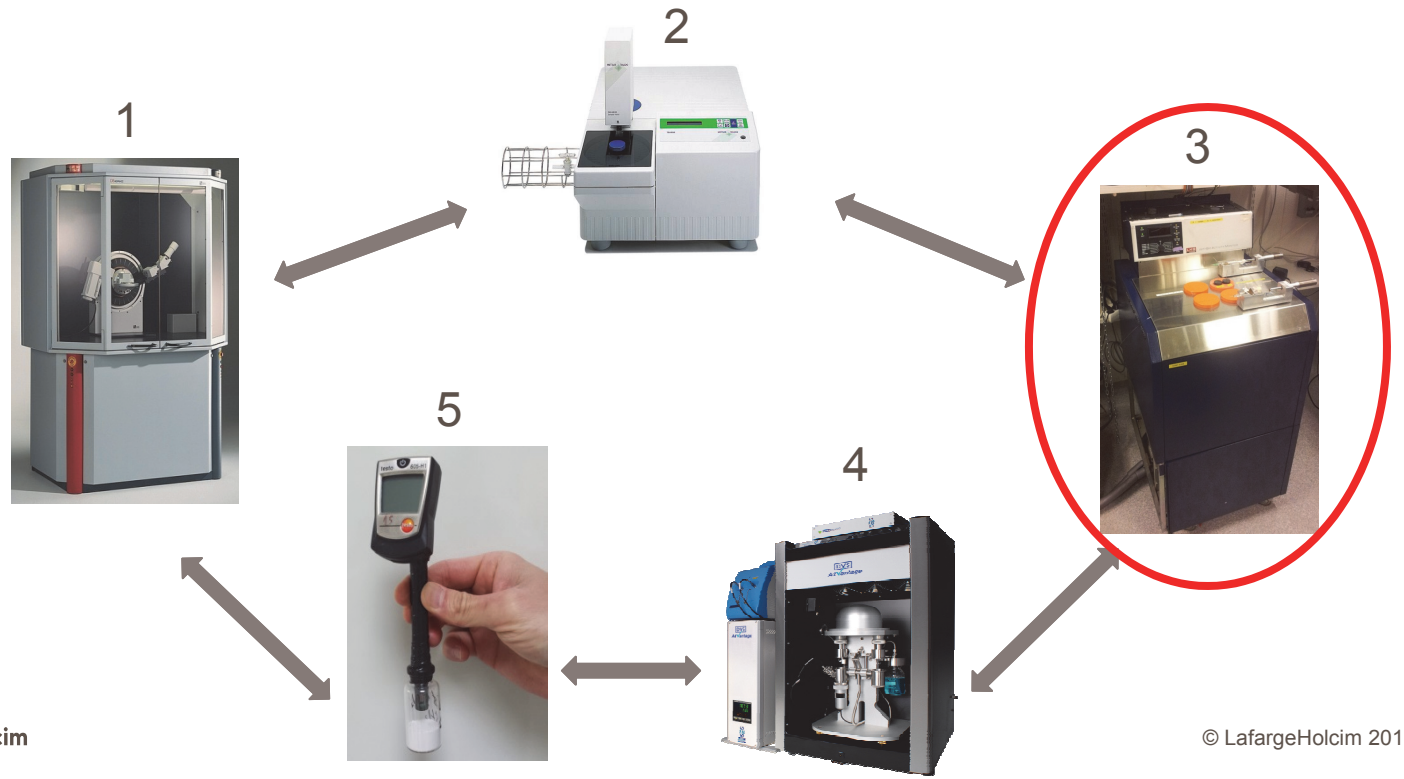




Methodology: Multi-method approach

1. **X-Ray diffraction (XRD)**
2. **Thermogravimetric analysis (TGA)**
3. **Sorption calorimetry**: collaboration Lund University
4. **Sorption balance**: collaboration Lund University
5. **Hydrate pair - humidity buffer method**

*Baquerizo, L.; Matschei, T.; Scrivener, K.; Saeidpour, M.; Thorell, A.; Wadsö, L. Methods to determine hydration states of minerals and cement hydrates, Cem. Concr. Res.



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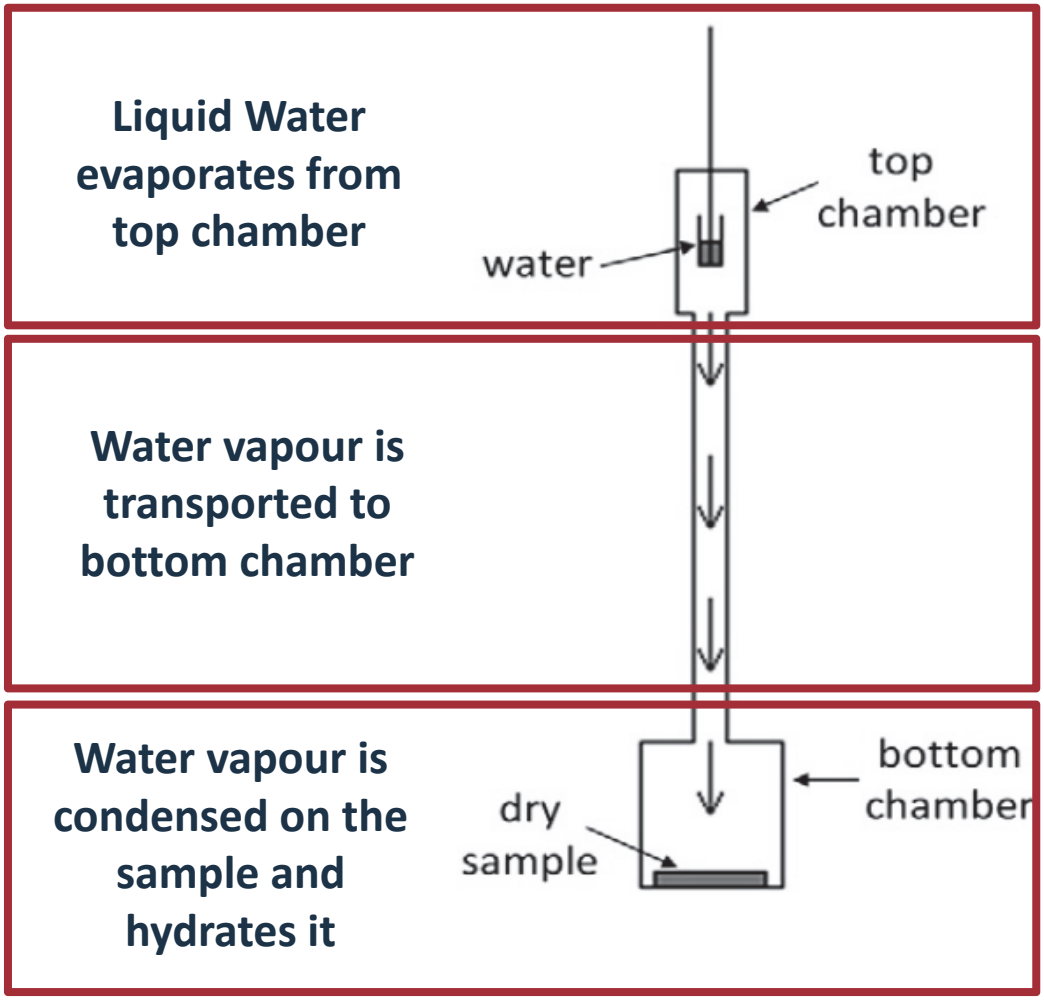
Sorption Calorimetry

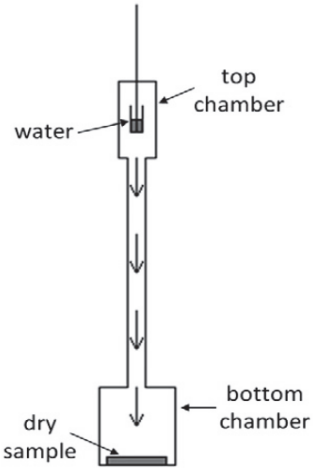
Calorimetry vessel

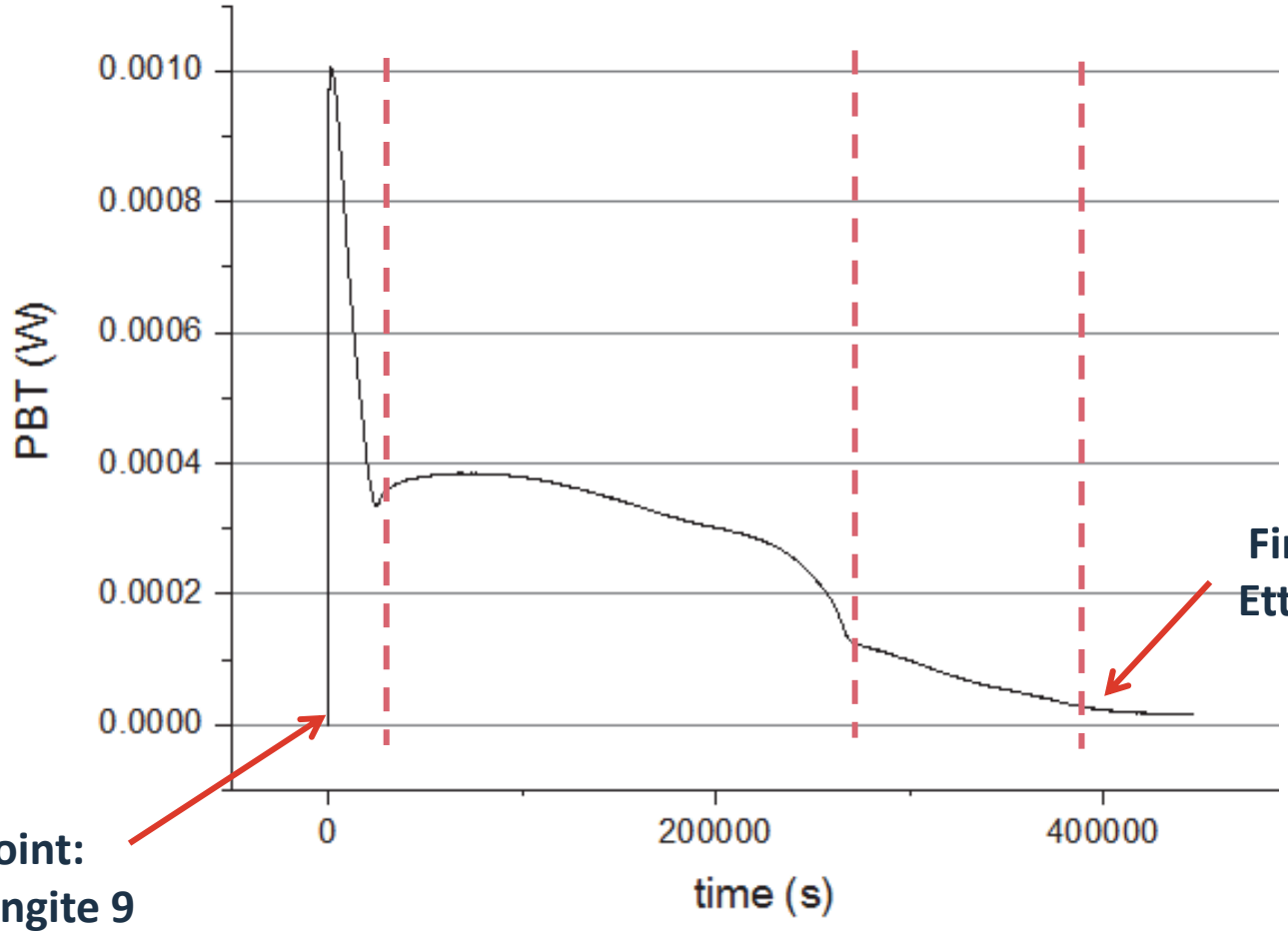


Sorption calorimetry (Lund University)

Sorption Calorimetry - Ettringite

- Raw data measured by the Sorption Calorimeter



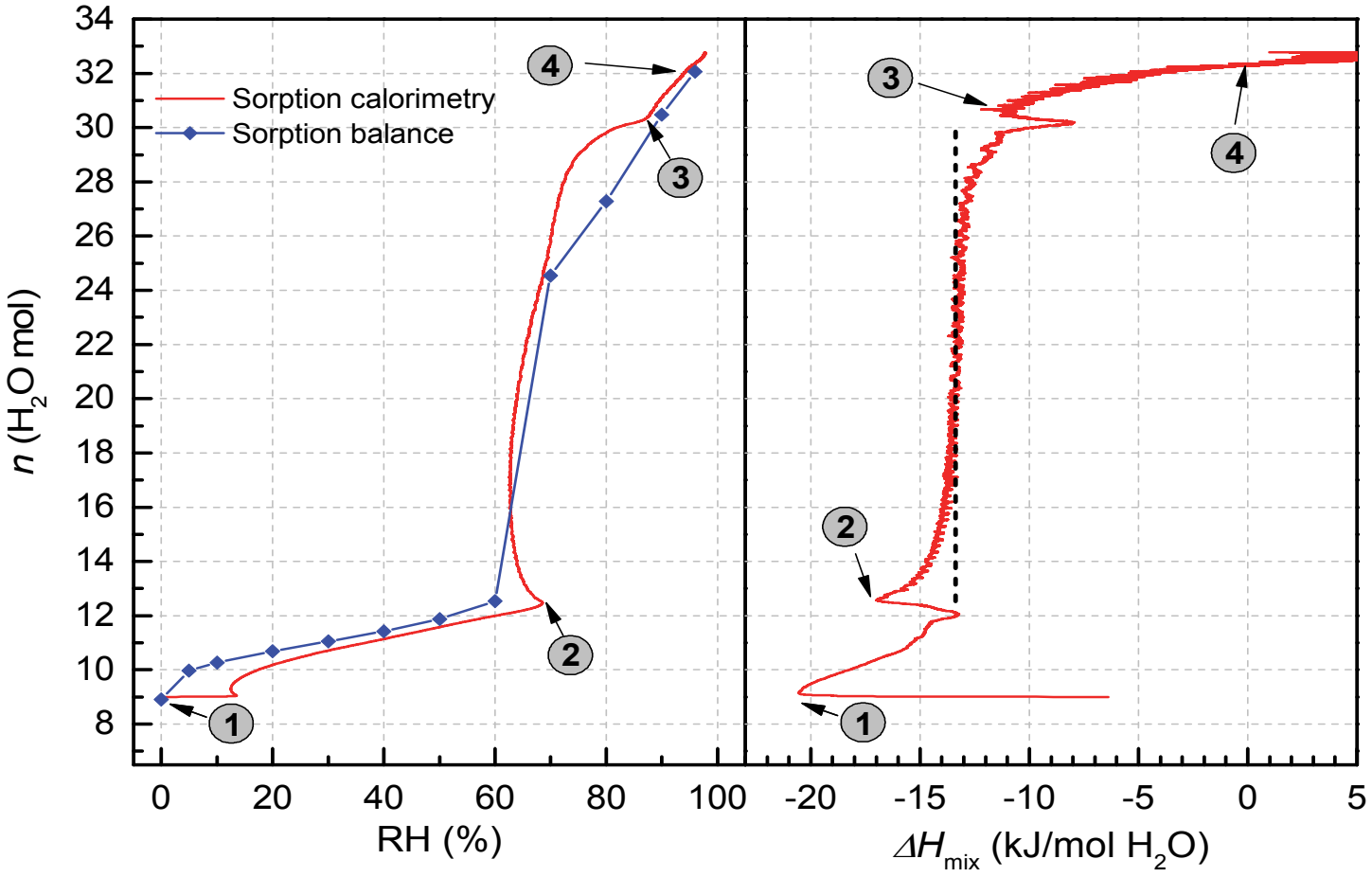


Start point:
Metaettringite 9

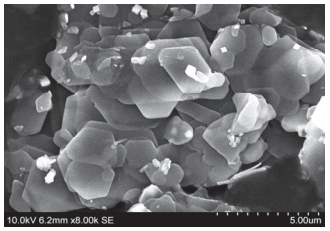
Final point:
Ettringite 32

Sorption calorimetry on Etrringite

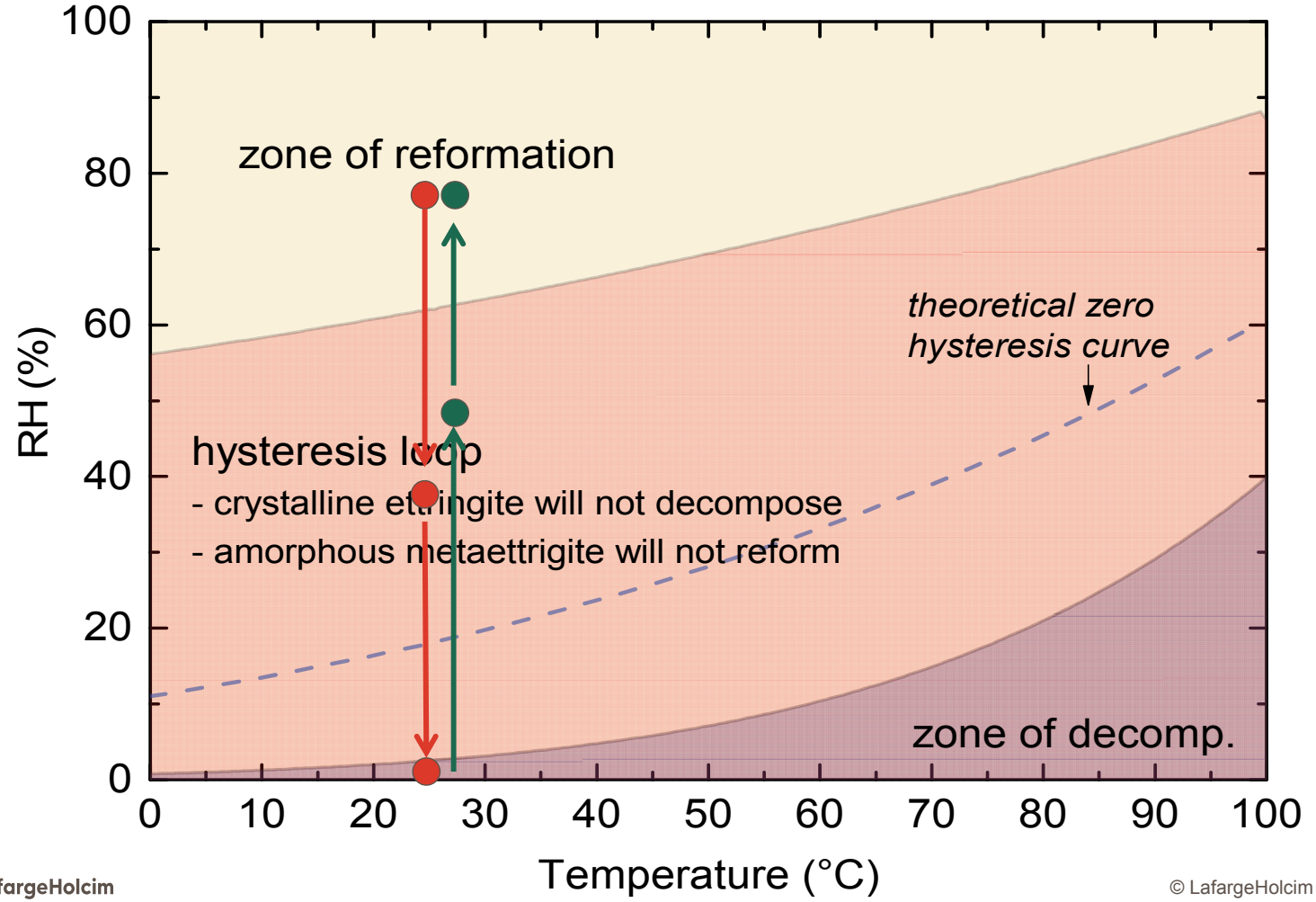
The absoprtion behaviour of etringite is clearly observed during the Sorption Calorimetry Tests

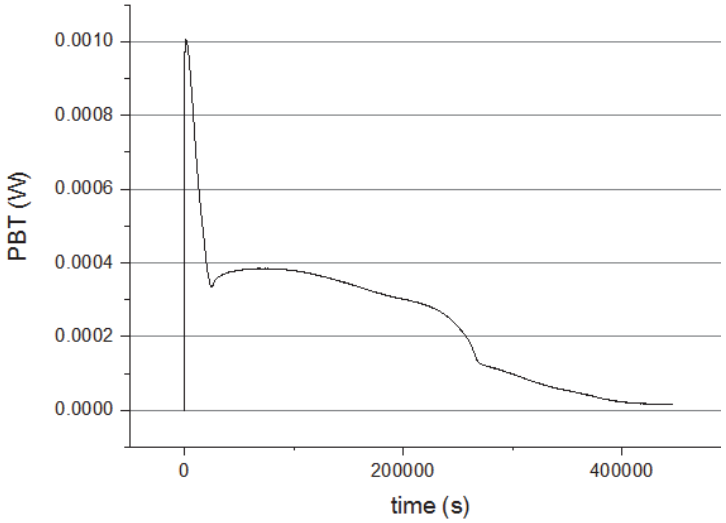


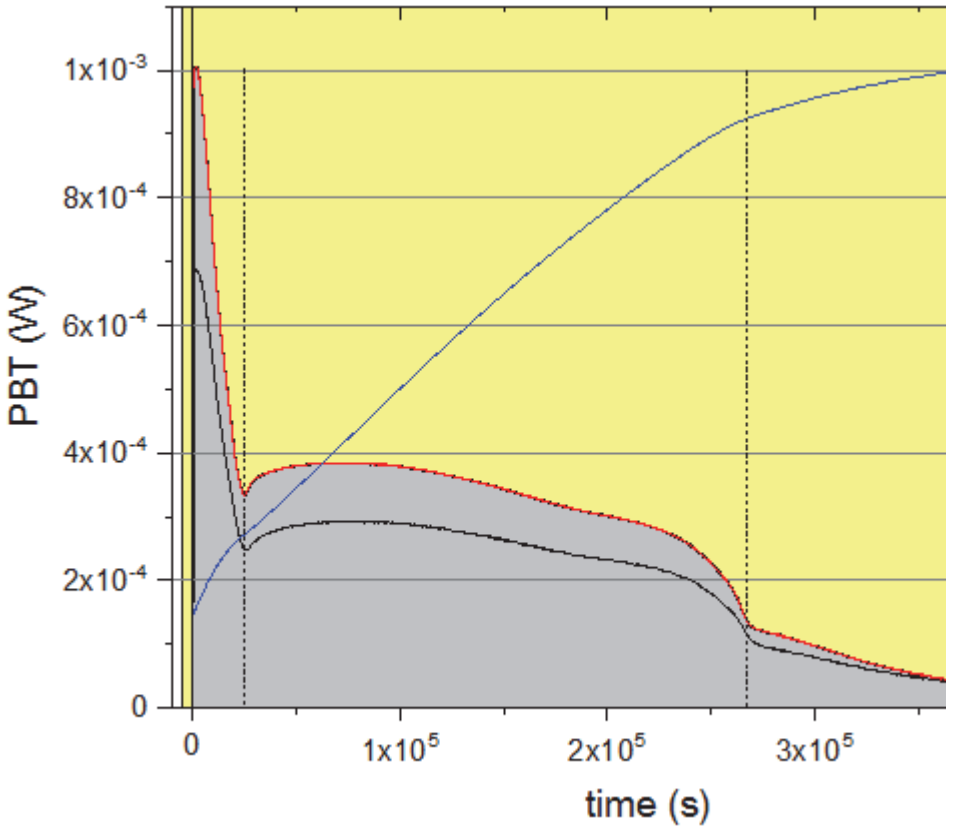
Stability of Ettringite



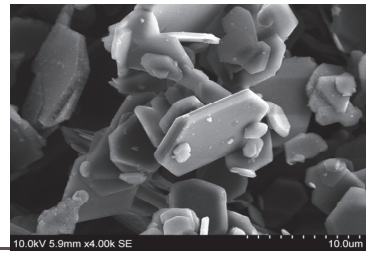
Stability RH vs T diagram of Ettringite



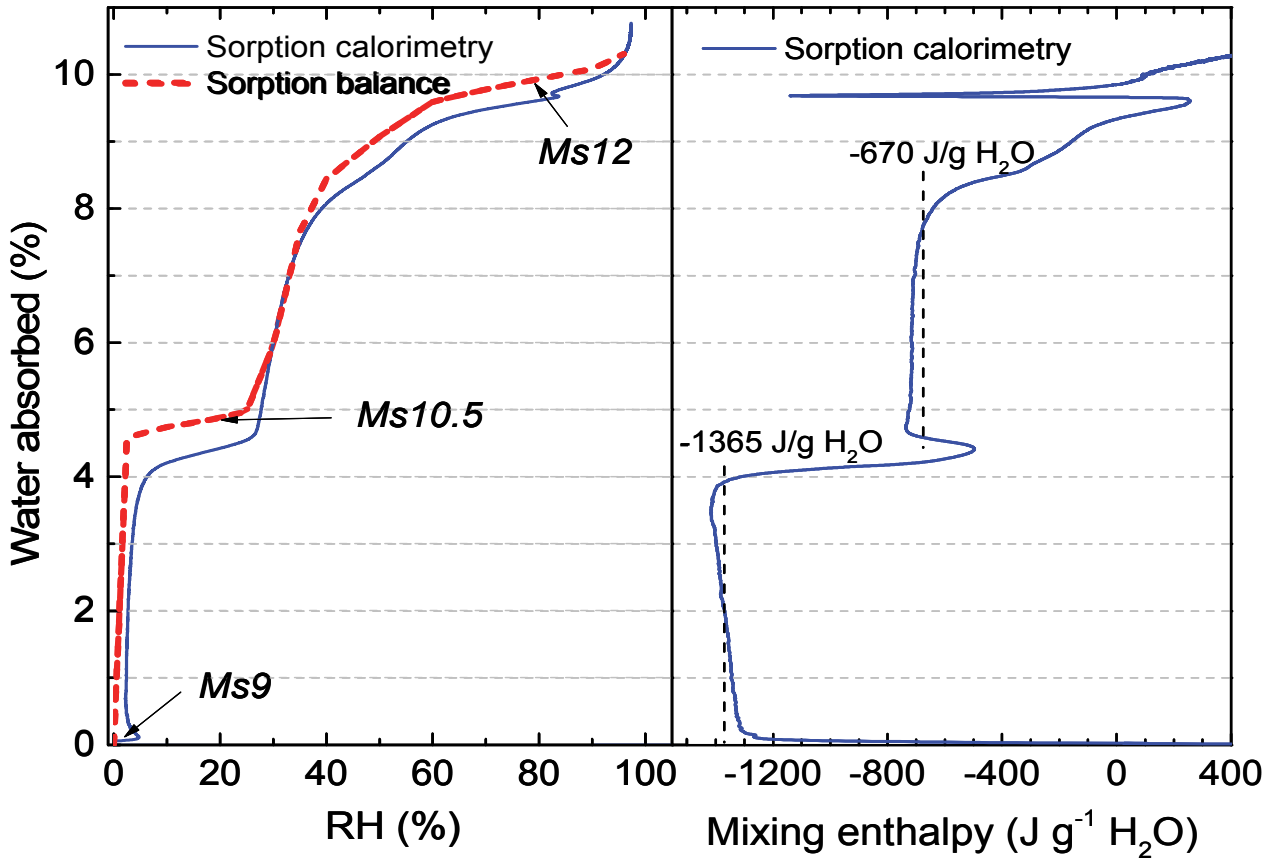




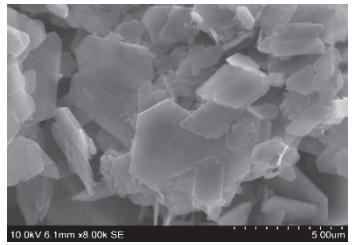
Sorption Calorimetry of Monosulfoaluminate



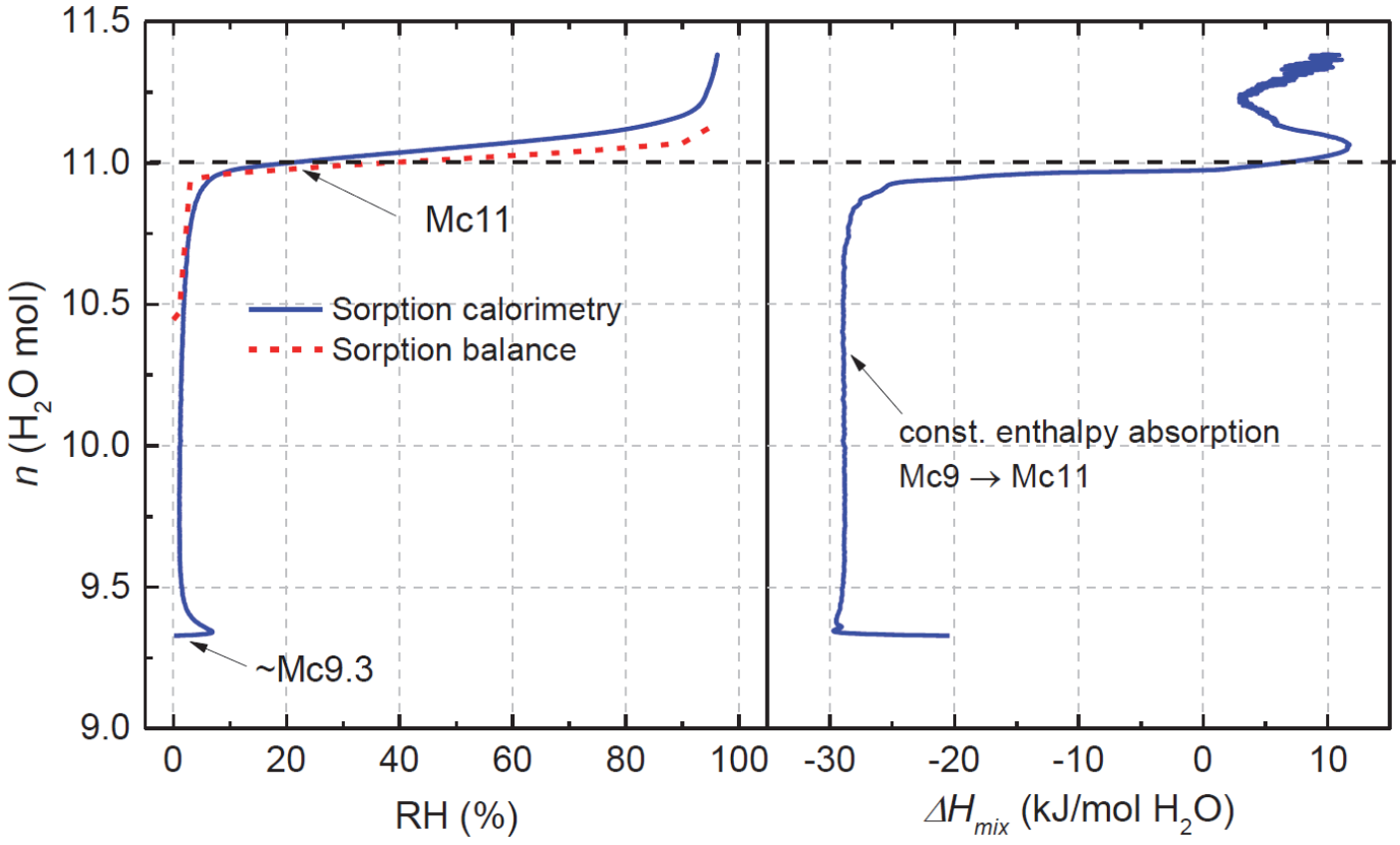
Good agreement between measurements from Sorption balance and Sorption Calorimetry



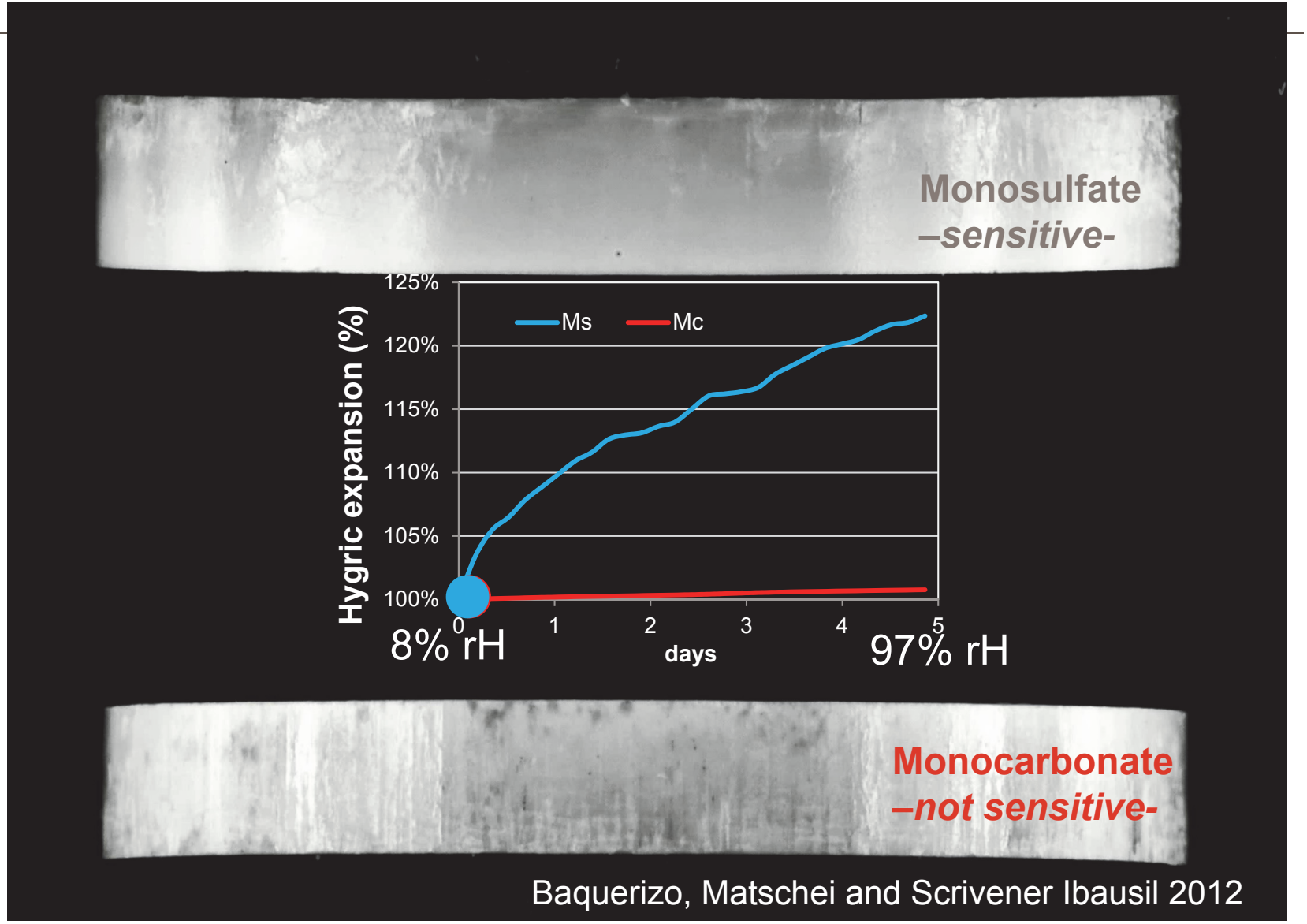
Sorption Calorimetry of Monocarboaluminate



Good agreement between measurements from Sorption balance and Sorption Calorimetry

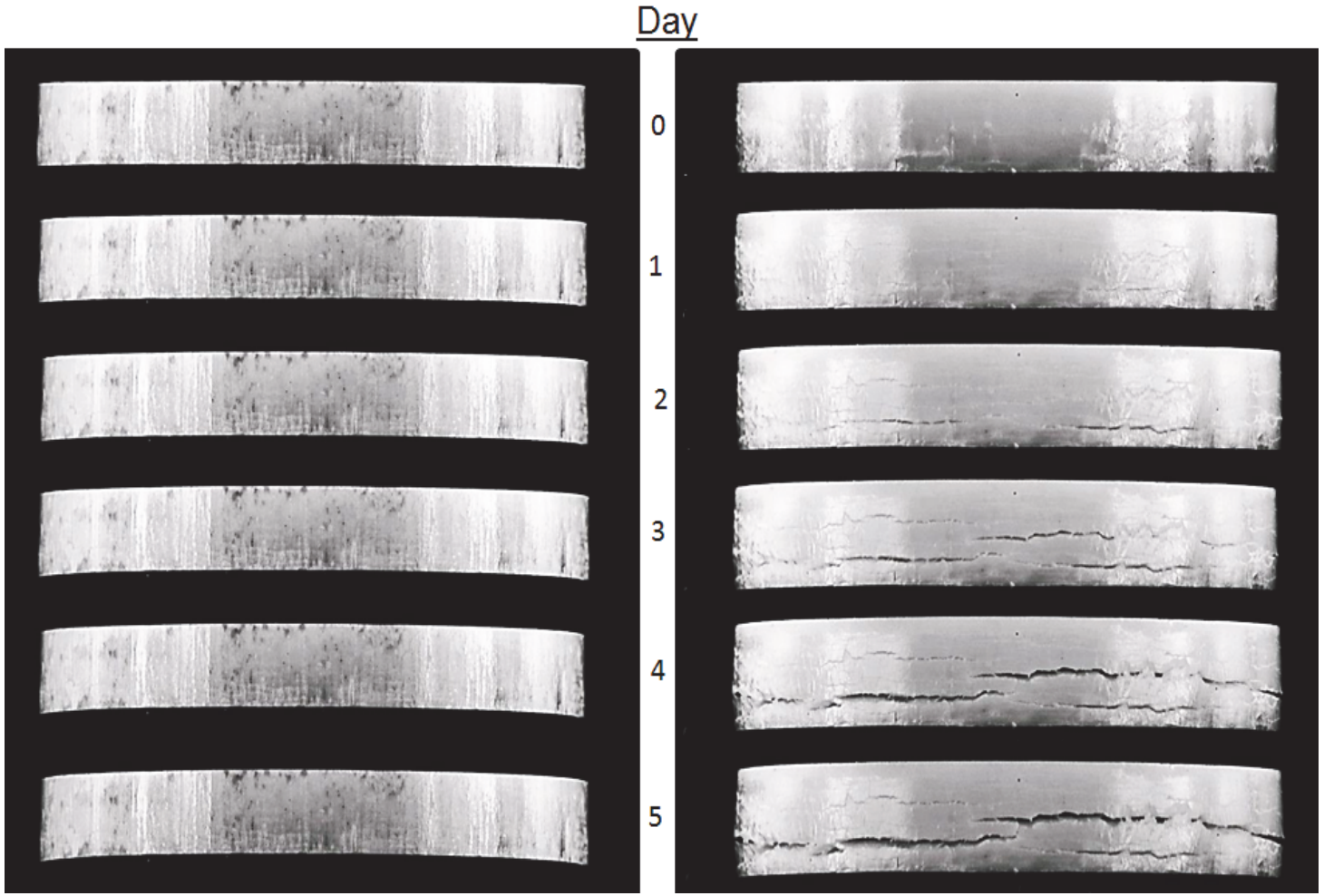


Volume stability Monosulfate vs Mocarbonate

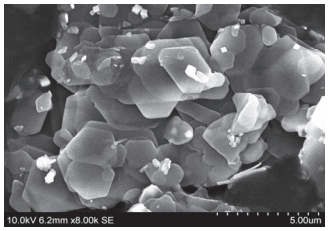


Monocarboaluminate
–not sensitive-

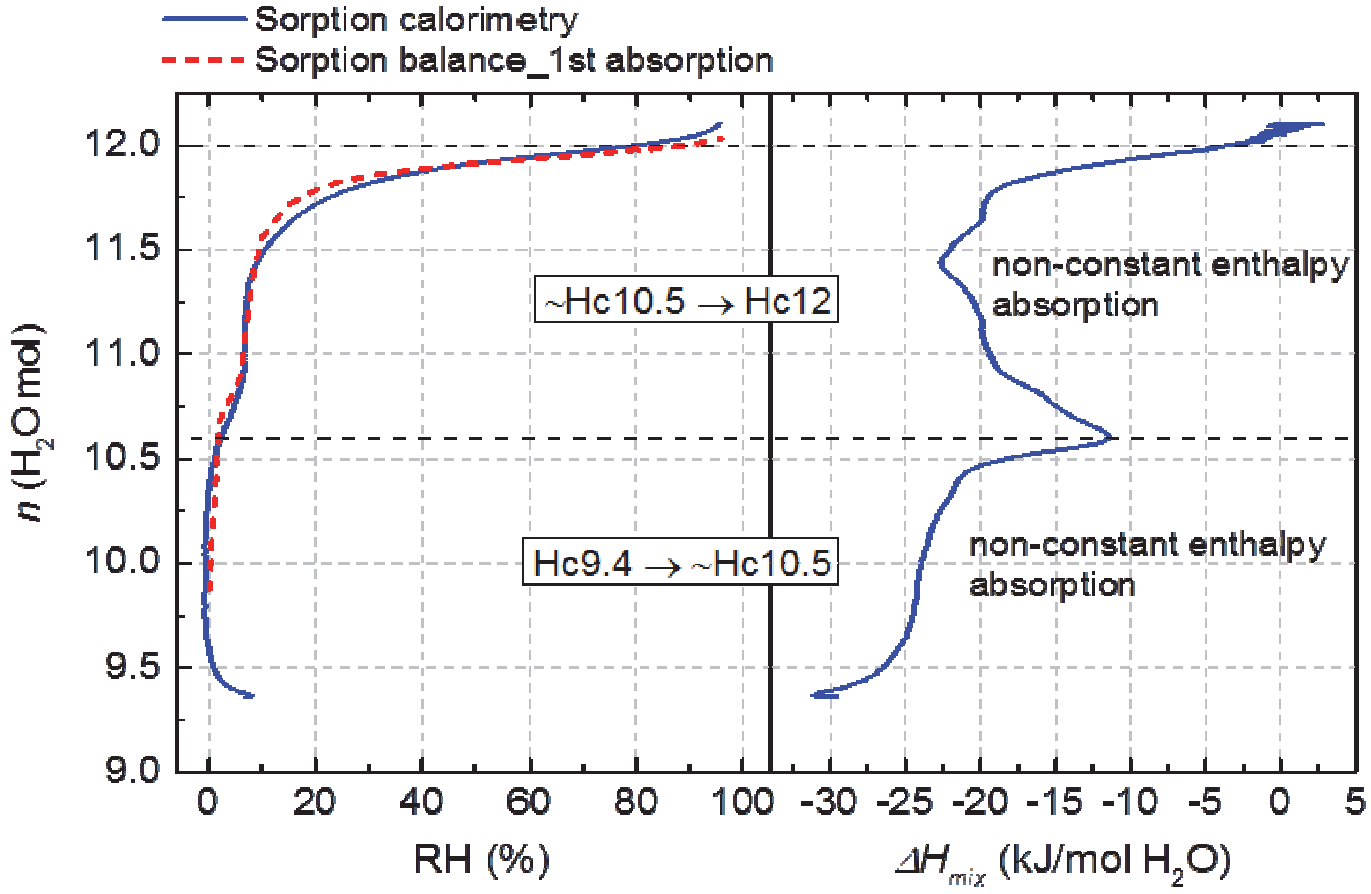
Monosulfoaluminate
–sensitive-



Sorption Calorimetry of Hemicarboaluminate



Good agreement between measurements from Sorption balance and Sorption Calorimetry

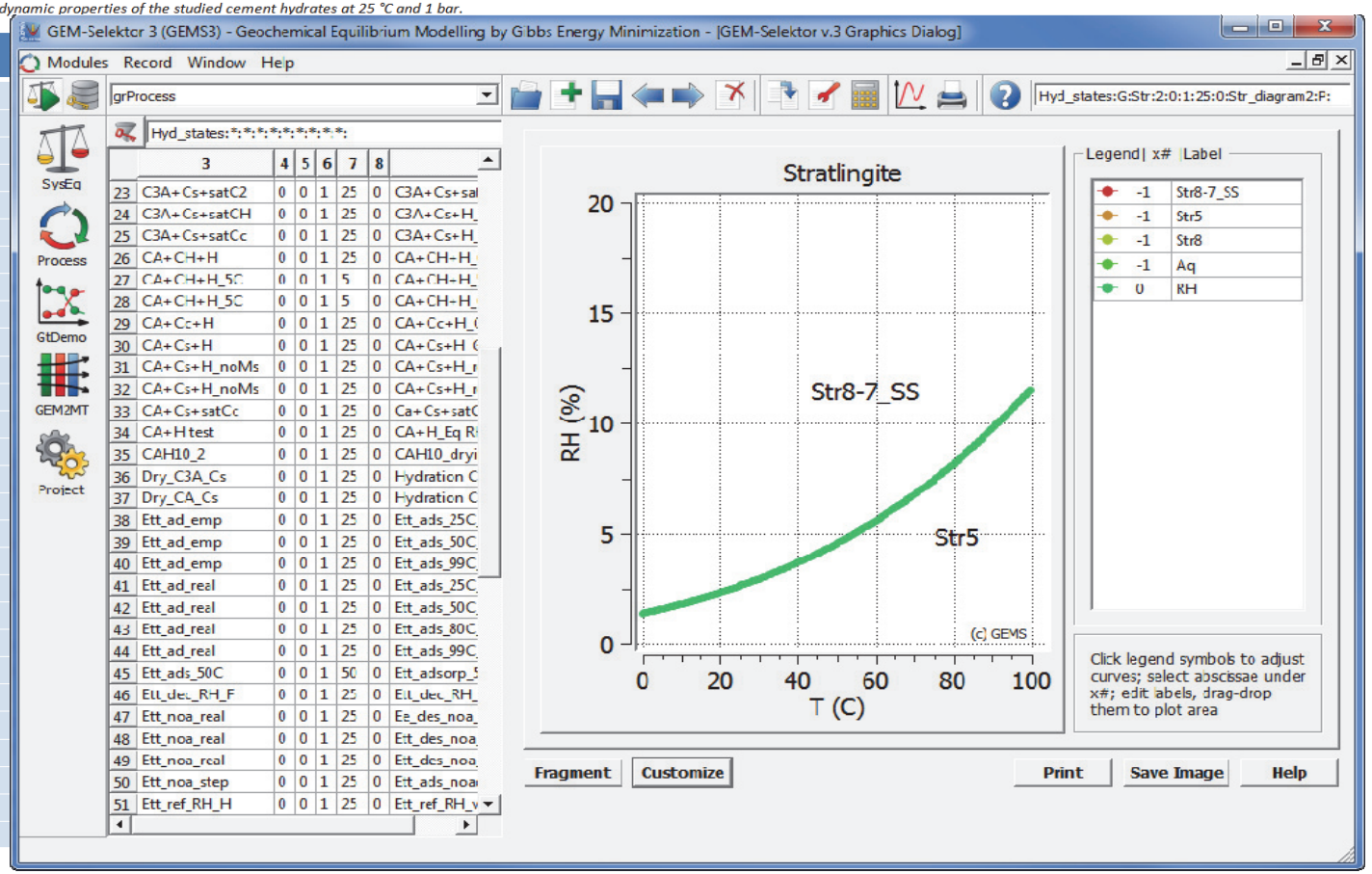


Now what?

Introduction of thermodynamic properties into database

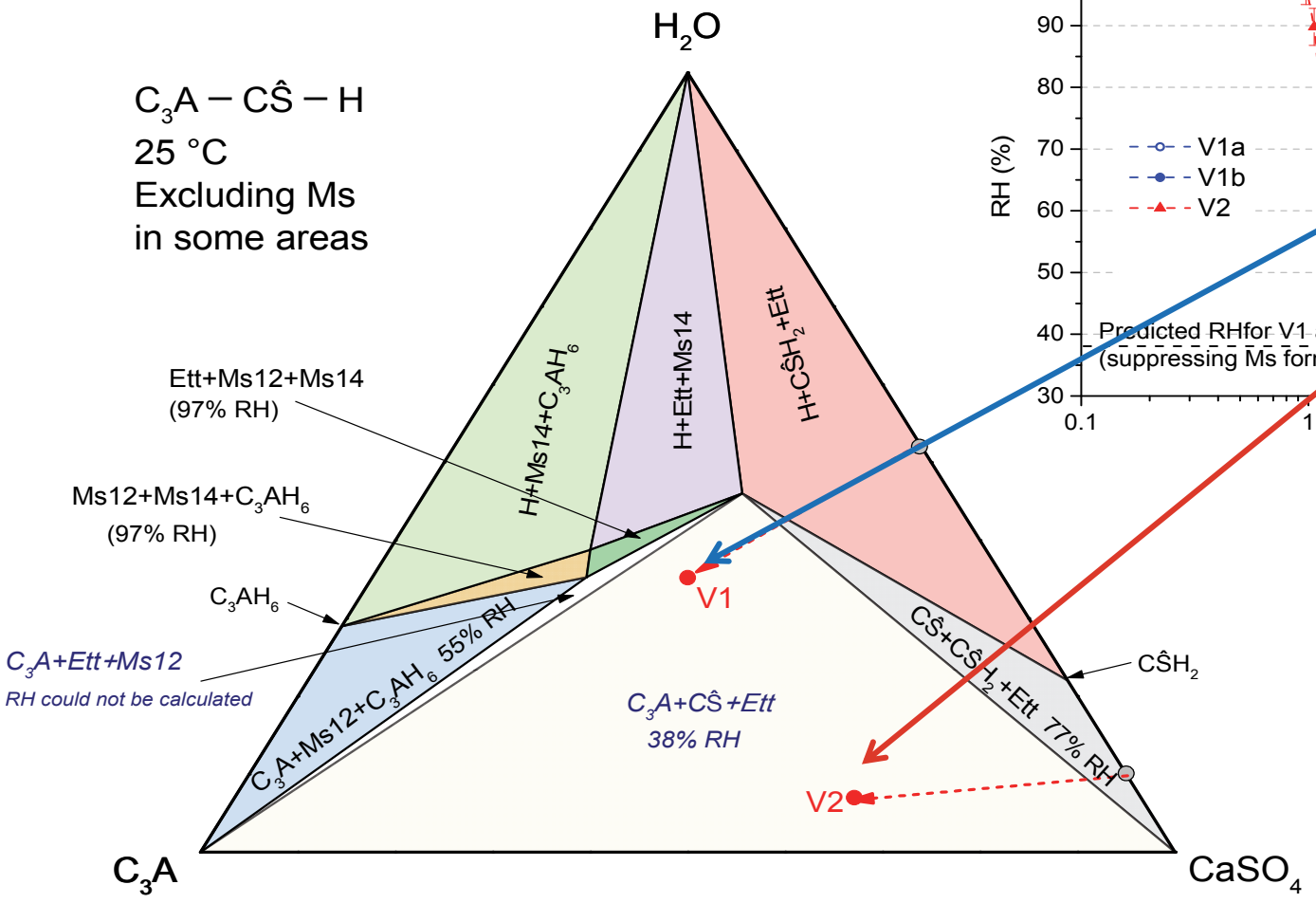
Table C:2 Standard molar thermodynamic properties of the studied cement hydrates at 25 °C and 1 bar.

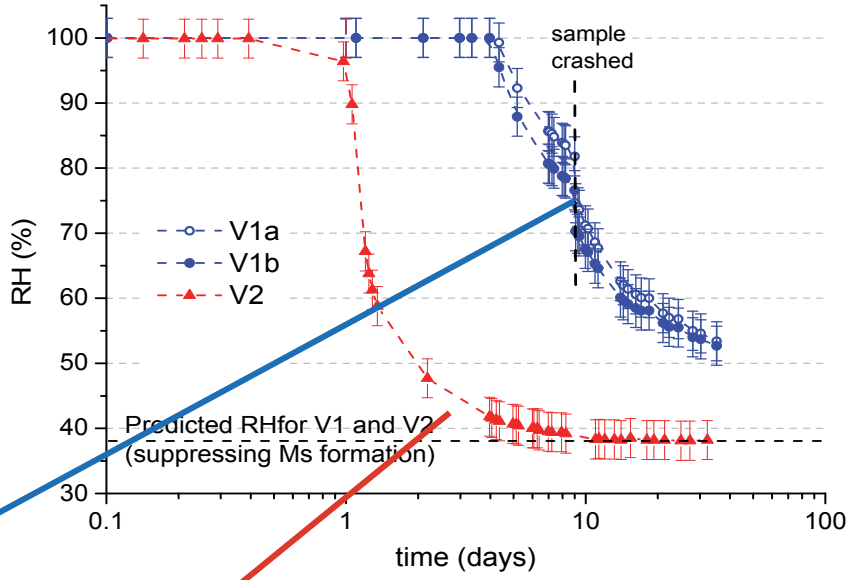
Phase	ΔG_f° (kJ/mol)
Ms16 – $C_4A\bar{S}H_{16}$	-8726.8
Ms14 – $C_4A\bar{S}H_{14}$	-8252.9
Ms12 – $C_4A\bar{S}H_{12}$	-7778.4
Ms10.5 – $C_4A\bar{S}H_{10.5}$ [b]	-7417.9
Ms10.5 – $C_4A\bar{S}H_{10.5}$ [c]	-7414.9
Ms9 – $C_4A\bar{S}H_9$	-7047.6
Mc11 – $C_4A\hat{C}H_{11}$	-7337.5
Mc9 – $C_4A\hat{C}H_9$	-6840.3
Hc12 – $C_4A\hat{C}_{0.5}H_{12}$	-7336.0
Hc10.5 – $C_4A\hat{C}_{0.5}H_{10.5}$	-6970.3
Hc9 – $C_4A\hat{C}_{0.5}H_9$	-6597.4
Str8 – C_2ASH_8	-5705.1
Str7 – C_2ASH_7 [d]	-5464.0
Str5.5 – $C_2ASH_{5.5}$	-5087.9
OH-AFm19 – C_4AH_{19}	-8749.9
OH-AFm13 – C_4AH_{13}	-7325.7
OH-AFm11 – C_4AH_{11}	-6841.4
Ett32	-15205.9
Ett30 [g]	-14728.1
Met13_desorption	-10540.6
Met13_absorption	-10678.2
Met9	-9540.4



What can we do with all this data?

Hydration of C_3A in the presence of $CaSO_4$



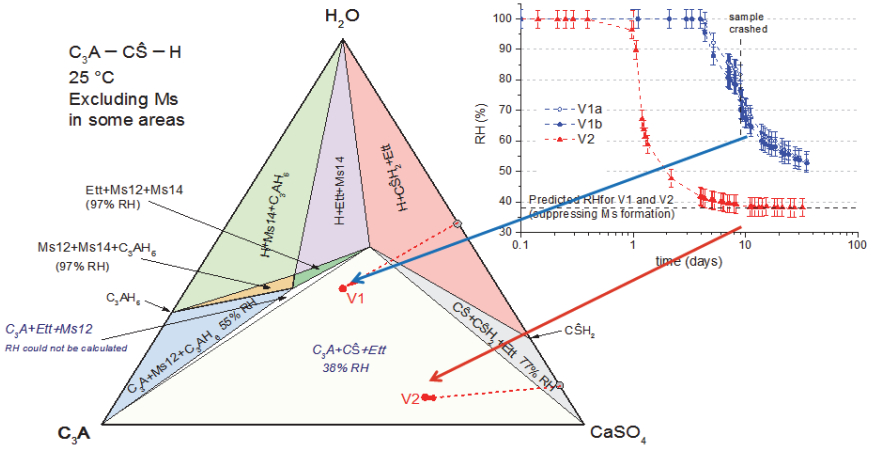


Where do we stand in our initial objectives?

Self-desiccation

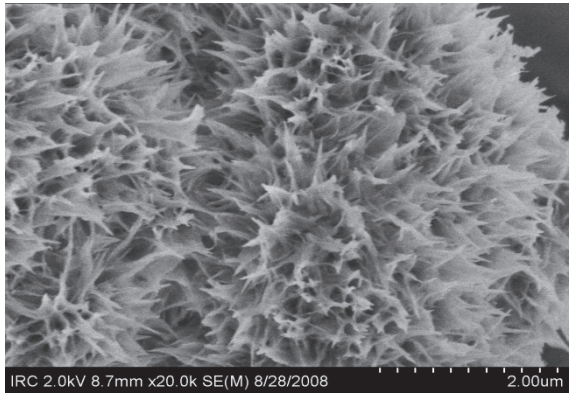
Can we estimate what will be the internal RH upon hydration? **Yes**

Can we estimate how long will it take? **No**



Have we answer all the questions important for OPC?

C-S-H*
(50-60% by volume), amorphous, varying water content, sensitive to RH.



Due to the complexity of C-S-H, this phase could not be part of our study……

Next steps:

Apply the developed methodology to C-S-H

Final remarks

- Cement hydrates are very sensitive to RH and T
- Some phases like Monocarbonate show high stability
- Ettringite is a rather stable phase, since very low humidity and/or high temperatures are need to decompose it.
  - But once it is dehydrated it is capable to completely rehydrate back to the initial state.
- The thermodynamic properties of the different phases can be used to predict more complex systems
  - Nevertheless kinetics play a big role and its prediction is not simple

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