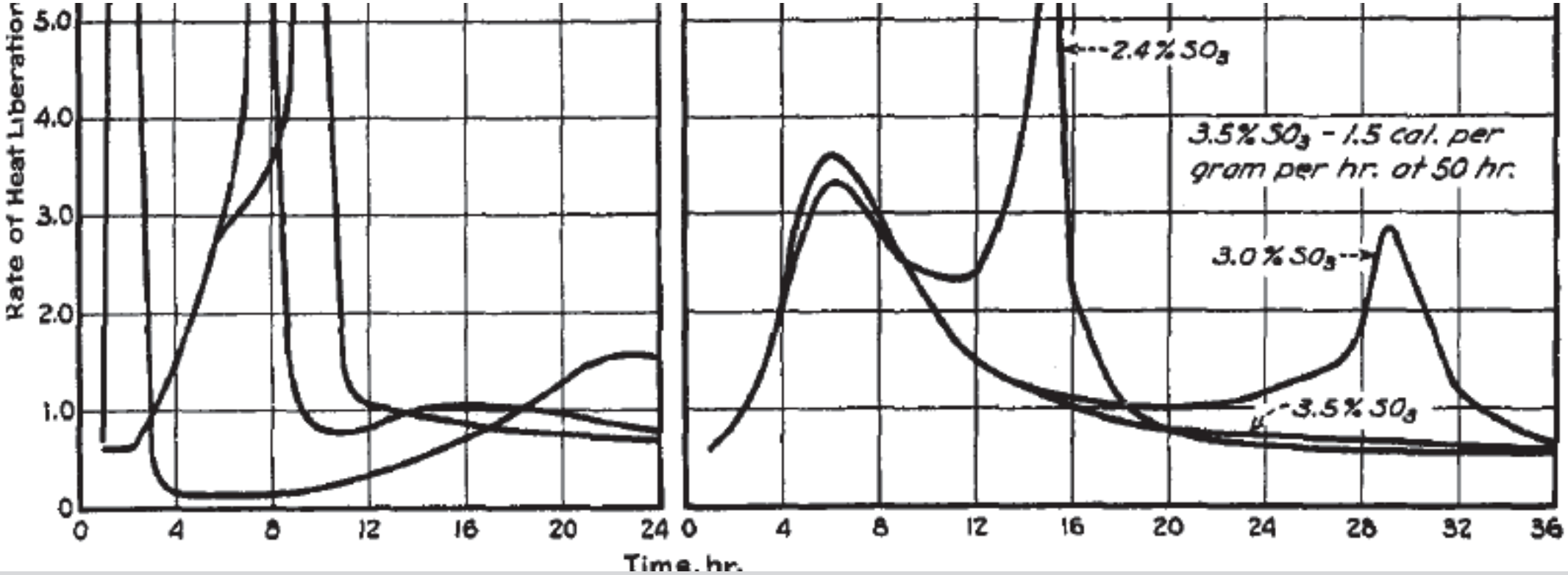



# „Towards understanding the optimum sulfate content of cement“

Thomas Matschei

HTW Dresden

4th European Cement Calorimetry Conference, Dec 11 and 12 2018

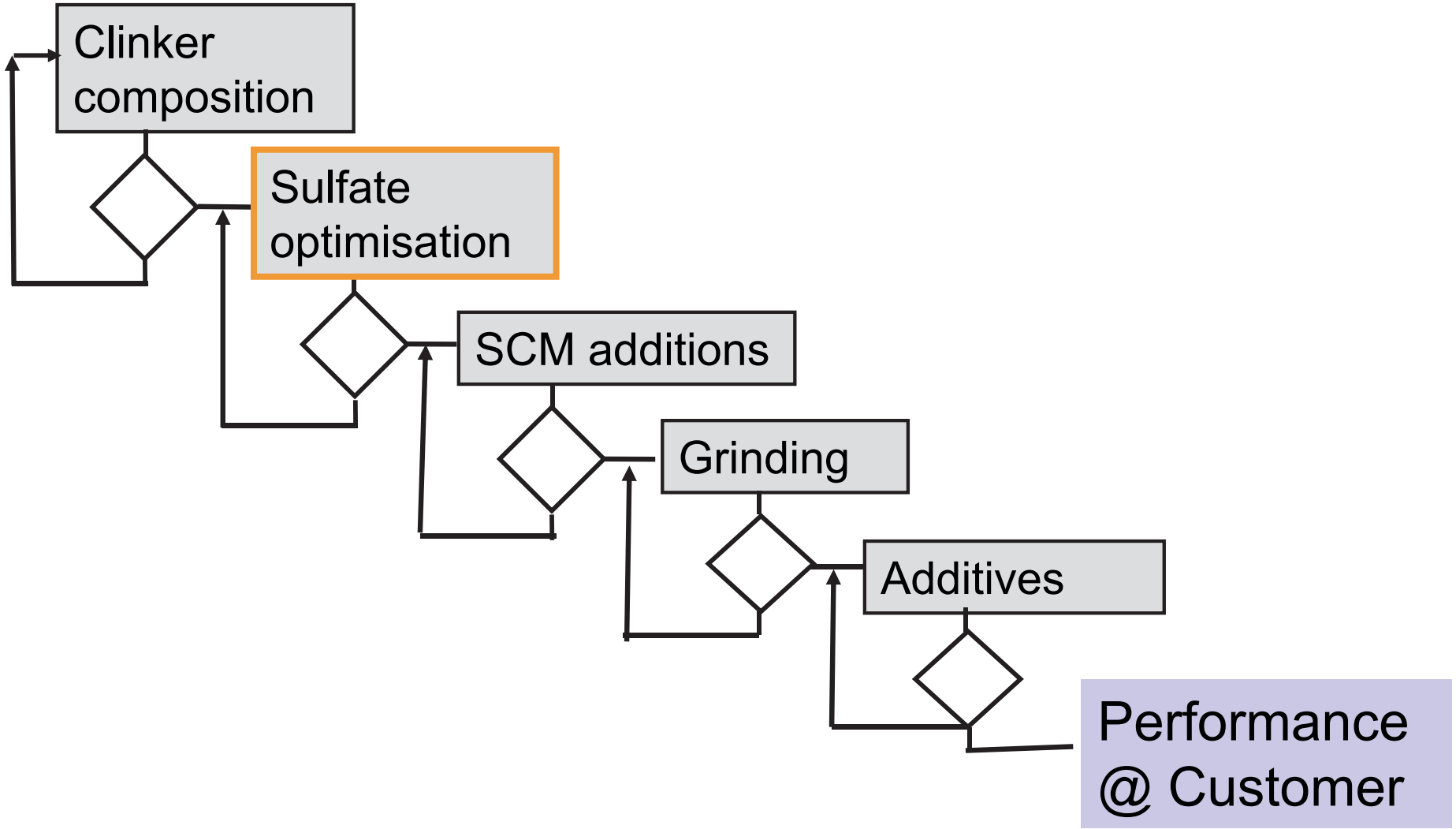
HOCHSCHULE FÜR TECHNIK UND WIRTSCHAFT DRESDEN
UNIVERSITY OF APPLIED SCIENCES

# Agenda

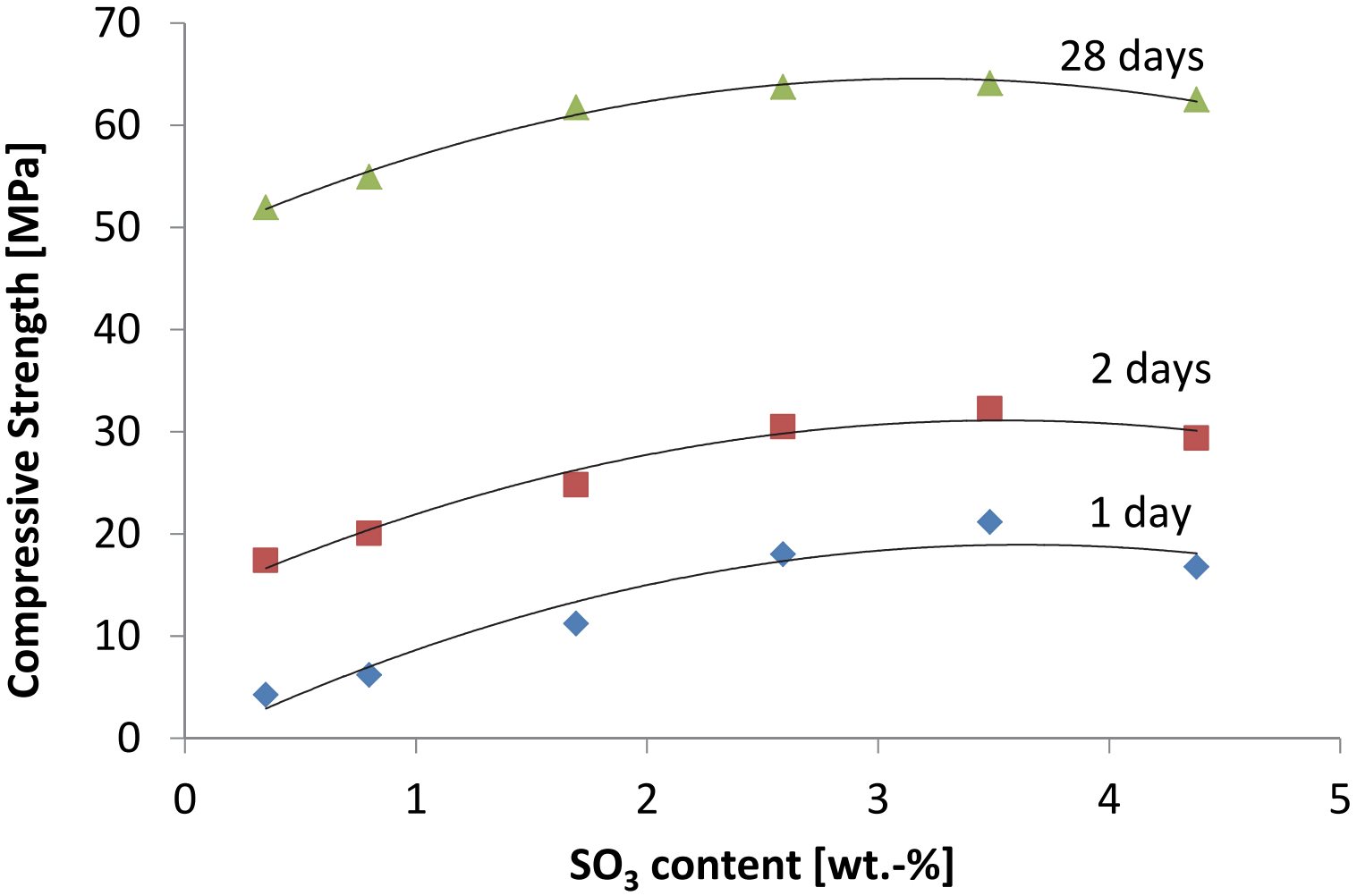
The talk will focus on:

1. Origin of aluminate – silicate interactions during alite hydration
2. The impact of sulfate on controlling aluminate – silicate interactions during cement hydration
3. The importance of phase equilibria to understand the role of sulfate during cement hydration

# Sulfate optimisation is one of the most important measures in cement design



# Importance of sulfate optimisation




*OPC*

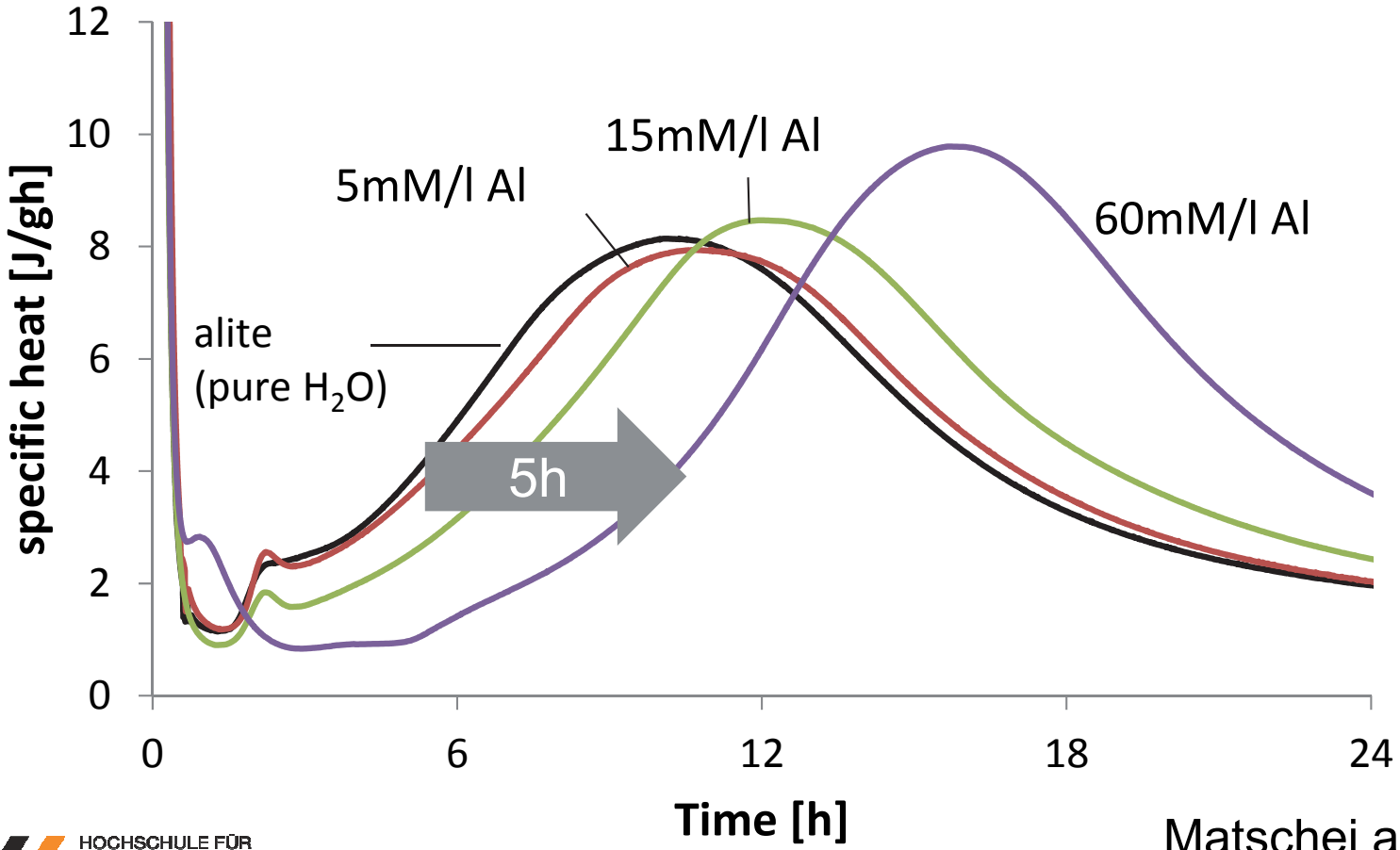
*w/c = 0.5*

*Own investigations*

- Sulfate additions have strong impact on strength development, especially at early ages

# Role of Alumina

Increasing alumina concentrations in the pore solution significantly retard alite hydration either due to suppression of C-S-H growth (Begarin et al 2009) and/or inhibition of $C_3S$ dissolution (Nicoleau et al 2014 and Pustovgar et al 2017)




*Own investigations*

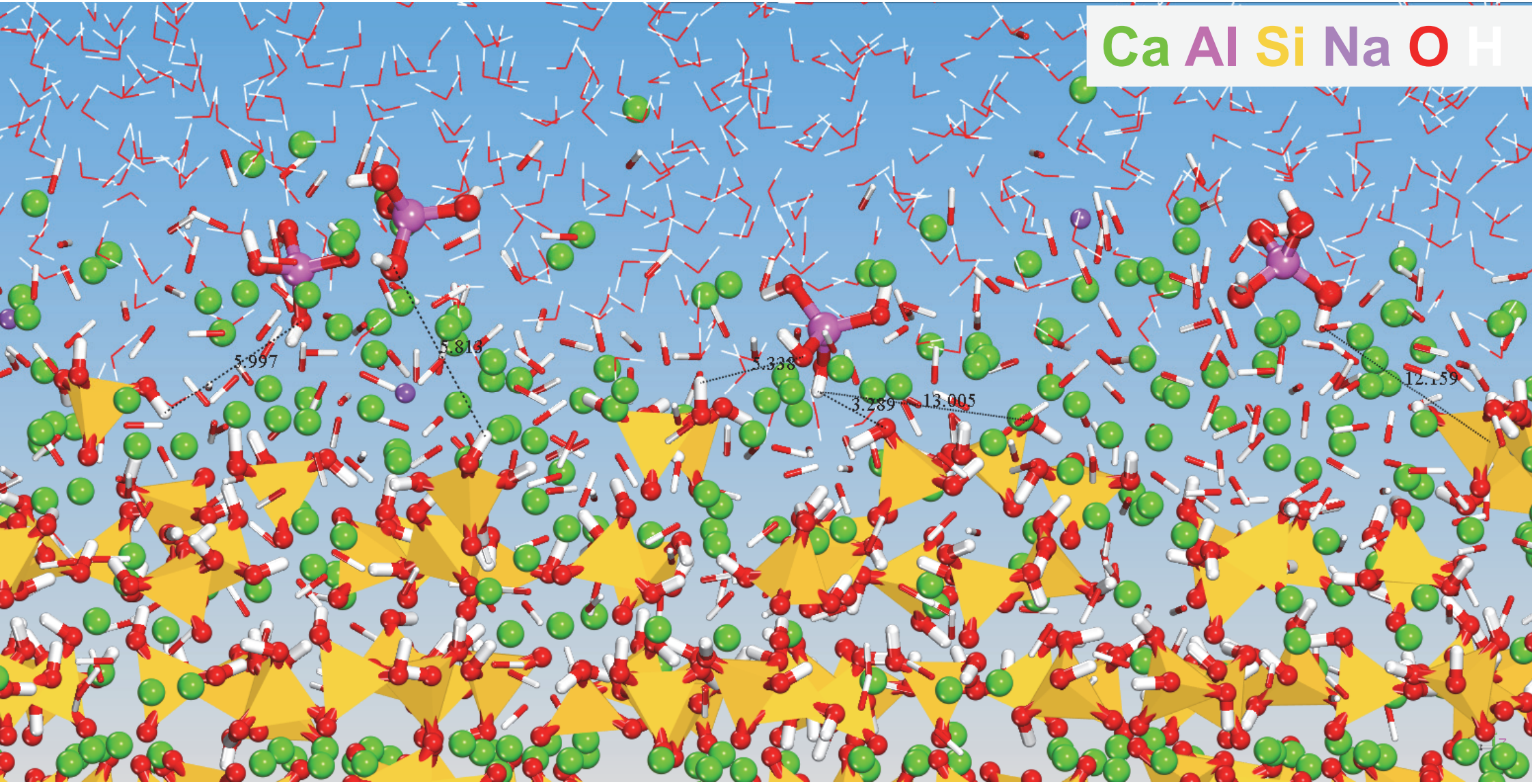
*Isothermal calorimetry (mixed externally)*

*Synthetic Alite + sodium aluminate solutions*

*w/s = 0.5*

Matschei and Costoya; Ibausil 2012

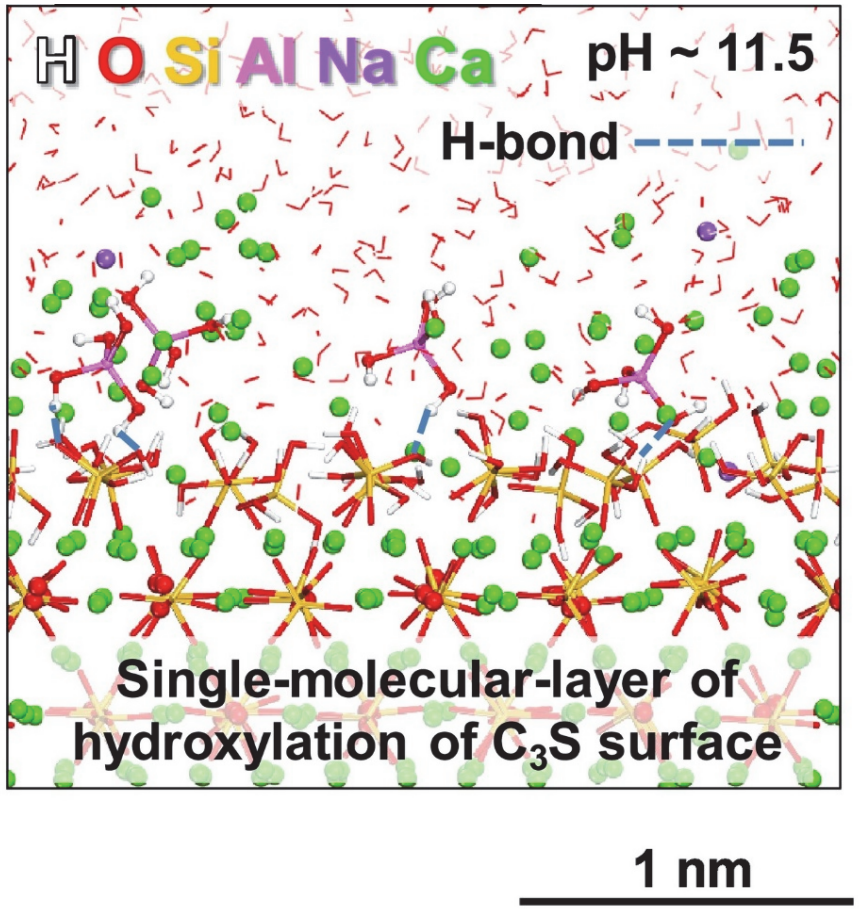
# Role of Alumina

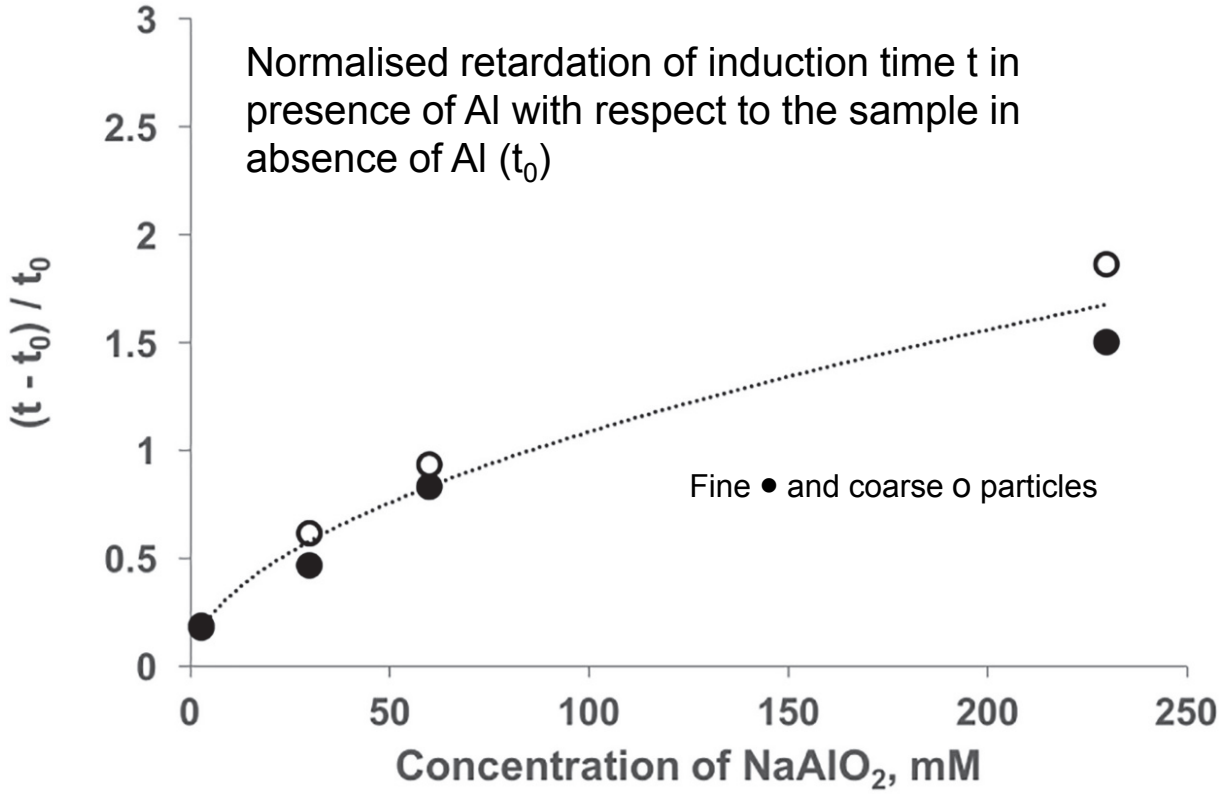



MD Simulations by R. Mishra in Pustovgar et al 2017

# Role of Alumina

At high Alumina concentrations formation of Calcium-Aluminate complexes that adsorb on reactive sites of hydroxylated $C_3S$ surface thereby hindering $C_3S$ dissolution

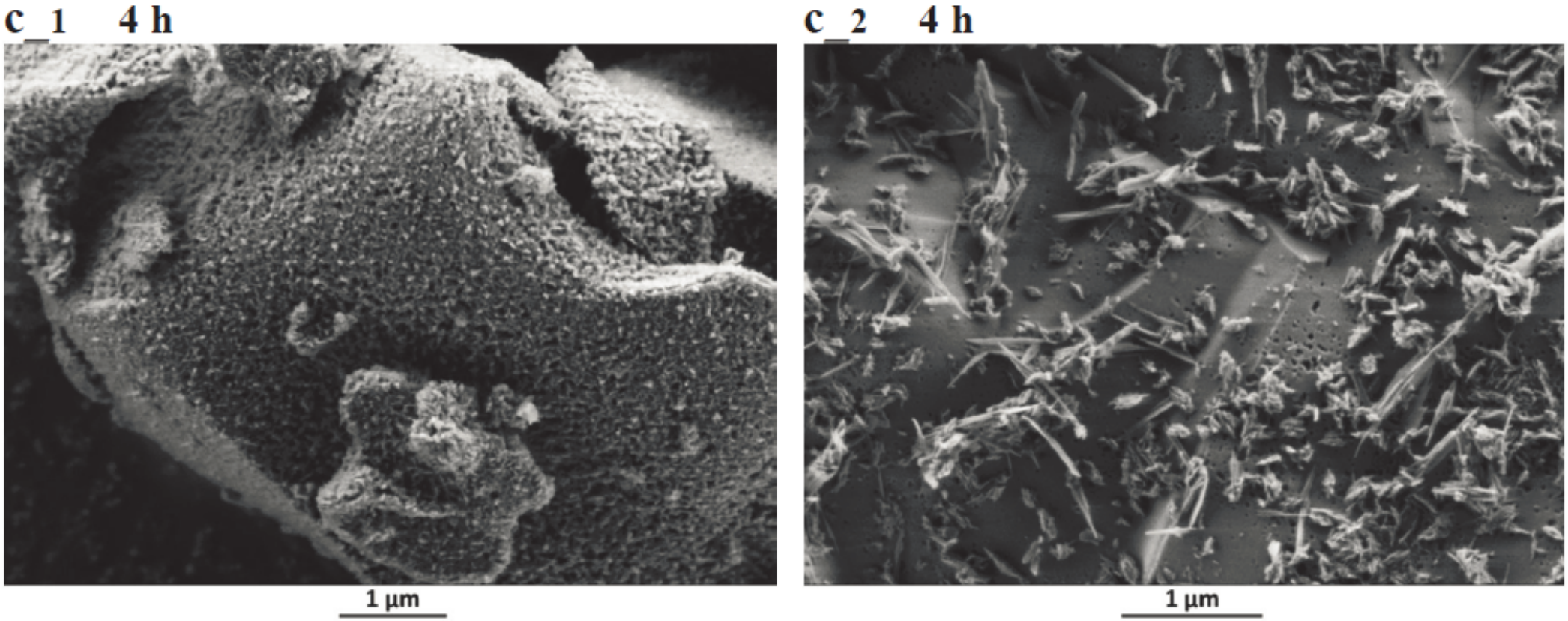



Pustovgar et al 2017

# Role of Alumina

At high Alumina concentrations formation of Calcium-Aluminate complexes that adsorb on reactive sites of $C_3S$ thereby hindering $C_3S$ dissolution



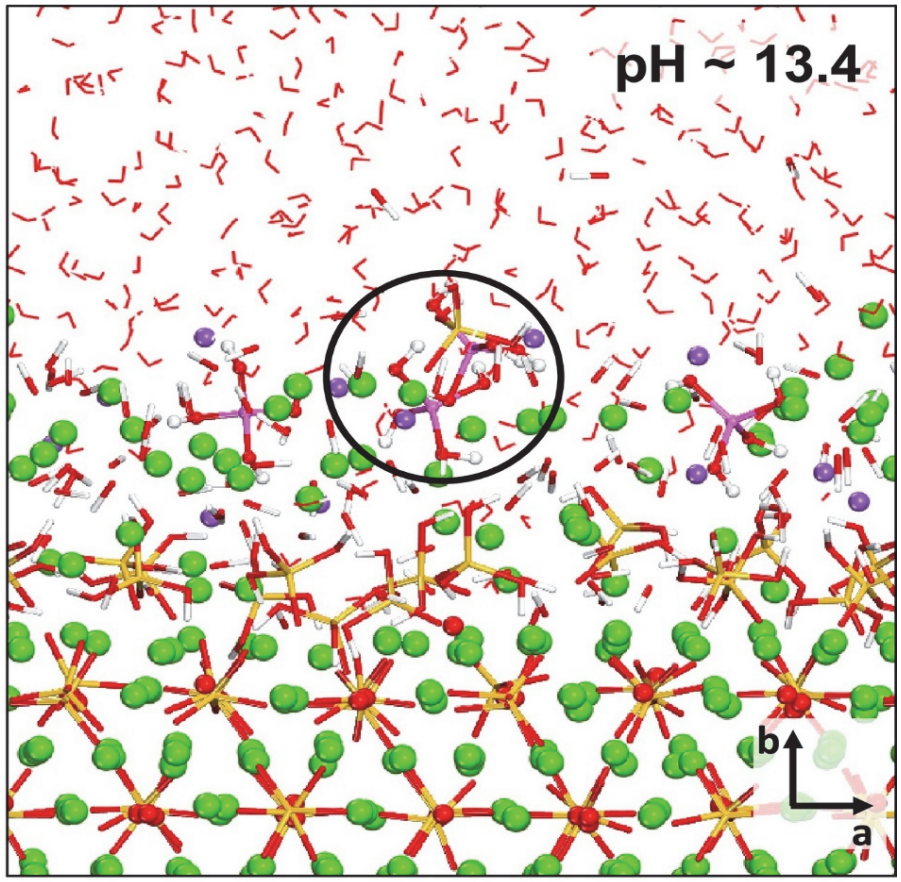

Water

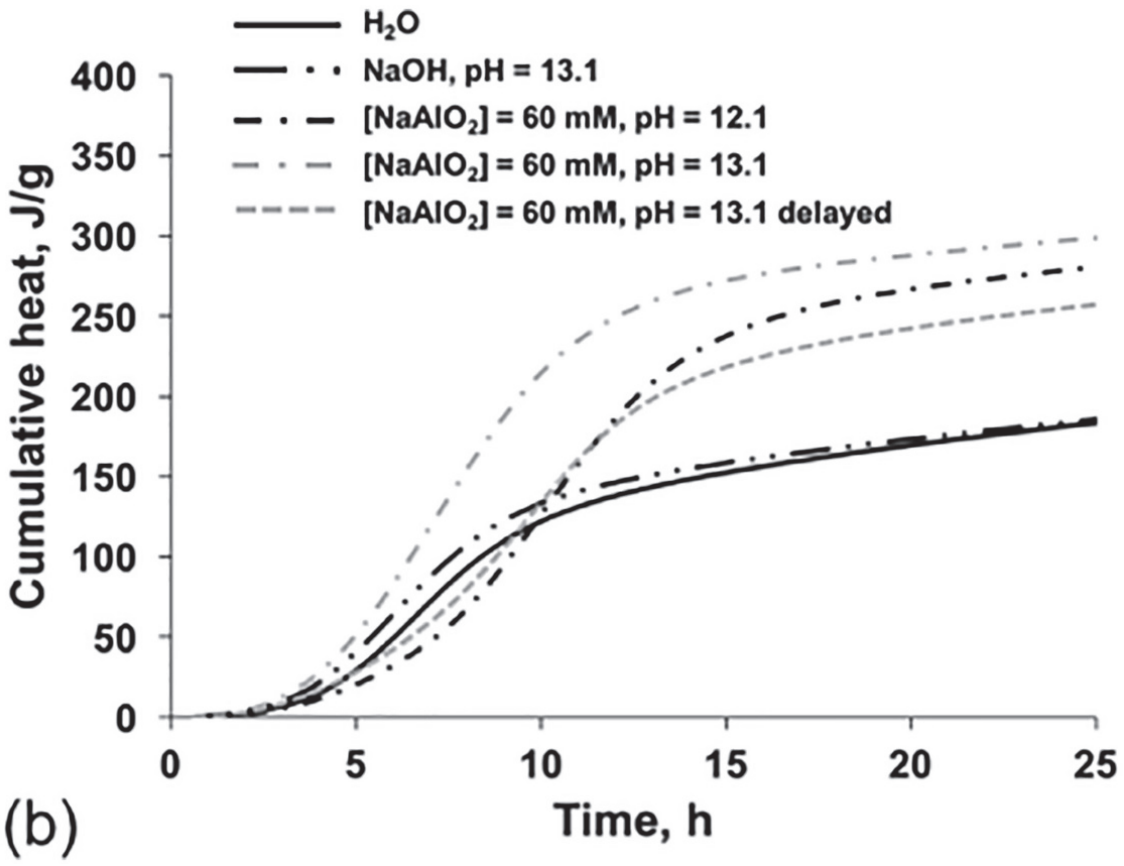
60mM $NaAlO_2$

Pustovgar 2017

# Role of Alumina – Role of pH

At higher pH-values formation of Al-Si-Complex; Sodium replaces Calcium thereby hindering adsorption of complexes on $C_3S$ sites → less retardation

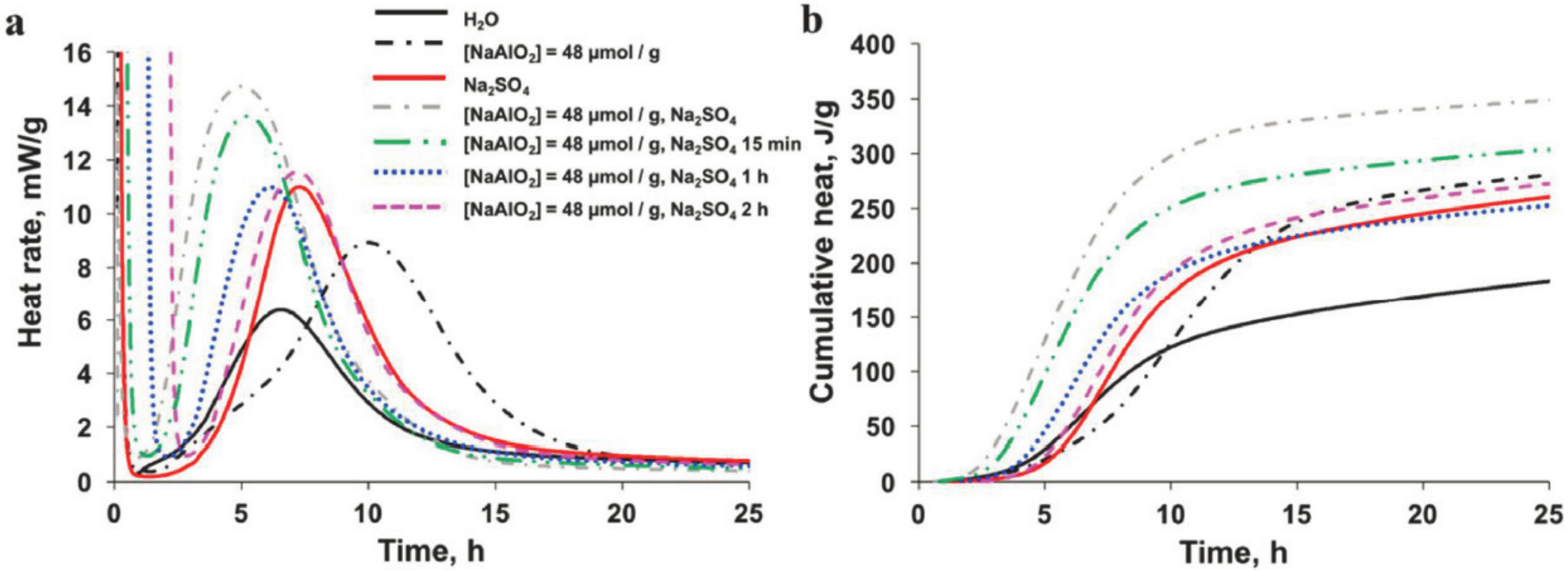



Pustovgar et al 2017

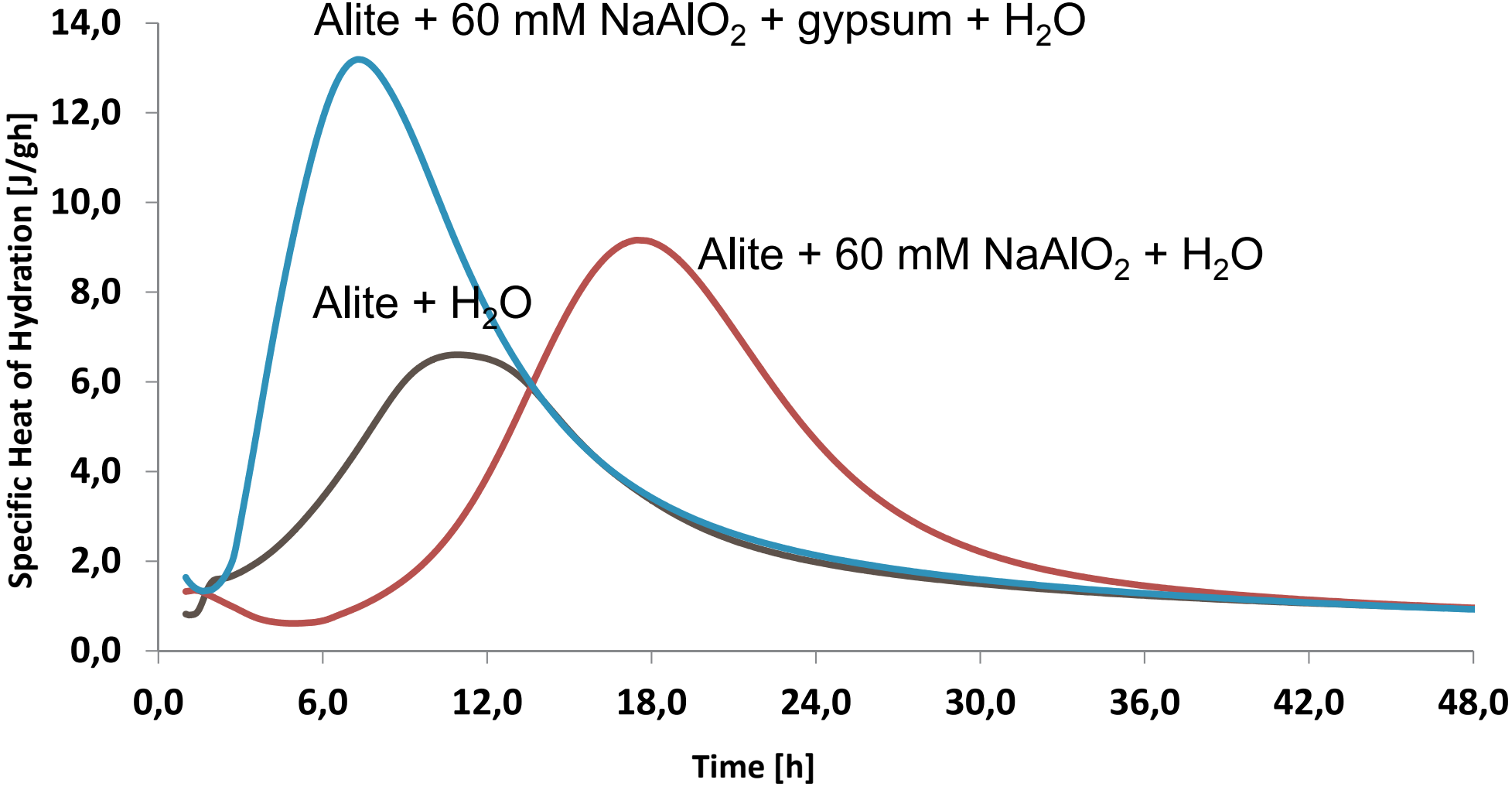
# What is the link between sulfate optimisation and alumina inhibition?

# The addition of sulfate “cancels” the alumina inhibition effect



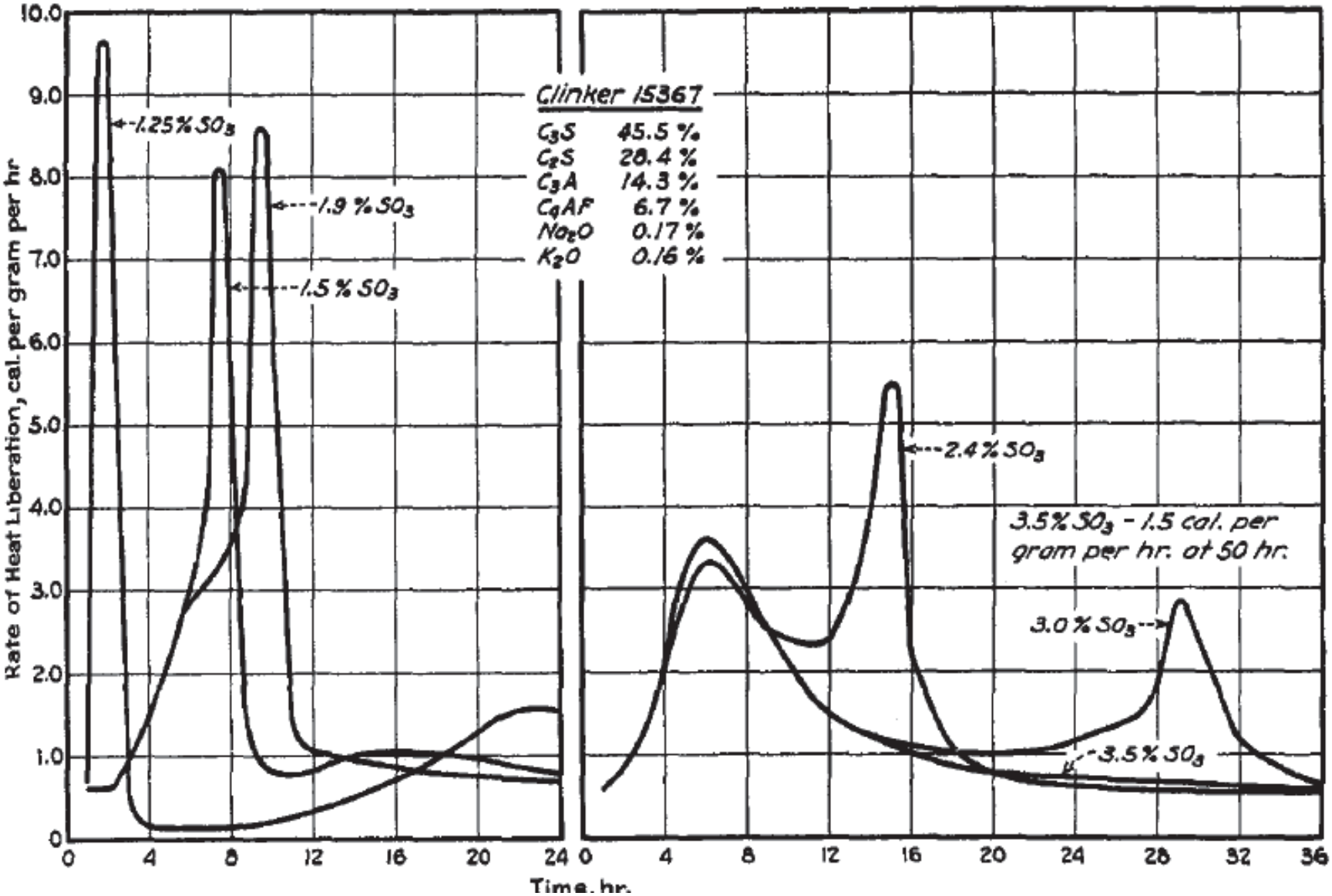

…but apparent impact of time of sulfate addition

# The addition of sulfate “cancels” the alumina inhibition effect



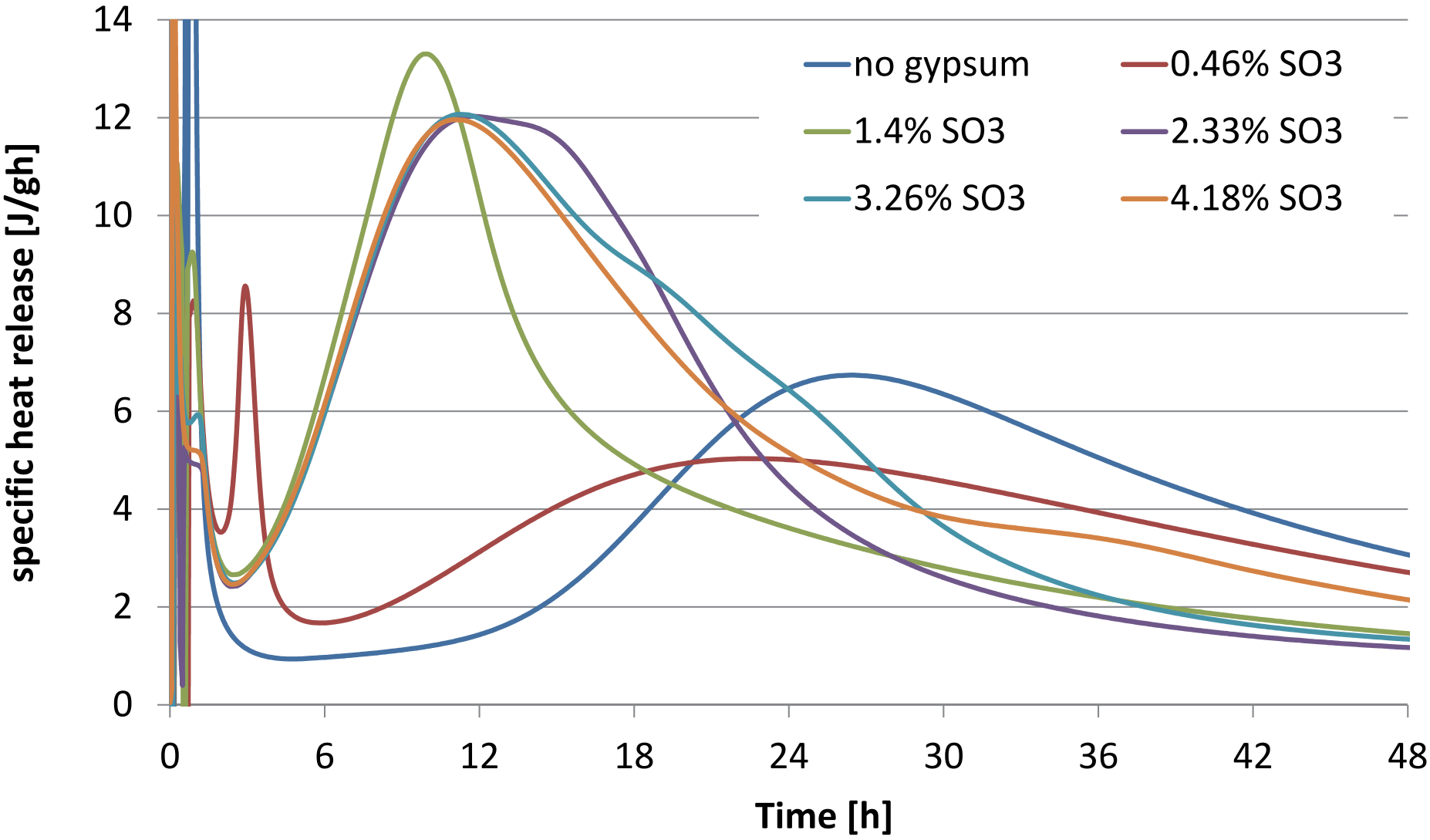
# From alite to cement

## *Lerch 1946*



# From alite to cement

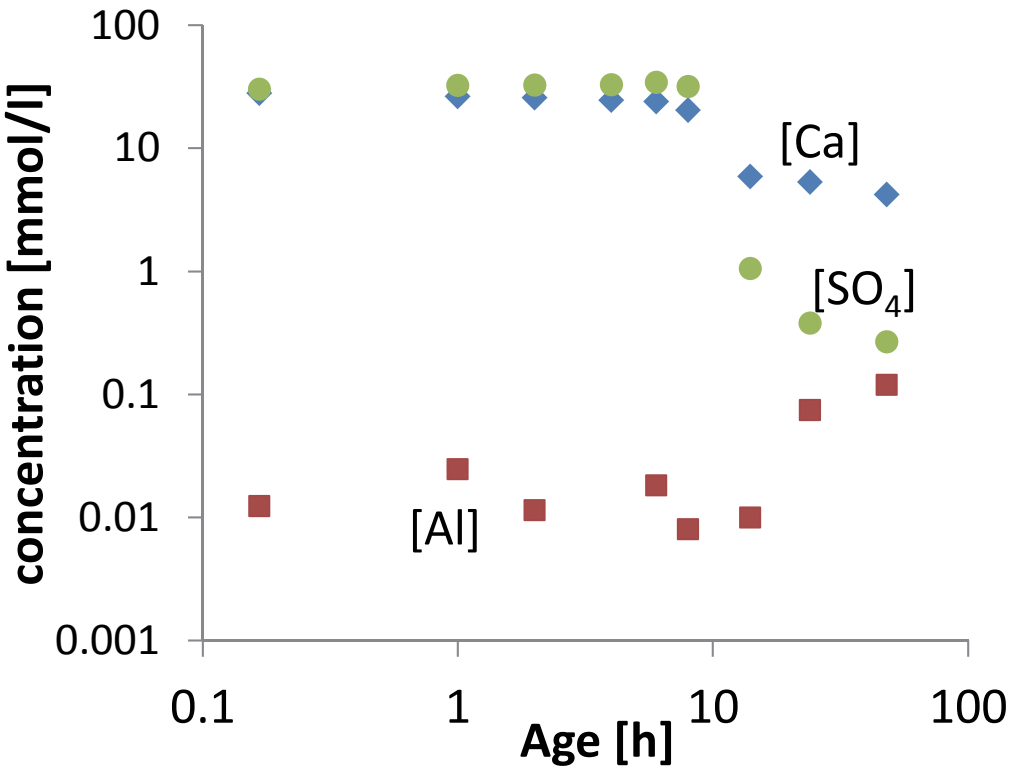
*own studies*



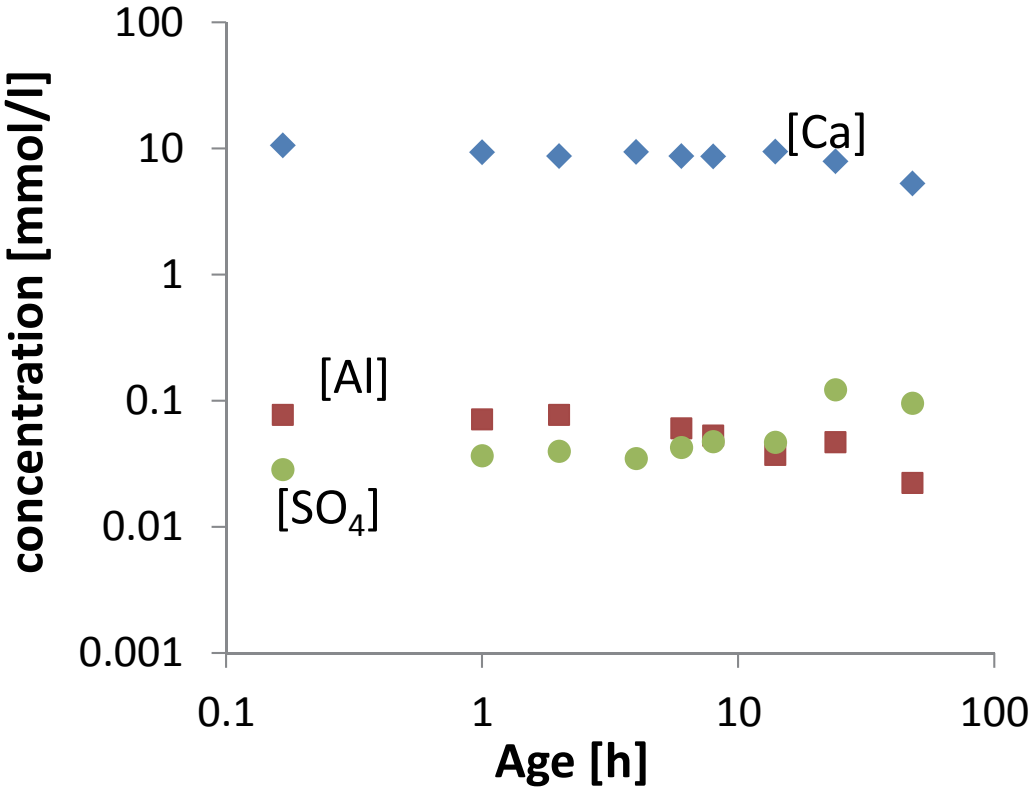

| Phase | $C_3S$ | $C_2S$ | $C_3A_{tot}$ | $C_4AF$ | $CaO_{free}$ | portlandite | periclase | $Na_2O_{eq}$ |
|---|---|---|---|---|---|---|---|---|
| *[wt.-%]* | 62.7 | 18.1 | 8.1 | 10.0 | <0.2 | <0.2 | 0.3 | 0.54 |

# What happens if gypsum is absent?

1.) Well sulfated system
(OPC with 5% gypsum; w/c=0.5)




2.) Undersulfated system
(pure clinker; gypsum absent, w/c=0.5)

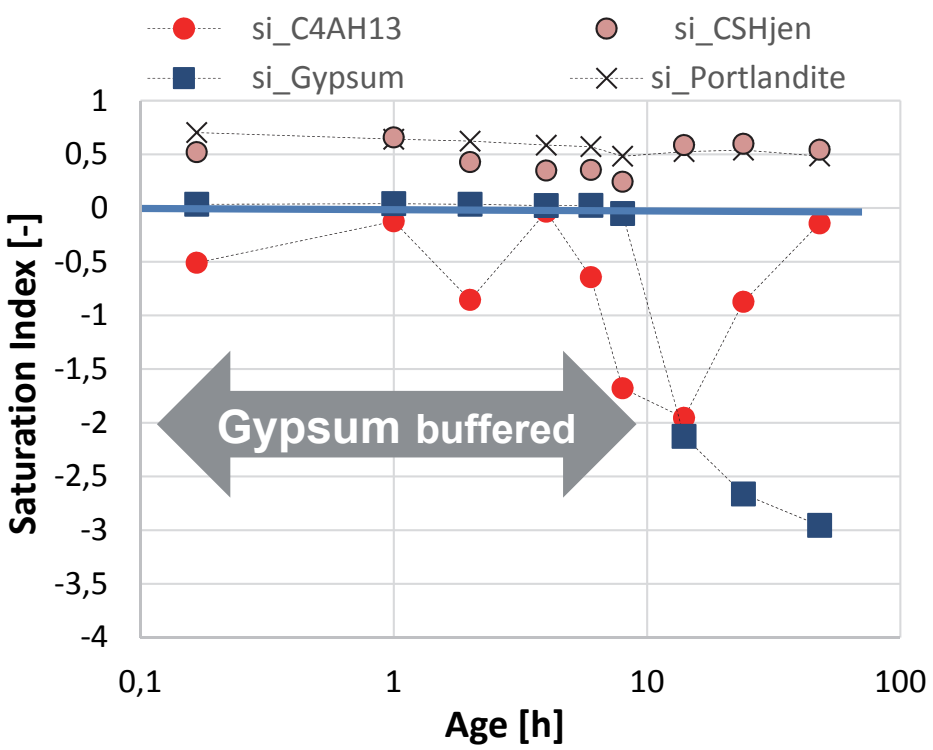



- alumina concentrations increase in gypsum depleted systems

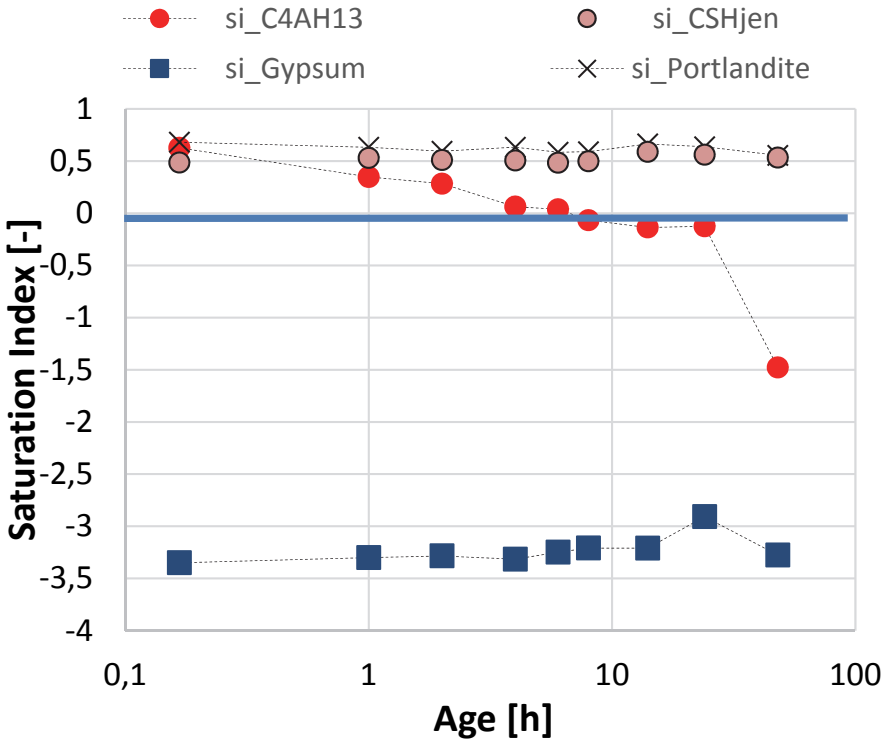
Matschei IBAUSIL 2012

# What happens if gypsum is absent?

## 1.) Well sulfated system
(OPC with 5% gypsum; w/c=0.5)

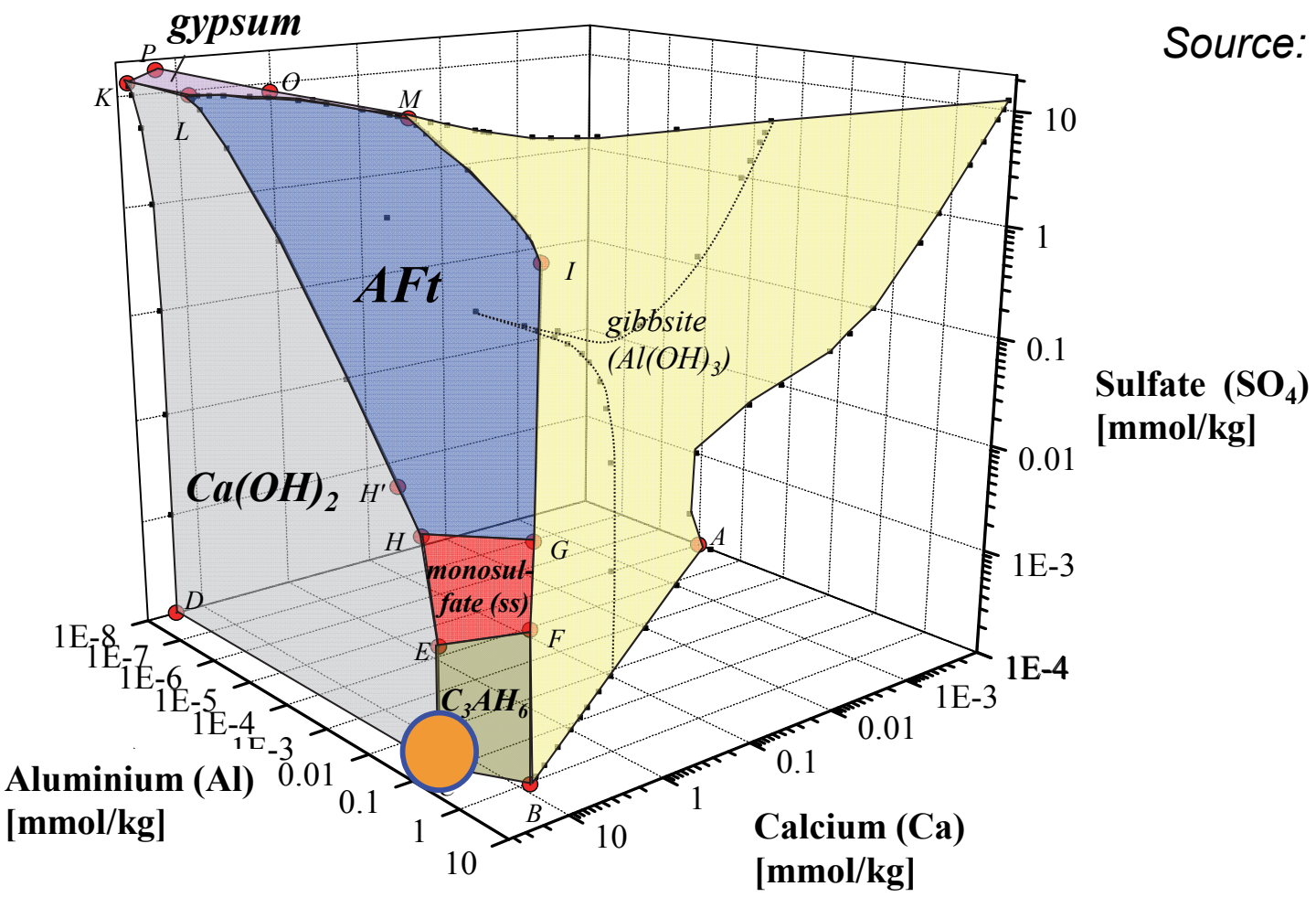



## 2.) Undersulfated system
(pure clinker; gypsum absent, w/c=0.5)




- Undersulfated System initially AFm buffered
- No impact on C-S-H or portlandite saturation

# Thermodynamic Phase Equilibria
# System $CaO-Al_2O_3-CaSO_4-H_2O$ and the role of gypsum

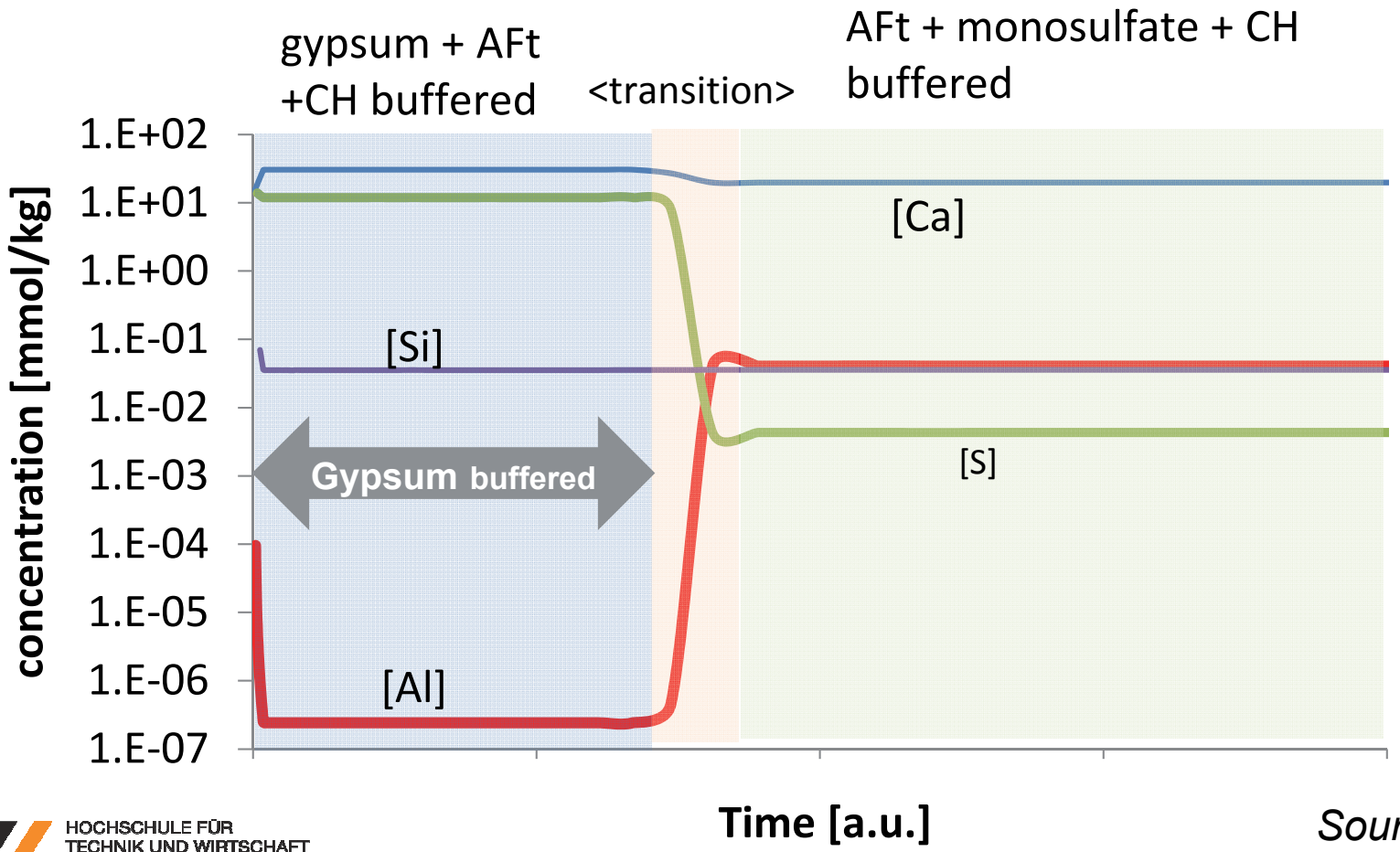



*Source: own calculations*

- The phase equilibria gypsum-portlandite-ettringite theoretically suppresses alumina concentrations to very low levels

# Thermodynamic Phase Equilibria
# Role of gypsum during cement hydration (kinetic model)

- Gypsum is a very good sulfate buffer in the early stages of hydration
- In presence of **gypsum, portlandite and ettringite** alumina concentrations should be theoretically suppressed to very low concentrations

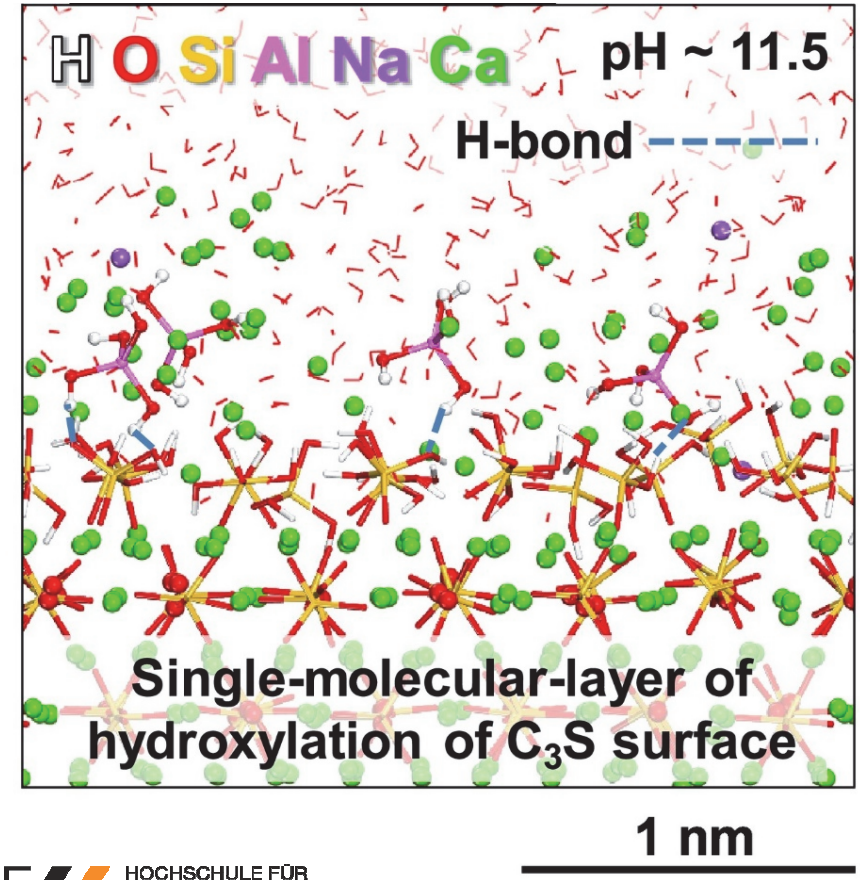



*Source: own calculations*

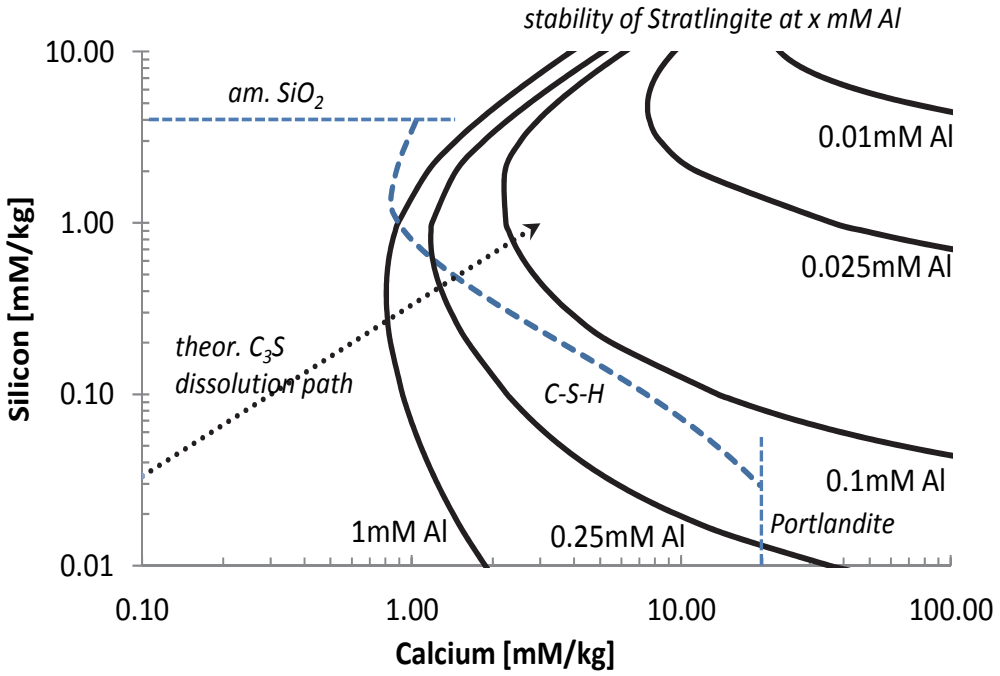
# Conclusion: Undersulfatisation causes an increase of [Al] due to a shift towards AFm based phase equilibria

This may cause:

1.) an initial inhibition of alite dissolution due to the formation of Calcium-aluminate complexes at ph< 13




2.) Stabilisation of C-A-S-H type phases rather than C-S-H → *growth problems of C-S-H as indicated by Begarin et al*




Matschei Ibausil 2012

## Summary

- The presence of sufficiently high alumina concentration in pore solution will cause a significant pertubation of the hydration of alite,
- In presence of sulfate the phase equilibria portlandite – gypsum – ettringite dominates the composition of the liquid phase at early stages of hydration
- This phase assemblage supresses the alumina concentration of the pore solution to a very low level, which does not interfere with the hydration of alite → allowing optimum performance at early ages