Influence of Sulfate Source and Content on Hydration Kinetics and Compressive Strength of Portland Cement

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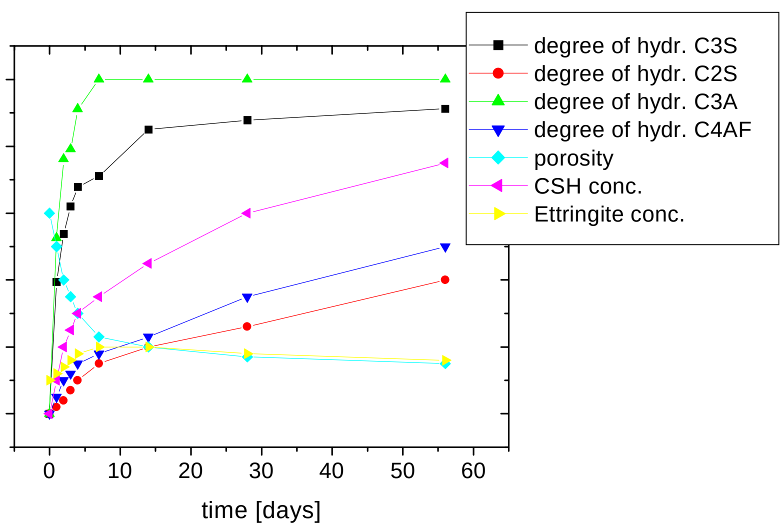
- Objectives of research
- Experimental results
    - heat of hydration
    - degree of hydration (C_3S and C_3A)
    - porosity, compressive strength
- Simulations
- Conclusions

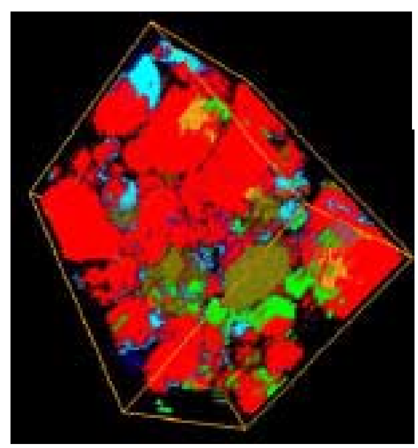
Objectives of research: Predict compressive strength
(of standard mortar; EN 196)

1st step: Simulate cement hydration

Characterize cement
(bogue composition, gypsum, fly ash, silica fume,...)

NIST simulation software CEMHYD3D

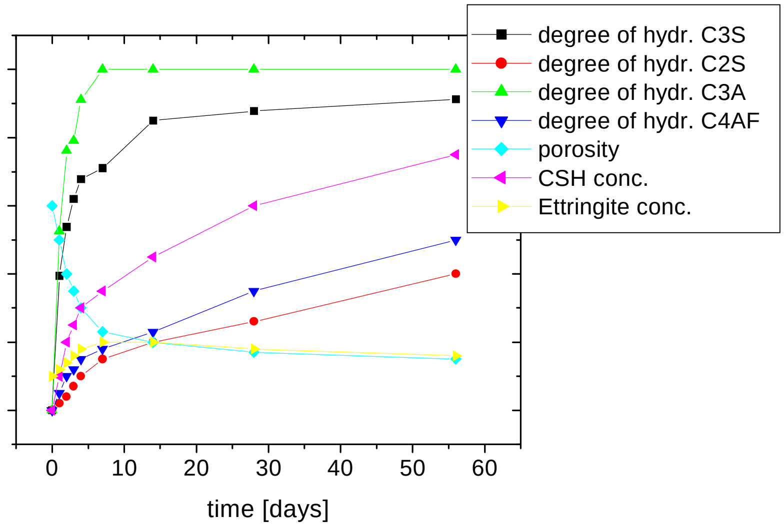


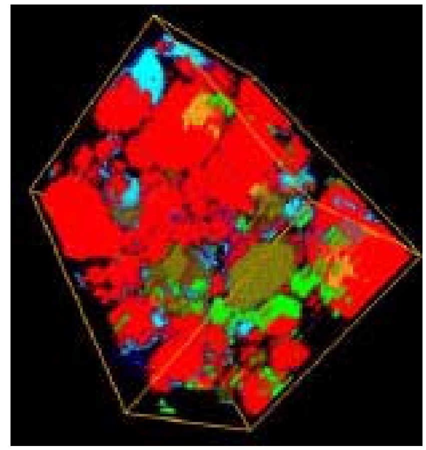


cement chemistry

3-D microstructure

2^{nd} step: calculate compressive strength

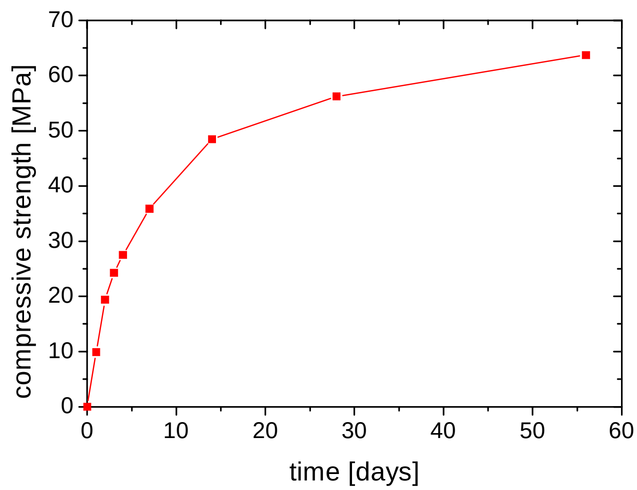




powers law: $\sigma = \sigma_0 X^A$

$$X = \frac{0.68\alpha}{0.32\alpha + w/c}$$

calibration using N2



Why does a cement producing company engage in modelling cement hydration?

1. Lower production costs

Quality control according to DIN 1164:

For every produced cement
- take two samples every week
- test compressive strengt after 2d, 7d, 28d

⇒ 312 tests/year for every cement

Reduce the number of tests
⇒ lower production costs

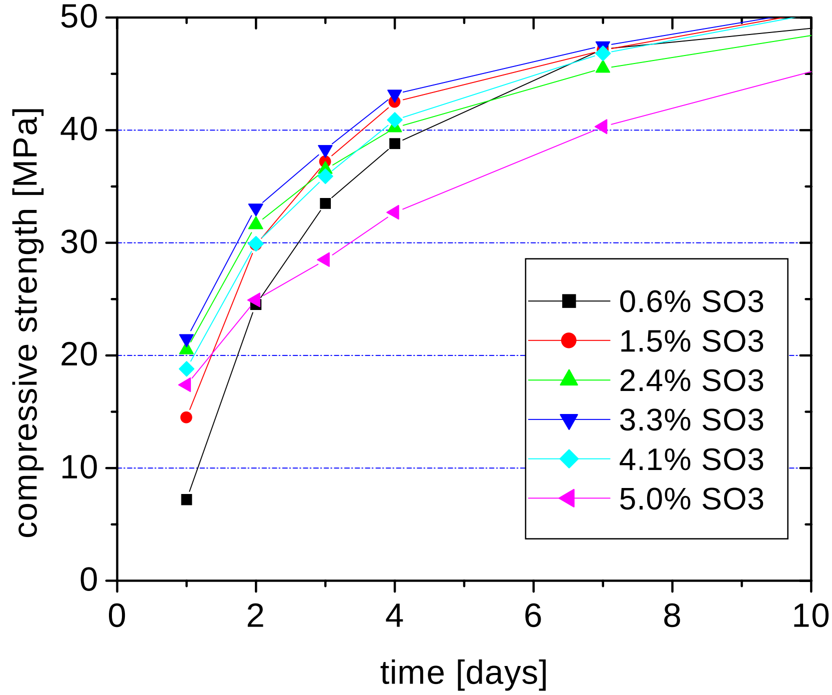
2. Speed up availability of information

Quality problems are evident after 28d
- what can be done if cement is already worked up?

In general simulated results are available after some h

Why have we investigated the influence of sulfate source on cement hydration?

$CaSO_4$ highly influences development of compressive strength (+ cement hydration)

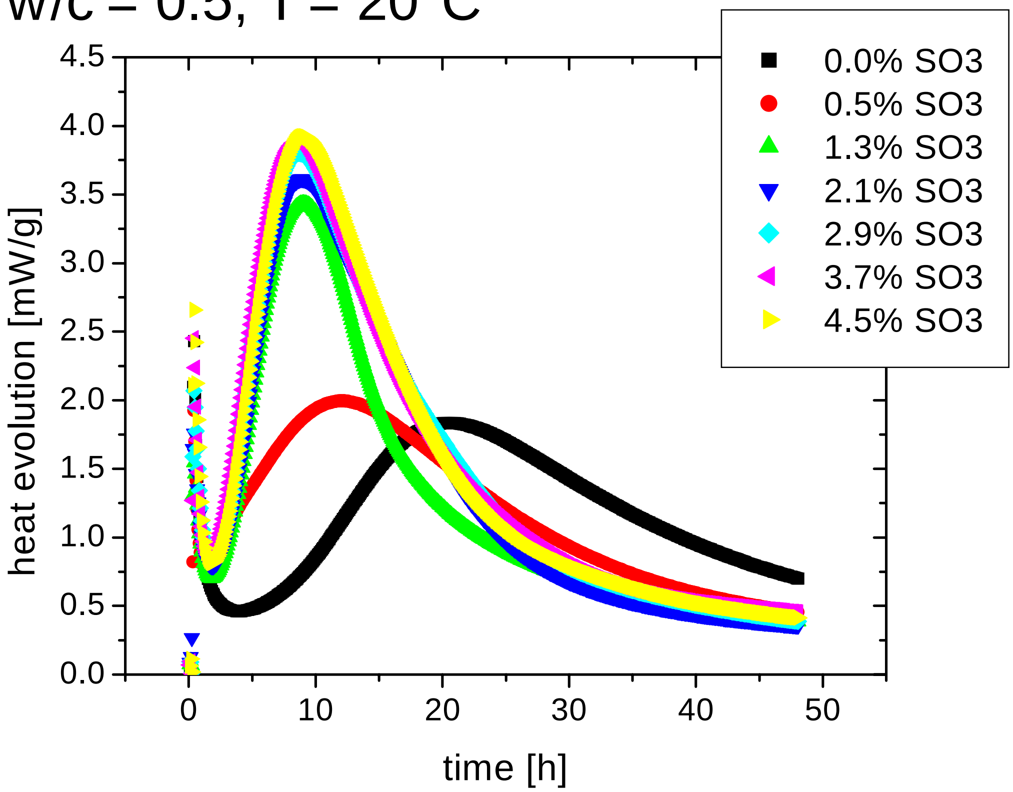


By our research we have tried

- to figure out the most important influences of $CaSO_4$ on the hydration kinetics of opc,
- to implement these results in CEMHYD3D and
- to develop a method to predict compr. strength for cements containing diff. amounts of $CaSO_4$

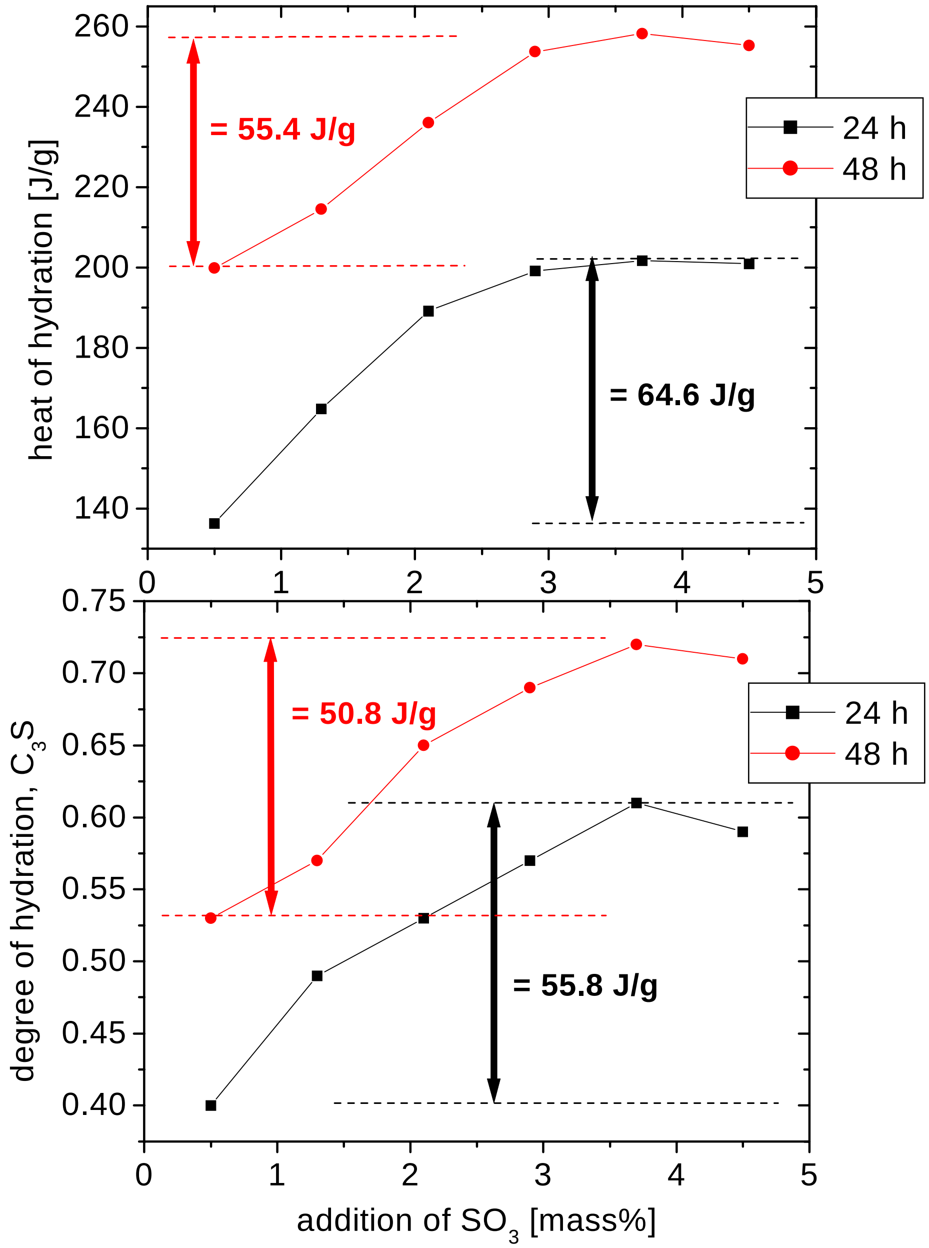
Experimental results

Ordinary portland clinker (5100 cm^2/g)
+ different amounts of anhydrite (10700 cm^2/g)
- w/c = 0.5; T = 20°C



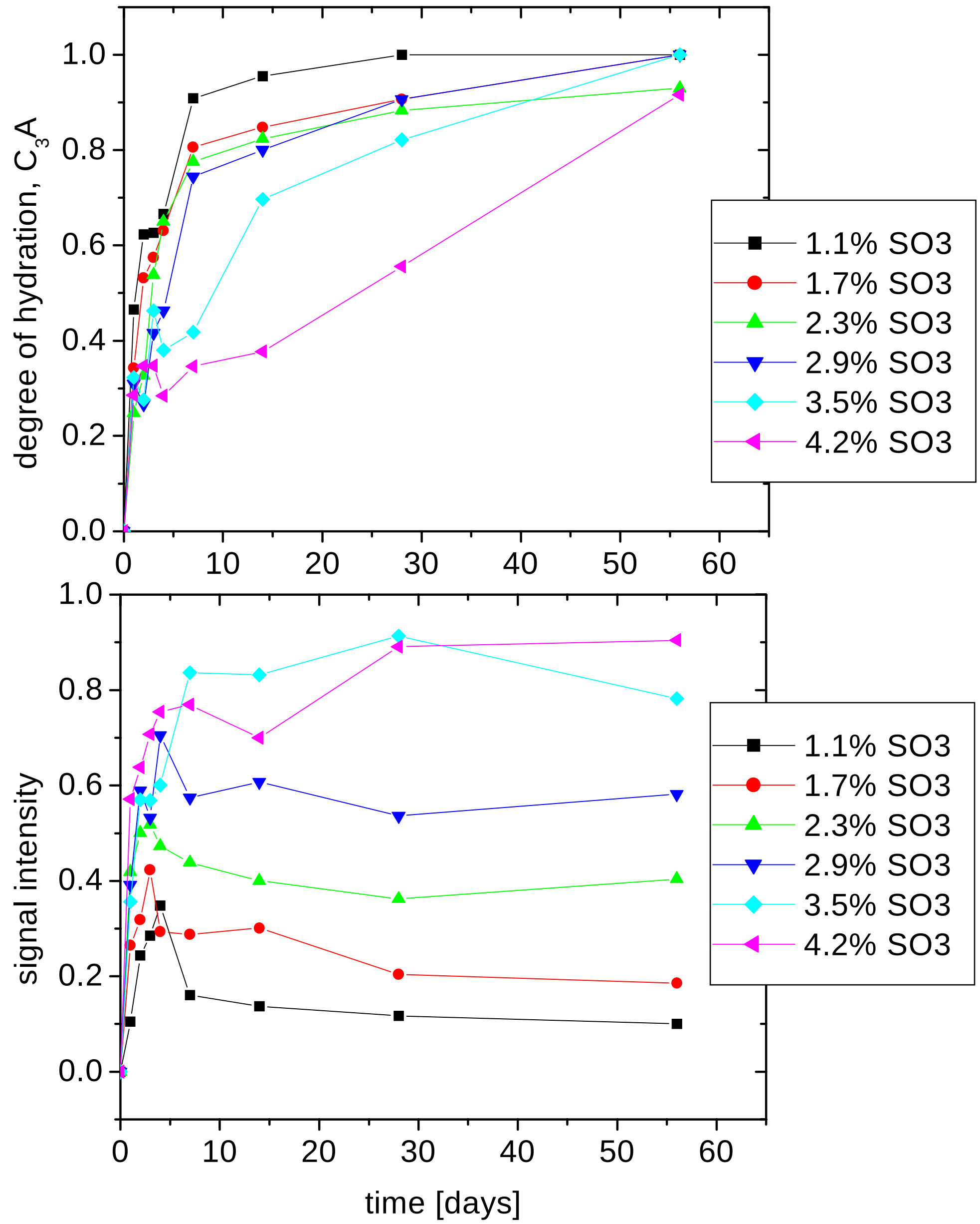
1. $CaSO_4$ accelerates cement hydration
2. A small amount of anhydrite (0.5% SO_3) shortens the induction period, maximum value is equal
3. Increasing amounts of $CaSO_4$ further accelerate the rate of hydration

Which reactions are responsible for the accelerated heat evolution?



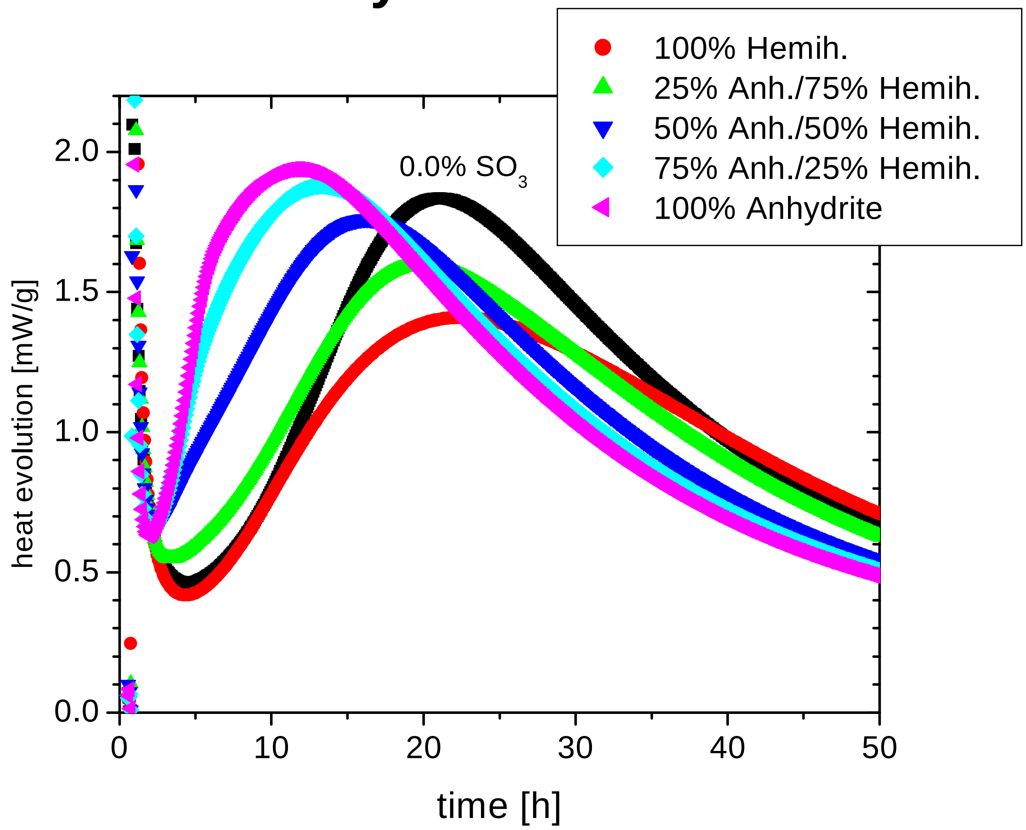
80%-90% of the acceleration can be attributed to the C_3S reaction

Different amounts of $CaSO_4$ - C_3A reactivity?



- High amounts of $CaSO_4$ retard the hydration of C_3A for more than 14 days
- Despite retardation more ettringite is formed

How do different modifications of $CaSO_4$ influence cement hydration?



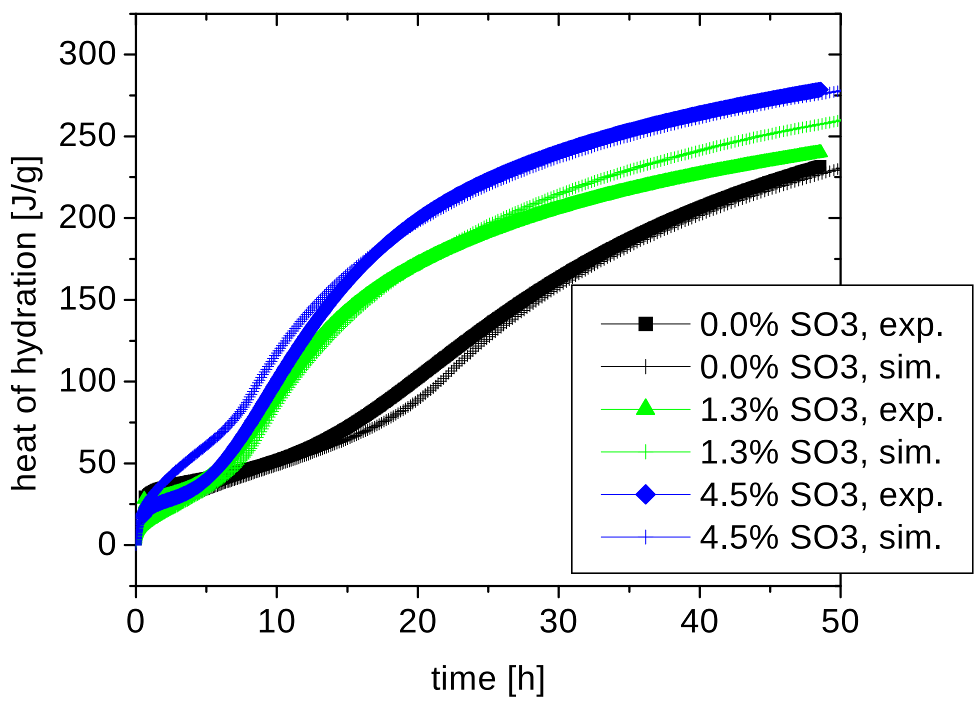
1. **Differences between hemihydrate and anhydrite** ⇒ different solubility
2. **$CaSO_4$ retards**
   higher solubility of hemihydrate ⇒ more ettringite
   retardation due to layer of „ ettringite“
3. **$CaSO_4$ accelerates**
   Nonat: $[Ca^{2+}]$ governs rate of reaction of C_3S
   High $[Ca^{2+}]$ ⇒ high rate of reaction
   Anhydrite reacts more slowly ⇒ longer available

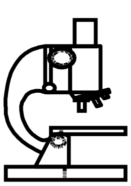
First attempts to simulate the influence of $CaSO_4$ on cement hydration

measured isothermal heat evolution of
- opc with different amounts of anhydrite
- w/c = 0.5

Simulations with NIST computer modelling software CEMHYD3D

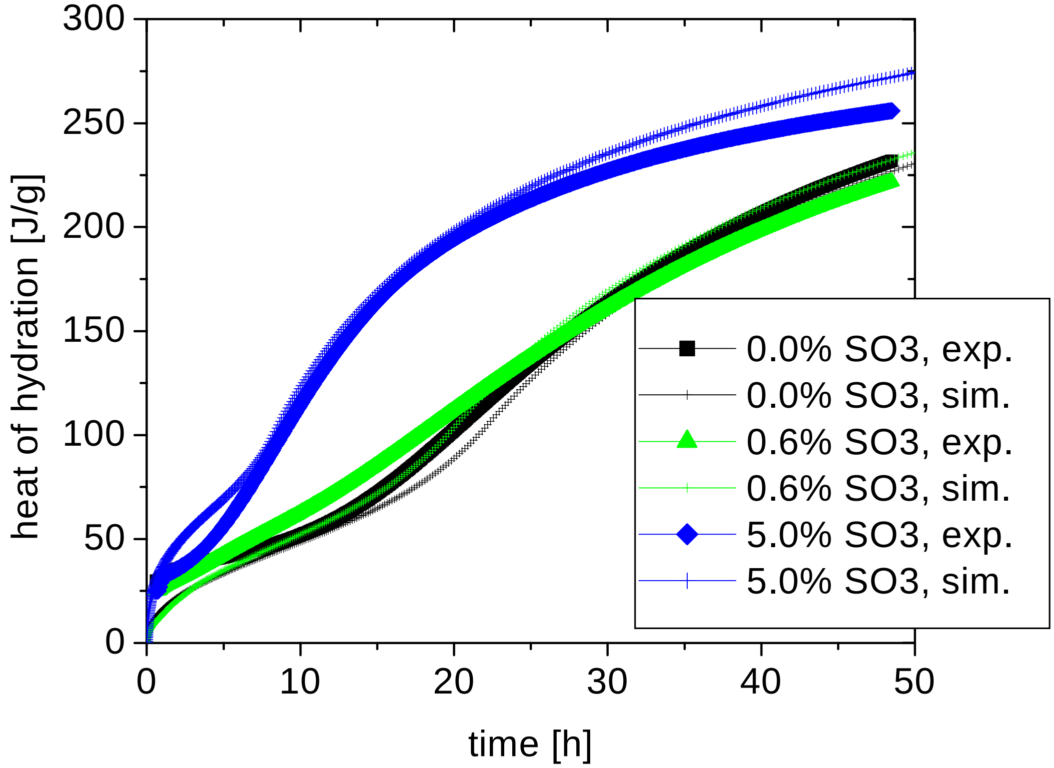
$$r_{nuc}(CSH) = f(c_{CaSO4\ in\ solution})$$



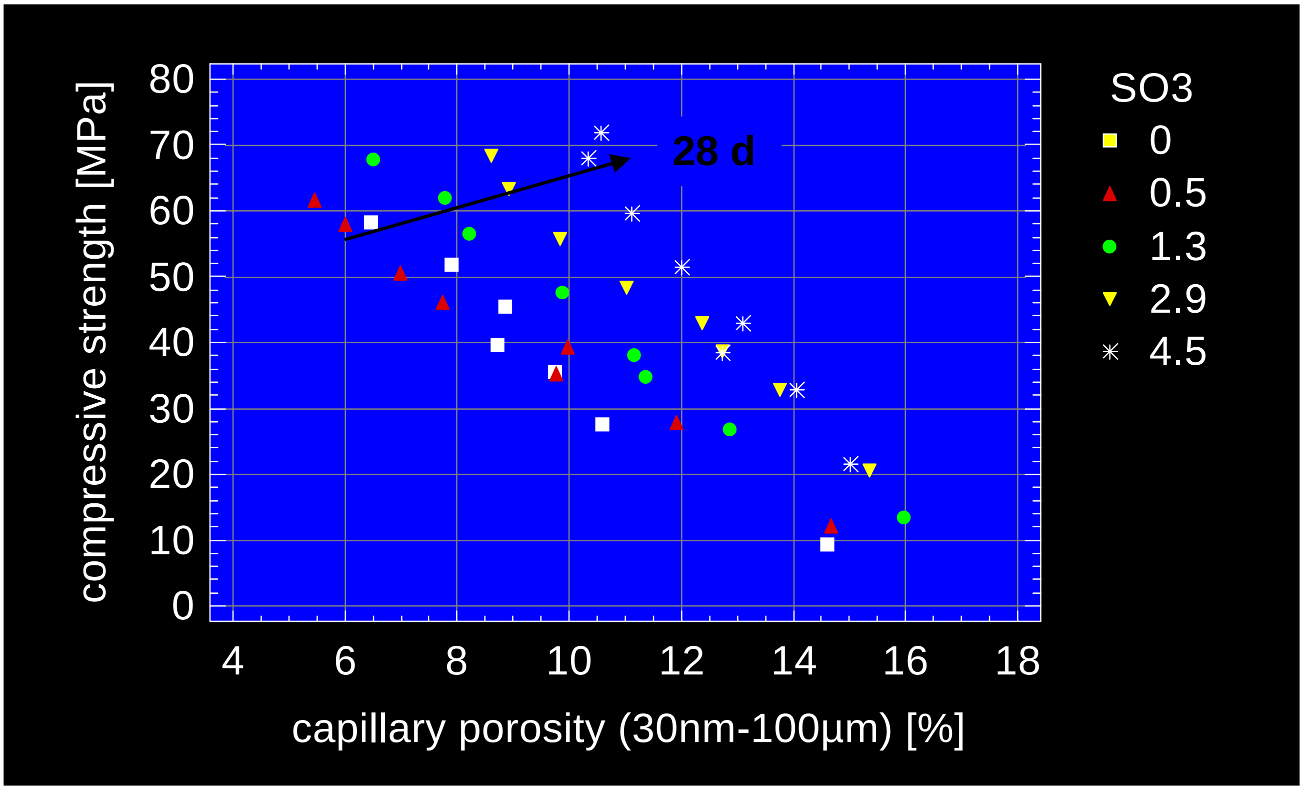


Simulations on the influence of hemihydrate on cement hydration

isothermal heat evolution of
- opc with different amounts of hemihydrate
- w/c = 0.5



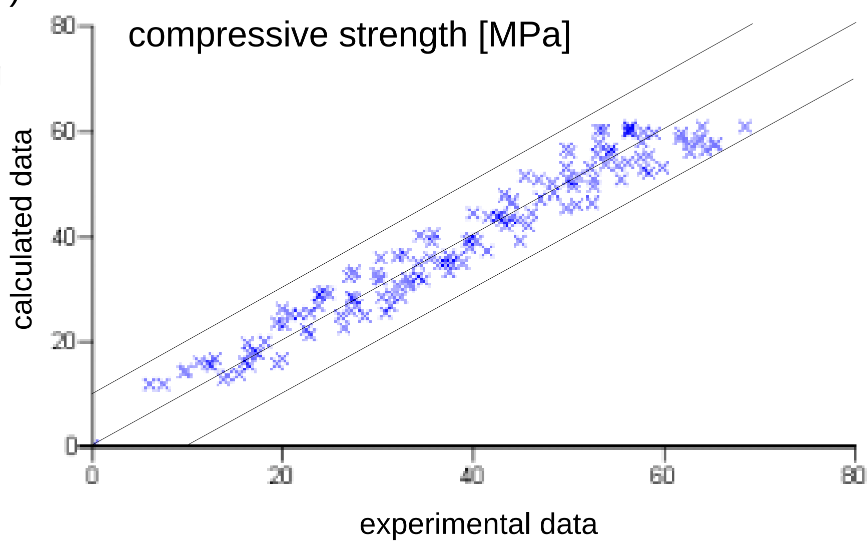
- Results look promising
- Model has still to be refined



- $CaSO_4$ modifies pore structure
- Poor overall correlation between strength and porosity
- Excellent correlation for each cement ⇒ calibrate each cement

Prediction of compressive strength

- Measured compressive strength according to EN 196
  - clinker composition (20 clinkers)
  - $CaSO_4$ content (0%-9%)
  - fineness (5µm-30µm)
- Simulation of cement hydration using CEMHYD3D
- Calibration of powers law using N2
- Predictions (1d - 56d)



maximum difference
≈ 10 N/mm²

average difference
< 3.0 N/mm²

Conclusions

Experimental results:

- $CaSO_4$ highly influences compressive strength
- $CaSO_4$ accelerates cement hydration
- The higher the amount of $CaSO_4$, the higher is the rate of hydration
- 80% - 90% of the acceleration can be attibuted to the acceleration of the C_3S hydration
- $CaSO_4$ retards the hydration of C_3A
- $CaSO_4$ increases capillary porosity + compressive strength

Simulations:

- First attemps to simulate the influence of $CaSO_4$ on cement hydration look promising

- Prediction of compressive strength is possible using CEMHYD3D and powers law (calibrated)
  Maximum deviation = 10 MPa
  Average deviation < 3.0 MPa