# Modeling pore solutions in the cement-water system

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Concrete and Construction Chemistry

EMPA

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# Motivation

- Concrete admixtures?
- Influence of composition?

**What happens during cement hydration?**

**Why?**

- Predict longterm behavior ?

→ **Thermodynamic Model**

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# Structure

1 Cement and concrete

2 Changes during hydration

3 Modeling

4 Results

5 Conclusions

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# Concrete

gravel/sand
cement
water

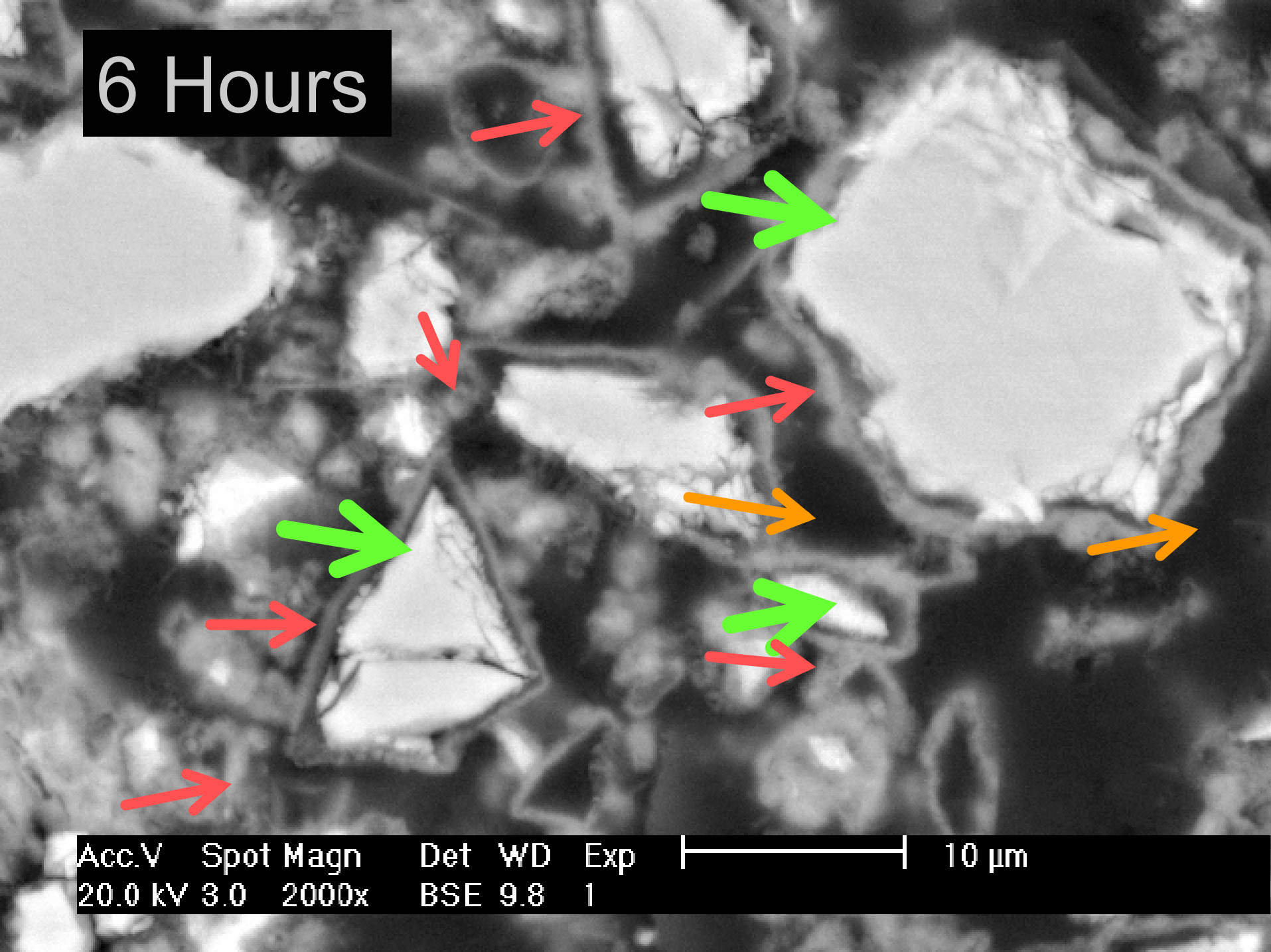
time ?

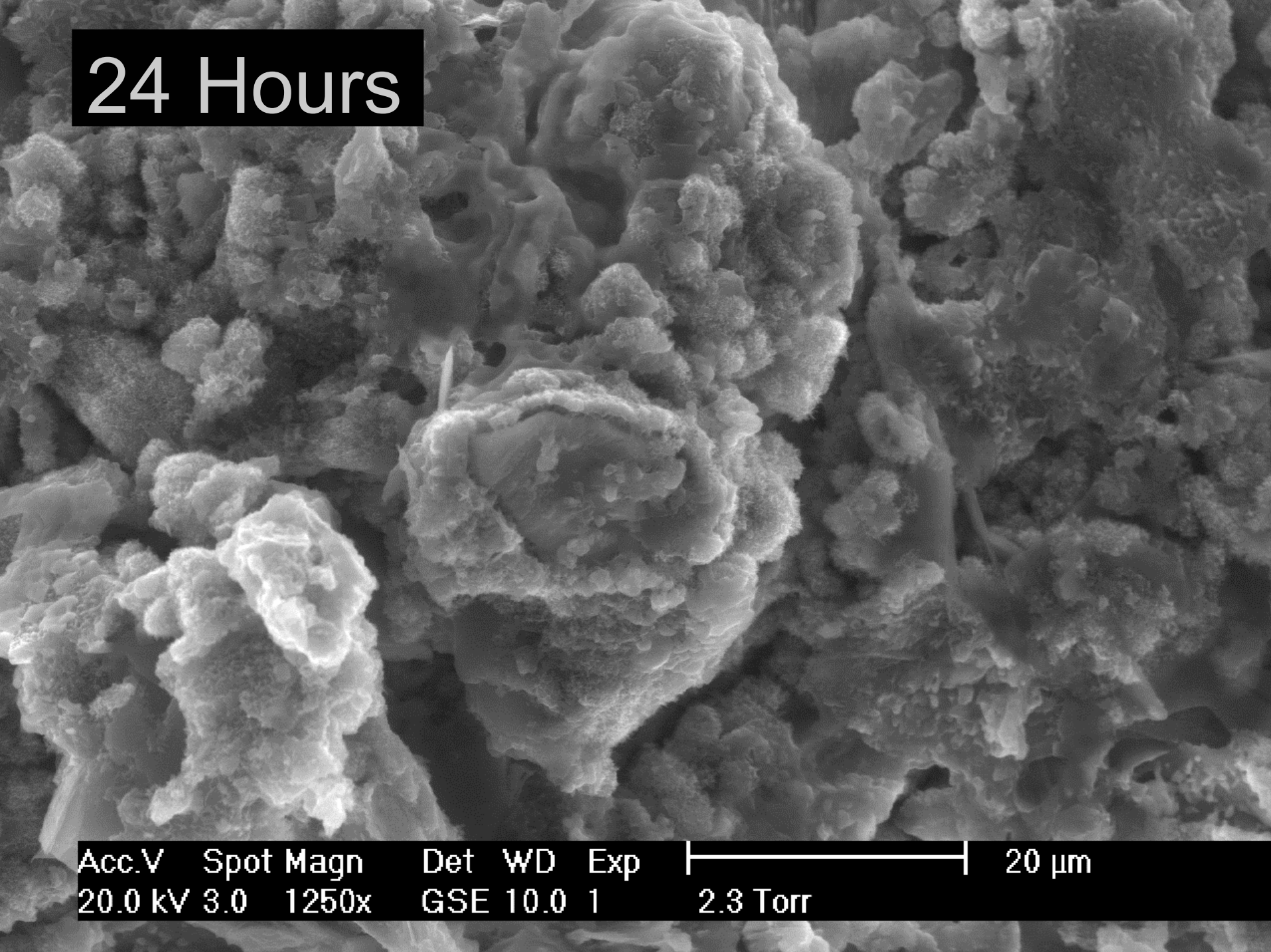
# Experiments

## Ordinary Portland Cement CEM I 42.5 N

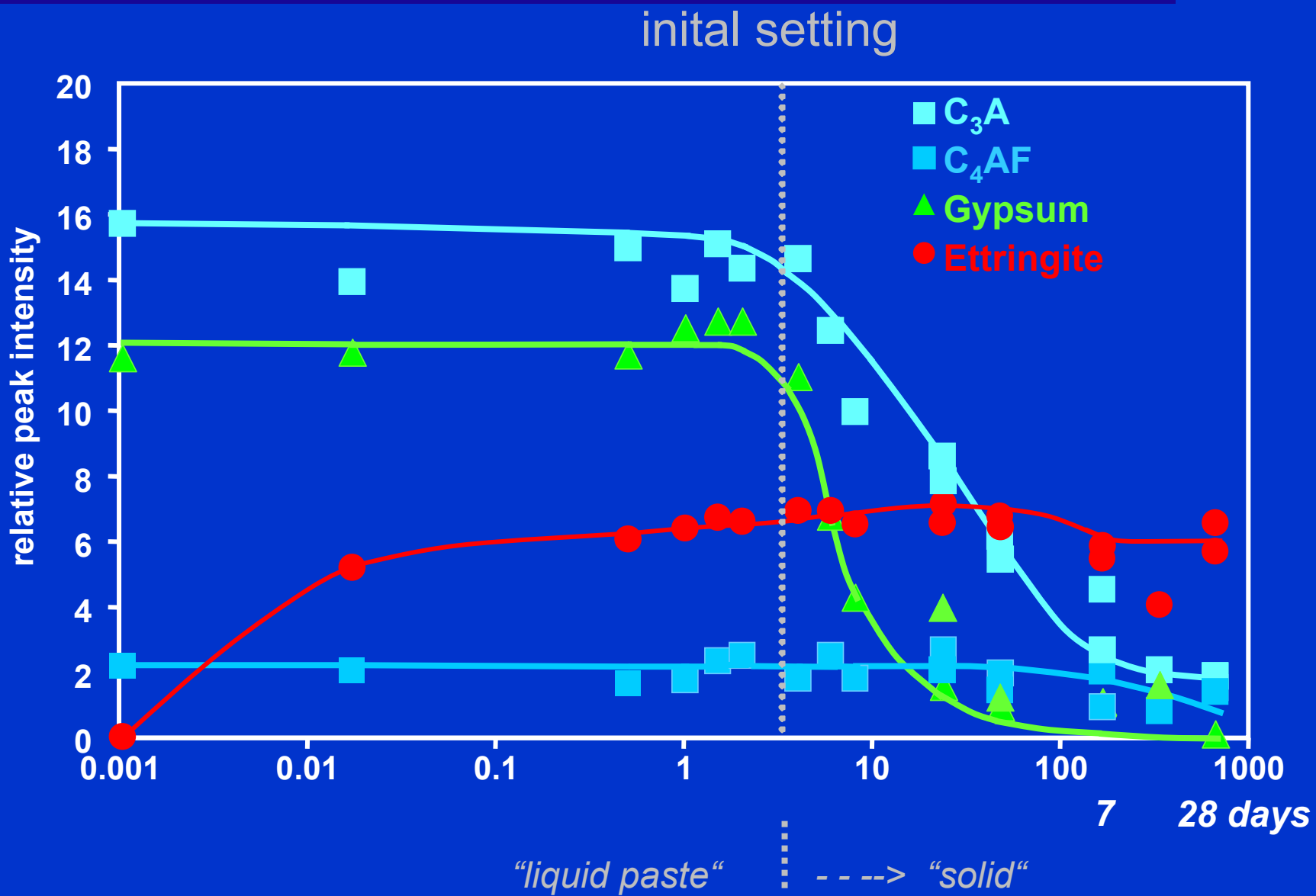
| Chemical analysis | g/100g |
|---|---|
| $CaO$ | 63 |
| $SiO_2$ | 20 |
| $Al_2O_3$ | 5 |
| $Fe_2O_3$ | 3 |
| $MgO$ | 2 |
| $Na_2O$ | 0.1 |
| $K_2O$ | 1 |
| $CO_2$ | 2 |
| $SO_3$ | 3 |

| Phase composition | | g/100g |
|---|---|---|
| $C_3S$ | $3CaO \cdot SiO_2$ | 55 |
| $C_2S$ | $2CaO \cdot SiO_2$ | 15 |
| $C_3A$ | $3CaO \cdot Al_2O_3$ | 8 |
| $C_4AF$ | $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ | 8 |
| $MgO$ | | 2 |
| $Na_2SO_4/K_2SO_4$ | | 2 |
| $Na_2O/K_2O$ | | 0.2 |
| $CaCO_3$ | | 4 |
| $CaSO_4$ | | 4 |

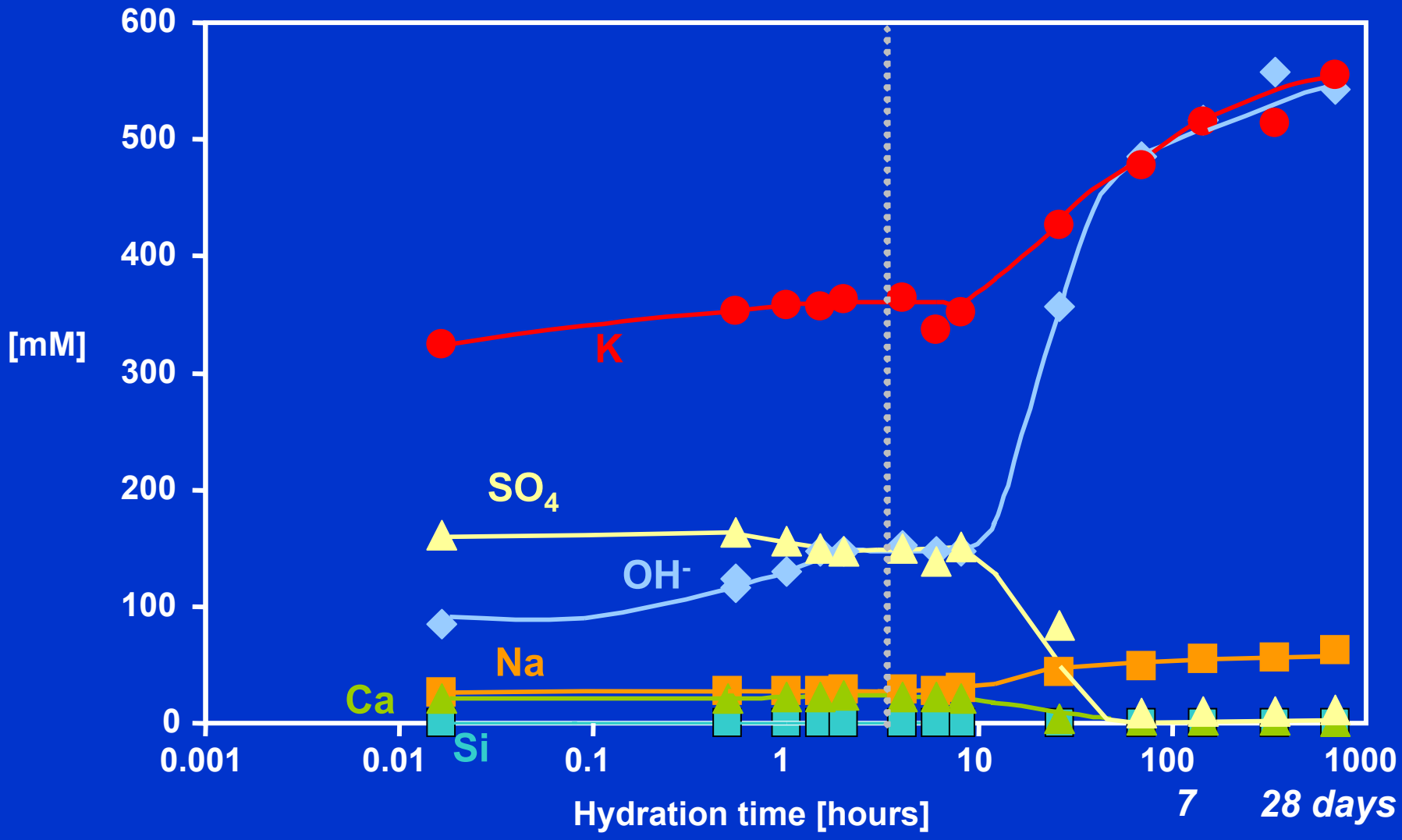

6 Hours
Acc.V Spot Magn Det WD Exp
20.0 kV 3.0 2000x BSE 9.8 1
10 µm


24 Hours
Acc.V Spot Magn Det WD Exp
20.0 kV 3.0 1250x GSE 10.0 1 2.3 Torr
20 µm

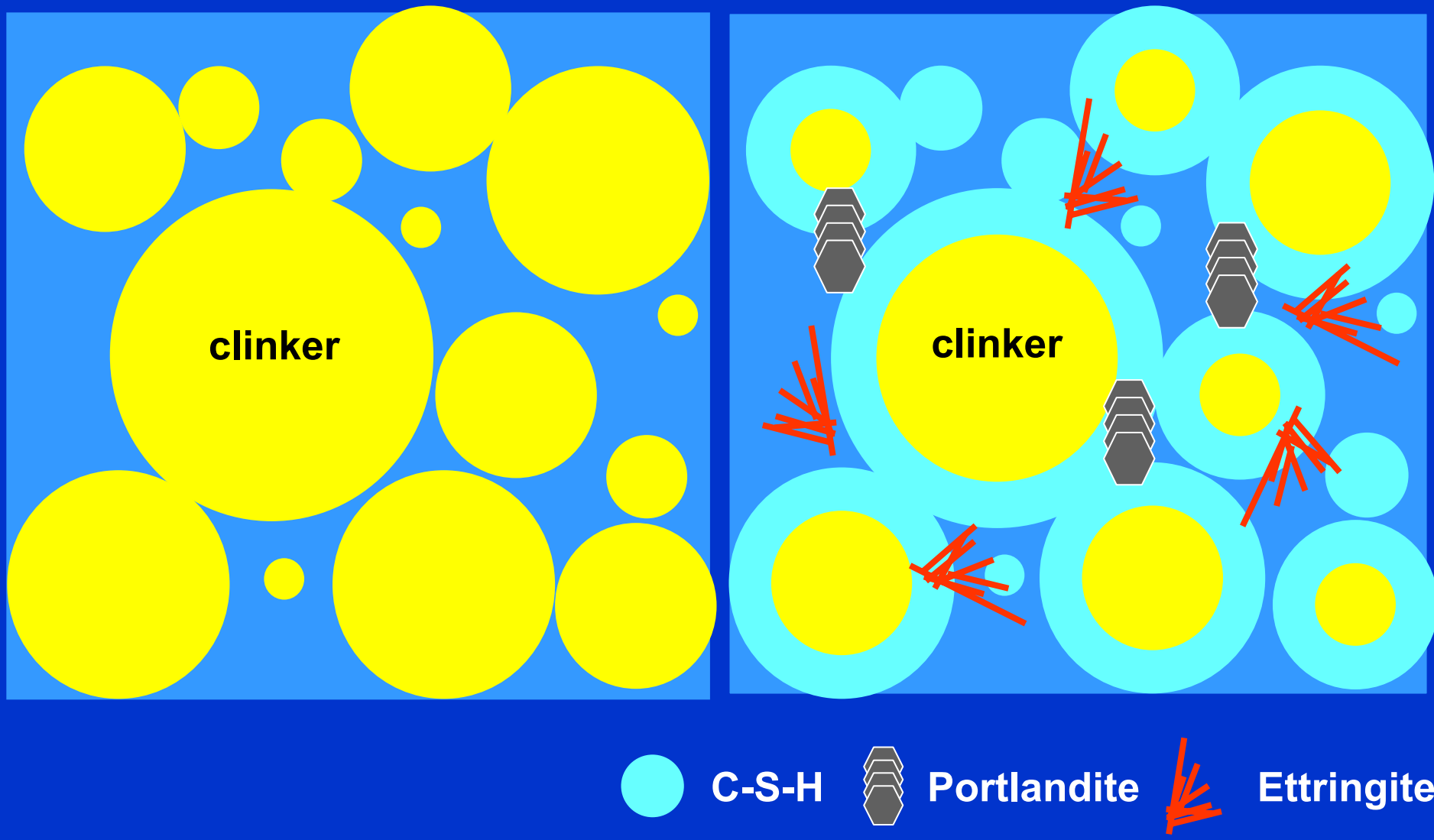
# Cement (XRD)


inital setting
relative peak intensity
20
18
16
14
12
10
8
6
4
2
0
0.001
0.01
0.1
1
10
100
1000
$C_3A$
$C_4AF$
Gypsum
Ettringite
7
28 days
"liquid paste"
- - --> "solid"

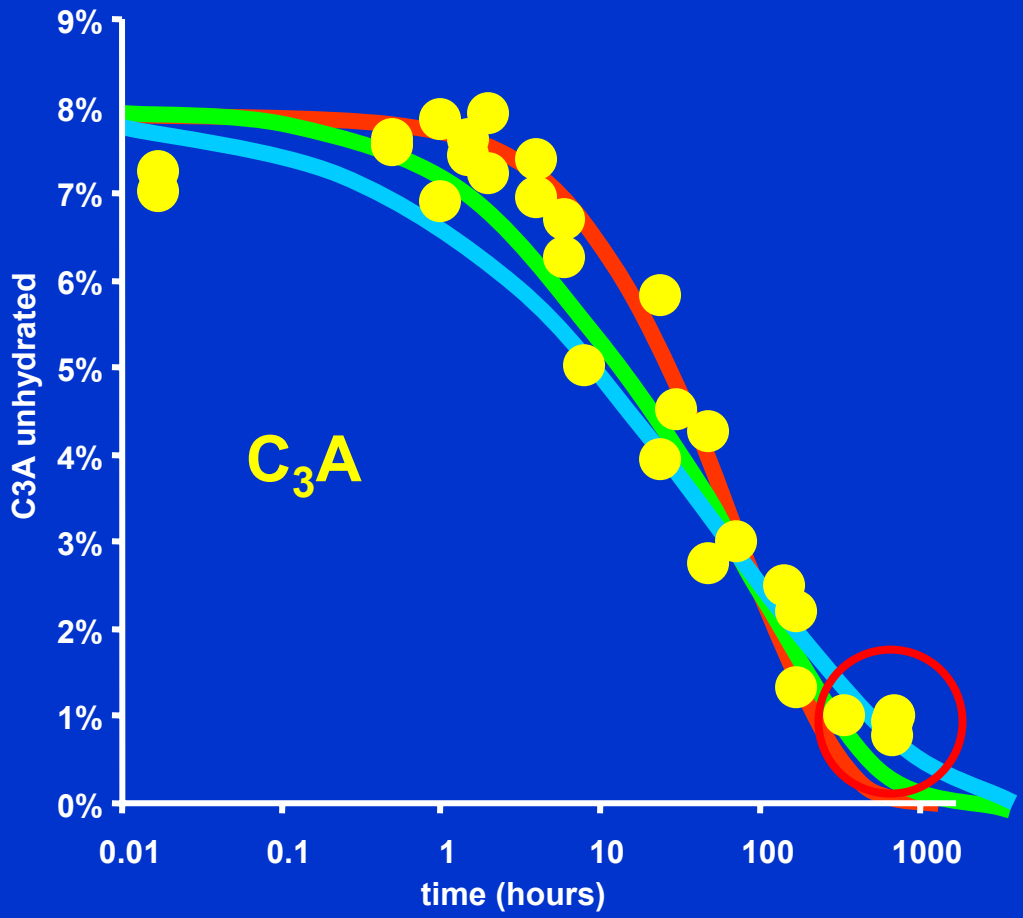
# Pore solution



# Hydration



# Dissolution kinetics




**Rate**

→ **Particle size distribution**

$R_i = k_i \times S(t)$

→ **Reactions**

$R_i = k'_i \times S(t) / \{OH^-\}^2$

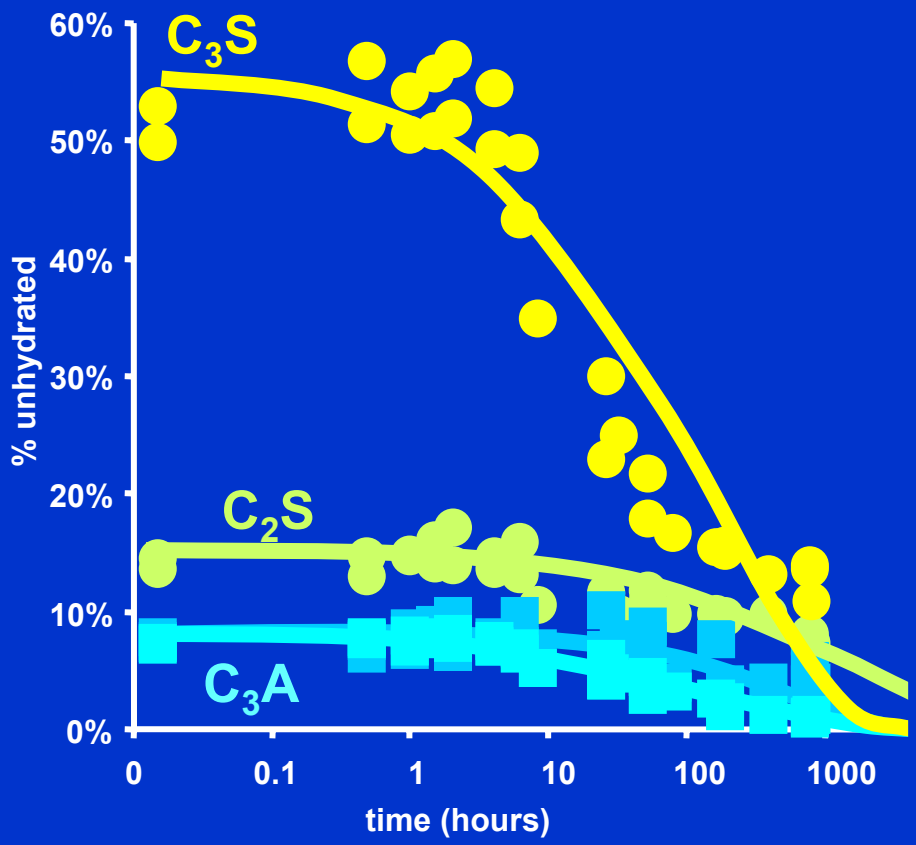
→ **Diffusion**

$R_i = k''_i \times S(t) \times t^{-0.5}$

# Modeling: Dissolution

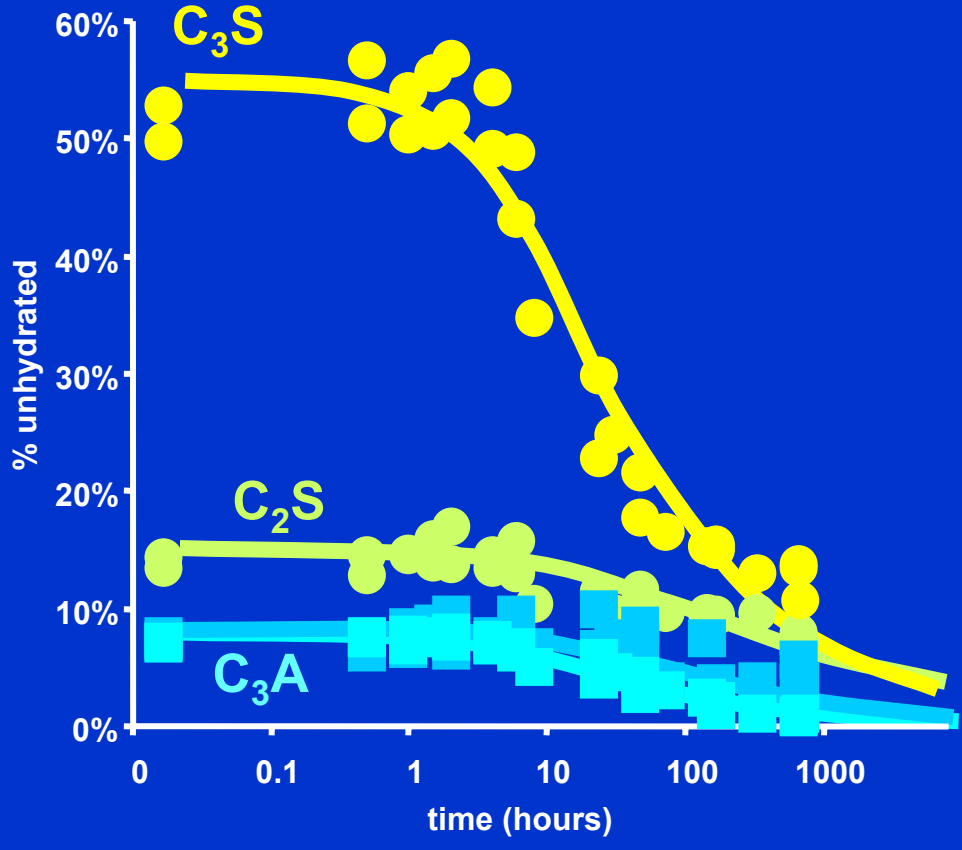
## I Surface reaction

$R_i = k_i \times S(t) / \{OH^-\}^2$




## II Empirical Approach

$R_j = k_j \times (1-\alpha_j(t))^B$ (1)




(1) Parrot and Killoh (1984)

# Thermodynamic calculations

**Multi-component input**

**I Slowly soluble clinkers**

$C_3S$ $C_2S$
$C_3A$ $C_4AF$

$K_2O$
$Na_2O$
$MgO$

**II Soluble solids**

$K_2SO_4$
$Na_2SO_4$
Hemihydrate
CaO

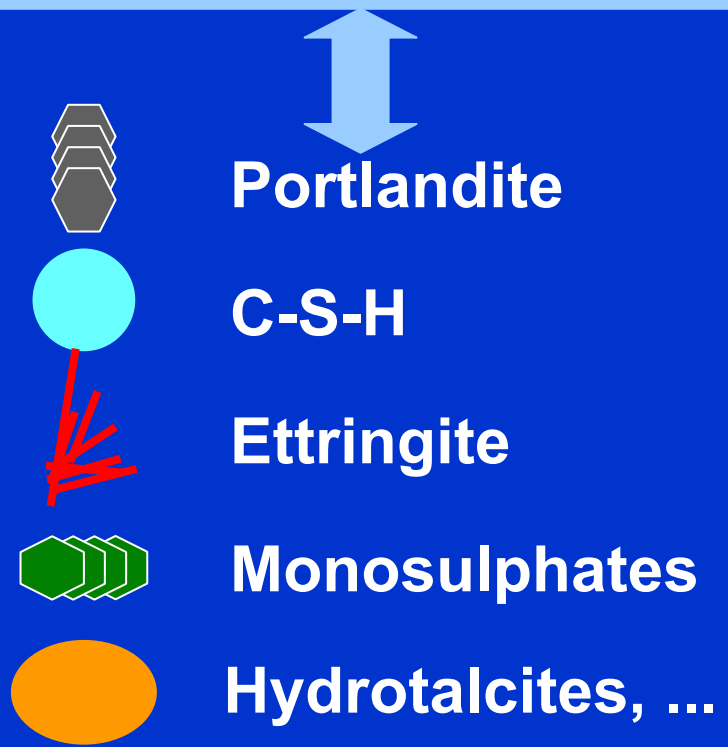
Gypsum
Anhydrite
Calcite

**III Water**

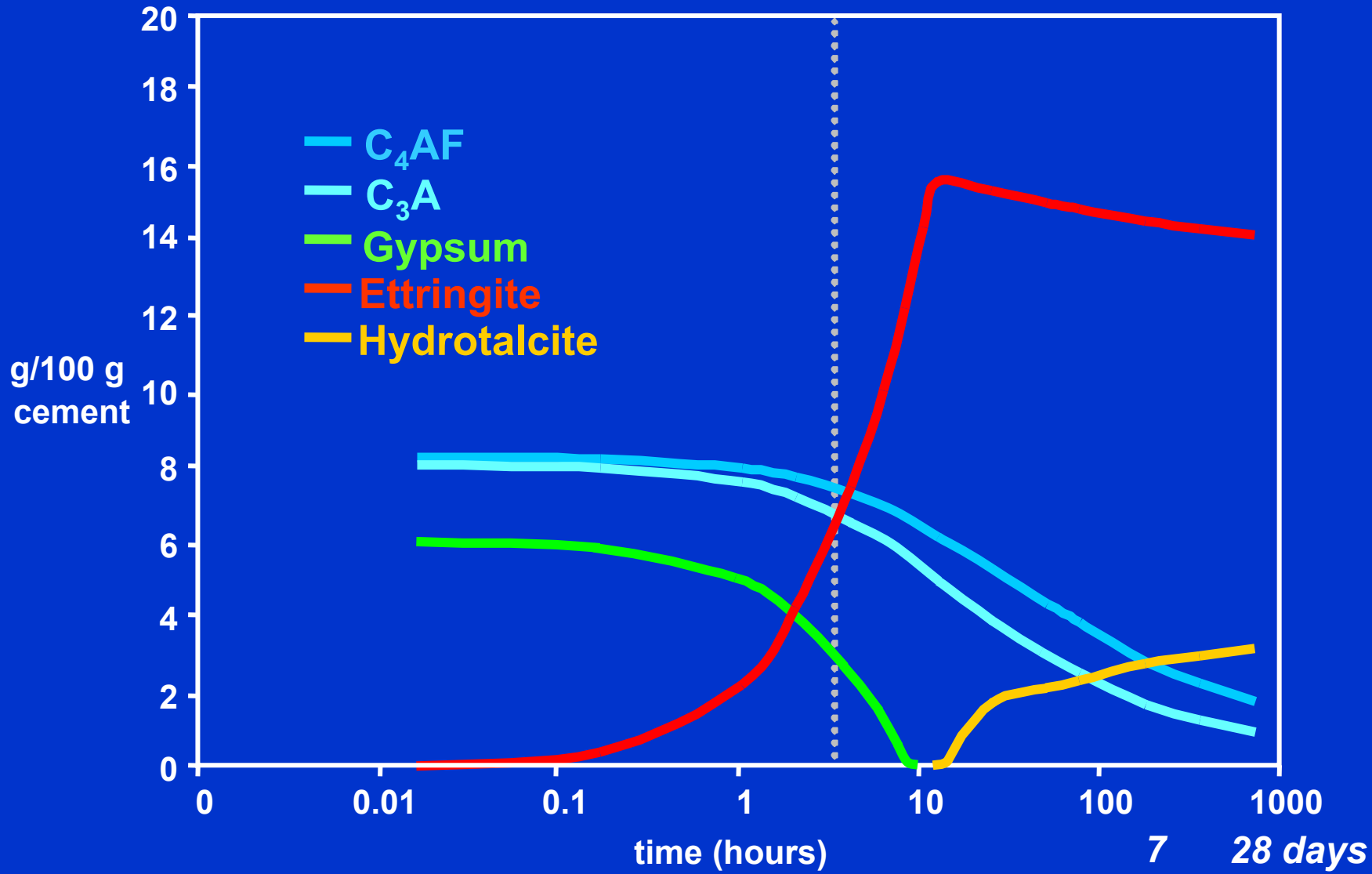
$H_2O$

**Thermodynamic modeling**
GEMS-PSI

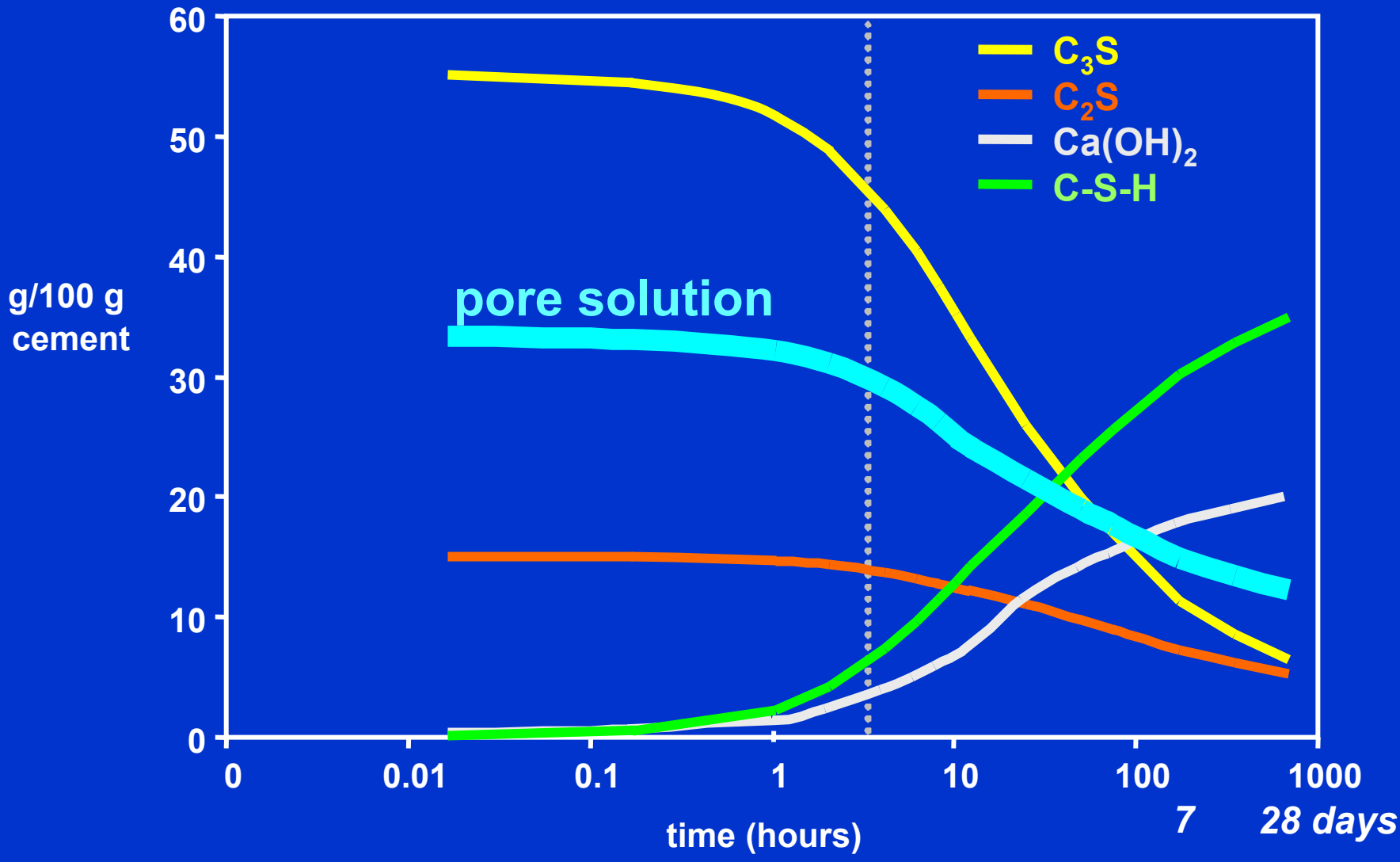
$Ca^{2+}$
$CaOH^+$
$CaSO_4^0$
**Speciation in solution**



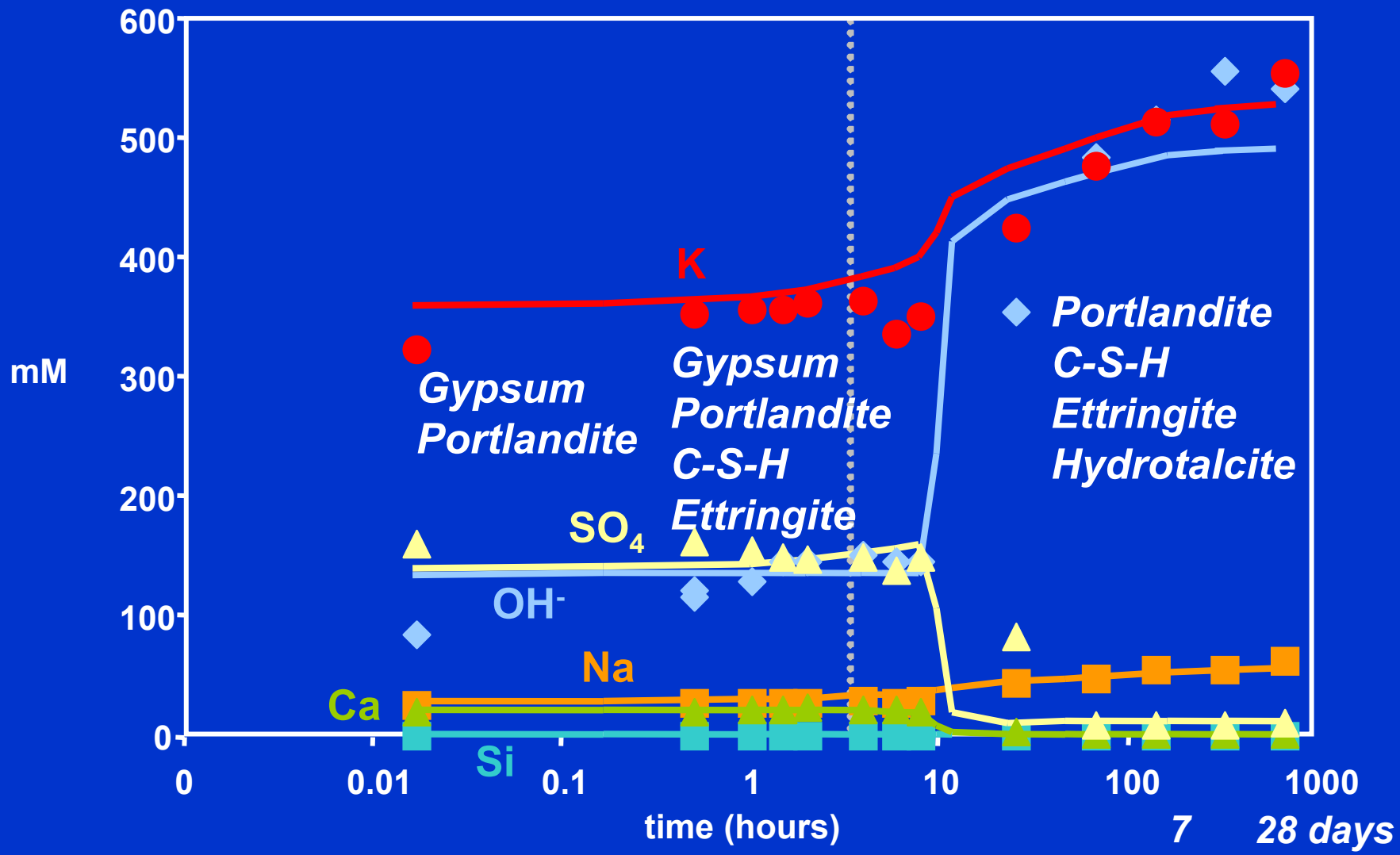
# Aluminate-, Sulphate Minerals



# Calcium- and Silicate Minerals



# Modeled pore solutions



# Conclusions

**Description of processes in a multi-component system**

**Model**

**Good agreement between prediction and experimental results**

**Slow dissolution of clinkers**
**Fast equilibration for newly formed minerals**

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