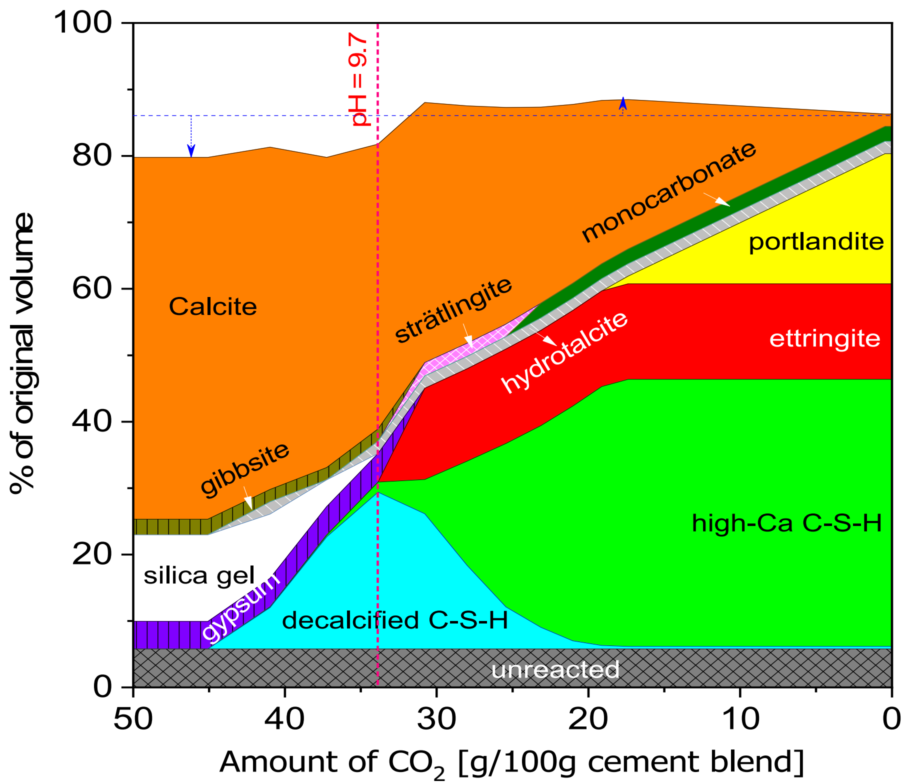
Thermodynamic modelling of cementitious systems



Lecture and hands-on computer simulations

Barbara Lothenbach, Frank Winnefeld, Bin Ma, Zhenguo Shi

Online course 2020
Preliminary programme: 15:00 h to ≈ 16:30

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Download and read the slides **before** each session

Monday, 24. Aug 2020: 01 Welcome, general introduction to cement chemistry

Tuesday, 25. Aug 2020: 02 First modelling, single systems
Wednesday, 26. Aug 2020: 03 Process
Thursday, 27. Aug. 2020: 04 Database
Friday, 28. Aug. 2020: 05 Hydration modelling +
Introduction to self studying excercises

4 groups

Monday , 31. Aug. 2020: 06 Durability
Tuesday, 1. Sept. 2020: self studying excercises
Wednesday, 2. Sept. 2020: self studying excercises
Thursday, 3. Sept. 2020: Student presentations
Friday, 4. Sept. 2020: Student presentations

4 groups

Friday, 4. December 2020: Hand in short reports of individual modelling project

1 Introduction cement chemistry

2 GEMS / Single calculations

3 Process calculations

…

Introduction cement chemistry 1

- Cement production
- Hydration of Portland cement
- Effect of limestone

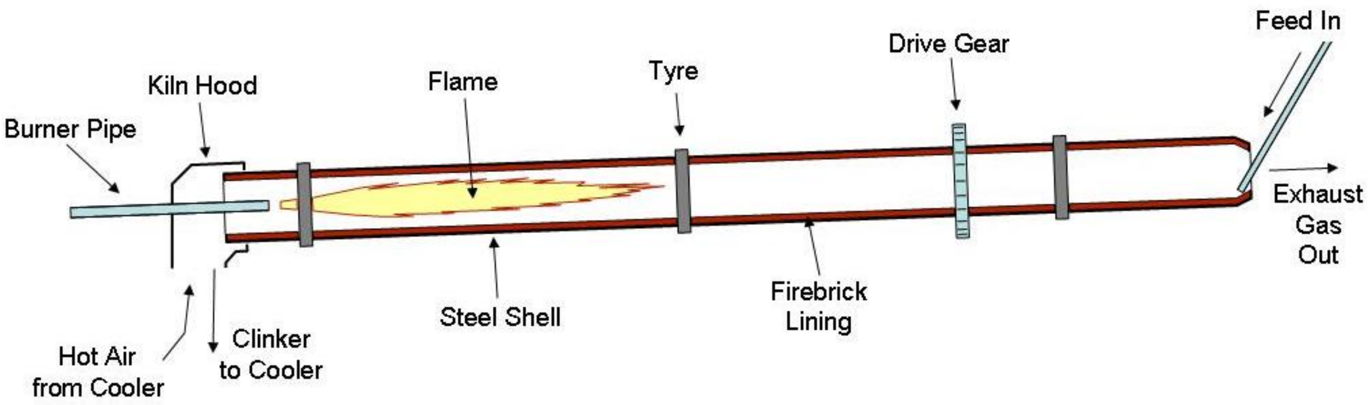
Portland cement (PC) production

limestone ($CaCO_3$)

clay + sand (Si, Al, Fe-oxides)

~ 1500°C ← increasing temperature

rotary kiln



clinker + gypsum → Ordinary Portland cement (OPC)

Rotary kiln

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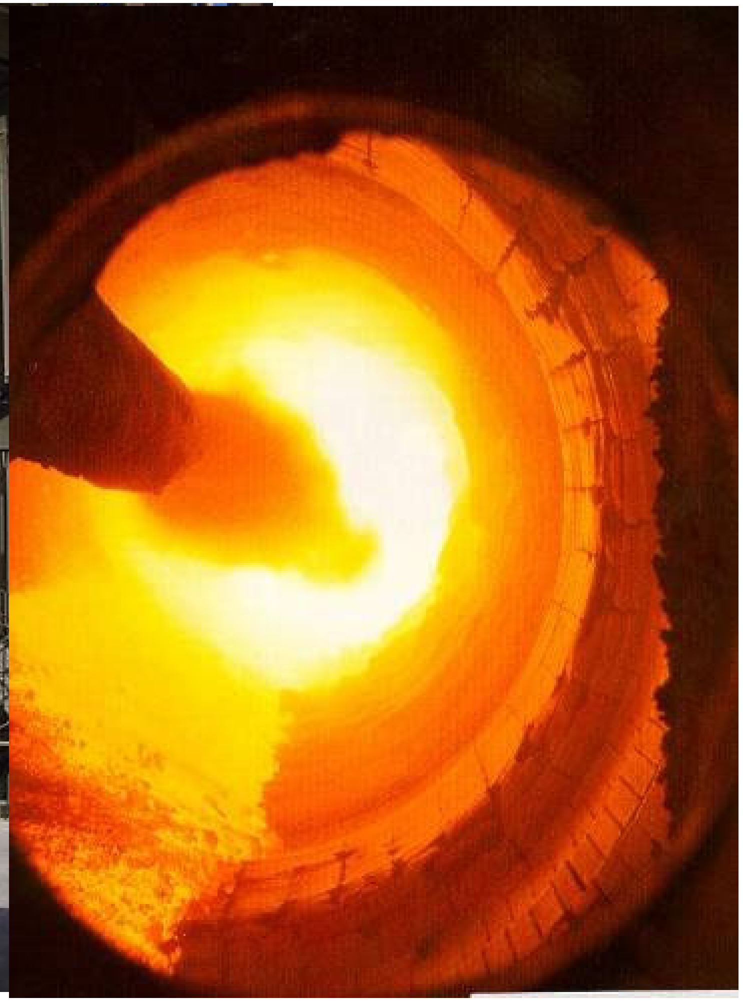
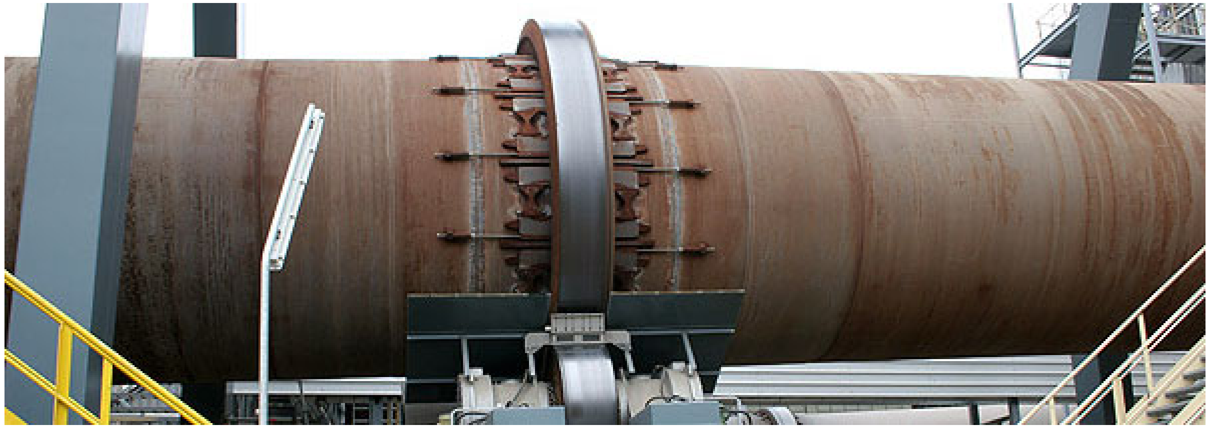
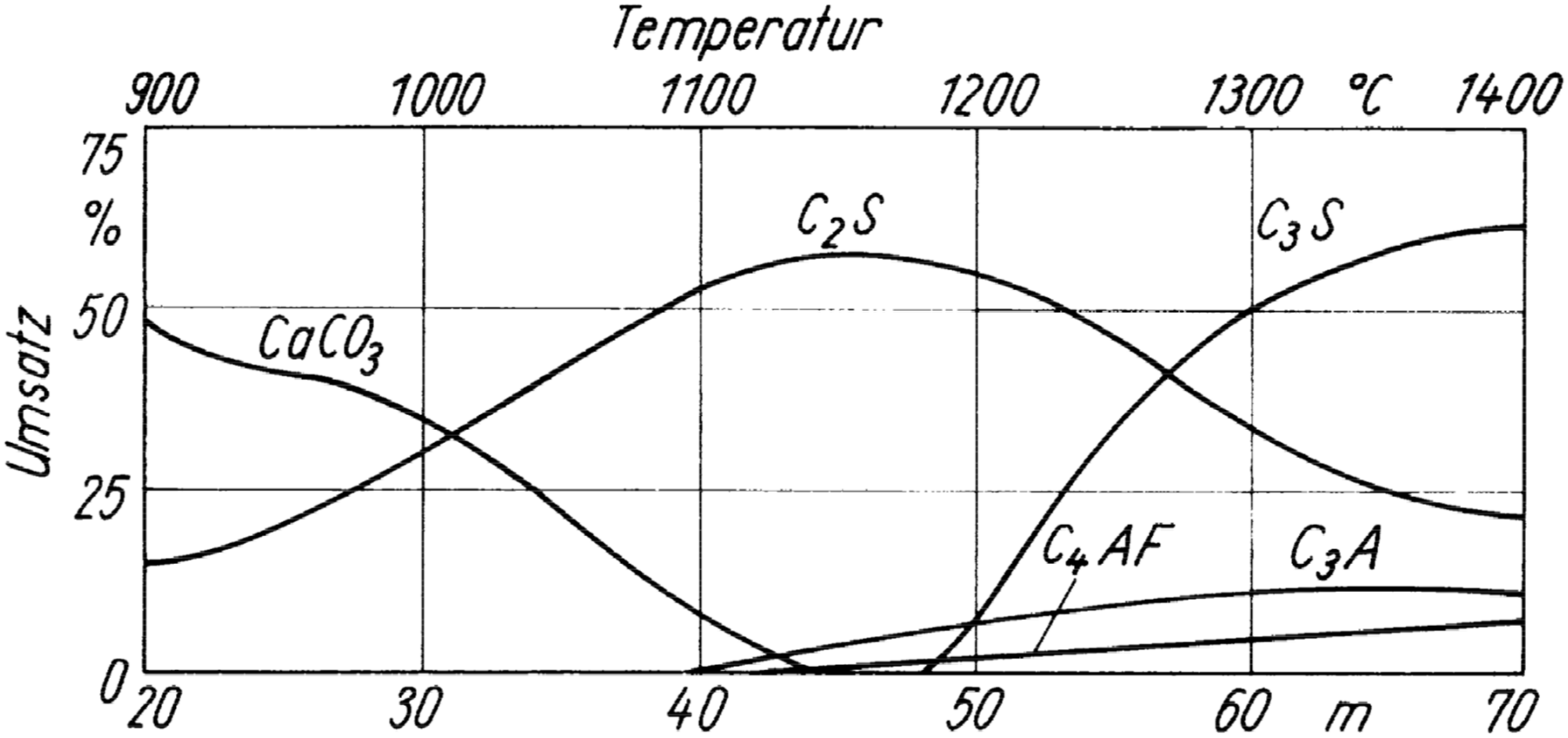


Rotary kiln

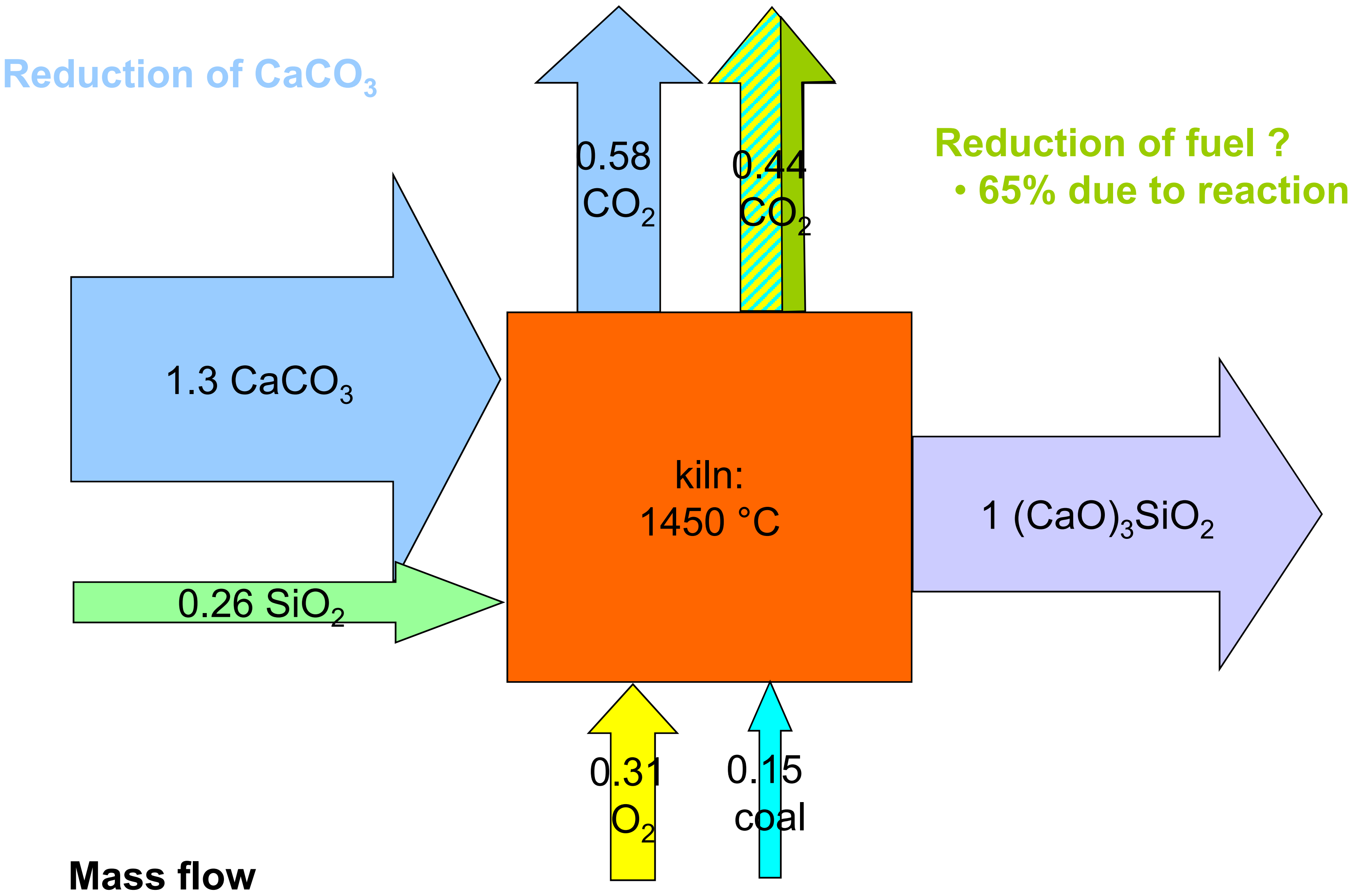


Fast cooling,
else:
$C_3S \rightarrow C_2S + C$ (free lime)



Distanz

CO_2 in OPC production ($(CaO)_3SiO_2$)



Data from Gartner (2004) CCR 34, 1489-1498

cement paste:

OPC

water

mortar:

+ sand

concrete:

+ gravel

= concrete

Portland cement: CEM I 42.5 N

Chemical analysis

SiO_2	19
Al_2O_3	4.4
Fe_2O_3	2.7
CaO	62
CaO_{free}	0.6
MgO	1.4
K_2O	0.95
Na_2O	0.10
SO_3	3.0
CO_2	2.1

Small amounts of titanium, manganese, phosphate and chromium

Bogue calculations →

Phases

Alite C_3S	58
Belite C_2S	10
alum. C_3A	7.6
ferrite C_4AF	7.5
$CaSO_4$	3.6
CaCO3	4.8
K_2SO_4	1.6
Na_2SO_4	0.1

Chemical reactions

Alite (C_3S) + water → C-S-H + portlandite

$(CaO)_3SiO_2 + 5.3H_2O \rightarrow Ca_{1.7}SiO_2(H_2O)_4 + 1.3Ca(OH)_2$

$C_3S + 5.3H \rightarrow C\text{-}S\text{-}H + 1.3CH$

C/S 1.5-2.0

Belite (C_2S) + water → C-S-H + portlandite

$(CaO)_2SiO_2 + 4.3H_2O \rightarrow Ca_{1.7}SiO_2(H_2O)_4 + 0.3Ca(OH)_2$

$C_2S + 4.3H \rightarrow C\text{-}S\text{-}H + 0.3CH$

Aluminate (C_3A) + anhydrite ($C\bar{s}$) + water → ettringite

$(CaO)_3Al_2O_3 + 3CaSO_4 + 32H_2O \rightarrow (CaO)_3(CaSO_4)_3Al_2O_3 \cdot 32H_2O$

$C_3A + 3C\bar{s} + 32H \rightarrow C_6A\bar{s}_3H_{32}$ **AFt**

Aluminate (C_3A) + calcite ($C\bar{c}$) + water → monocarbonate

$(CaO)_3Al_2O_3 + CaCO_3 + 12H_2O \rightarrow (CaO)_3(CaCO_3) Al_2O_3 \cdot 12H_2O$

$C_3A + C\bar{c} + 12H \rightarrow C_4A\bar{c}H_{12}$ **AFm**

AFt + AFm contain a lot of water -> high volume

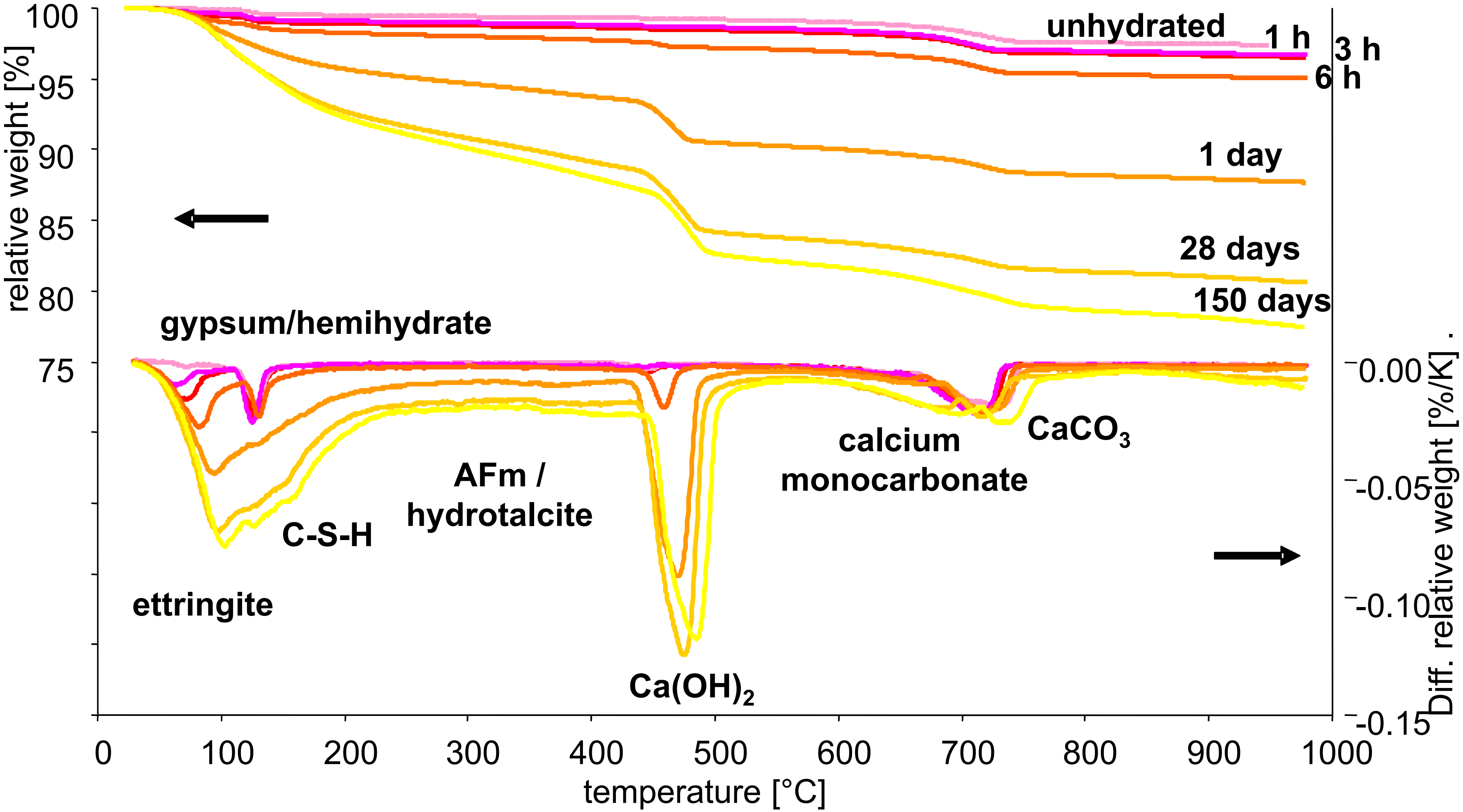
C	CaO
S	SiO_2
A	Al_2O_3
F	Fe_2O_3
H	H_2O
$\bar{c}$	CO_2
$\bar{s}$	SO_3
N	Na_2O
K	K_2O
M	MgO
T	TiO_2

What is cement?

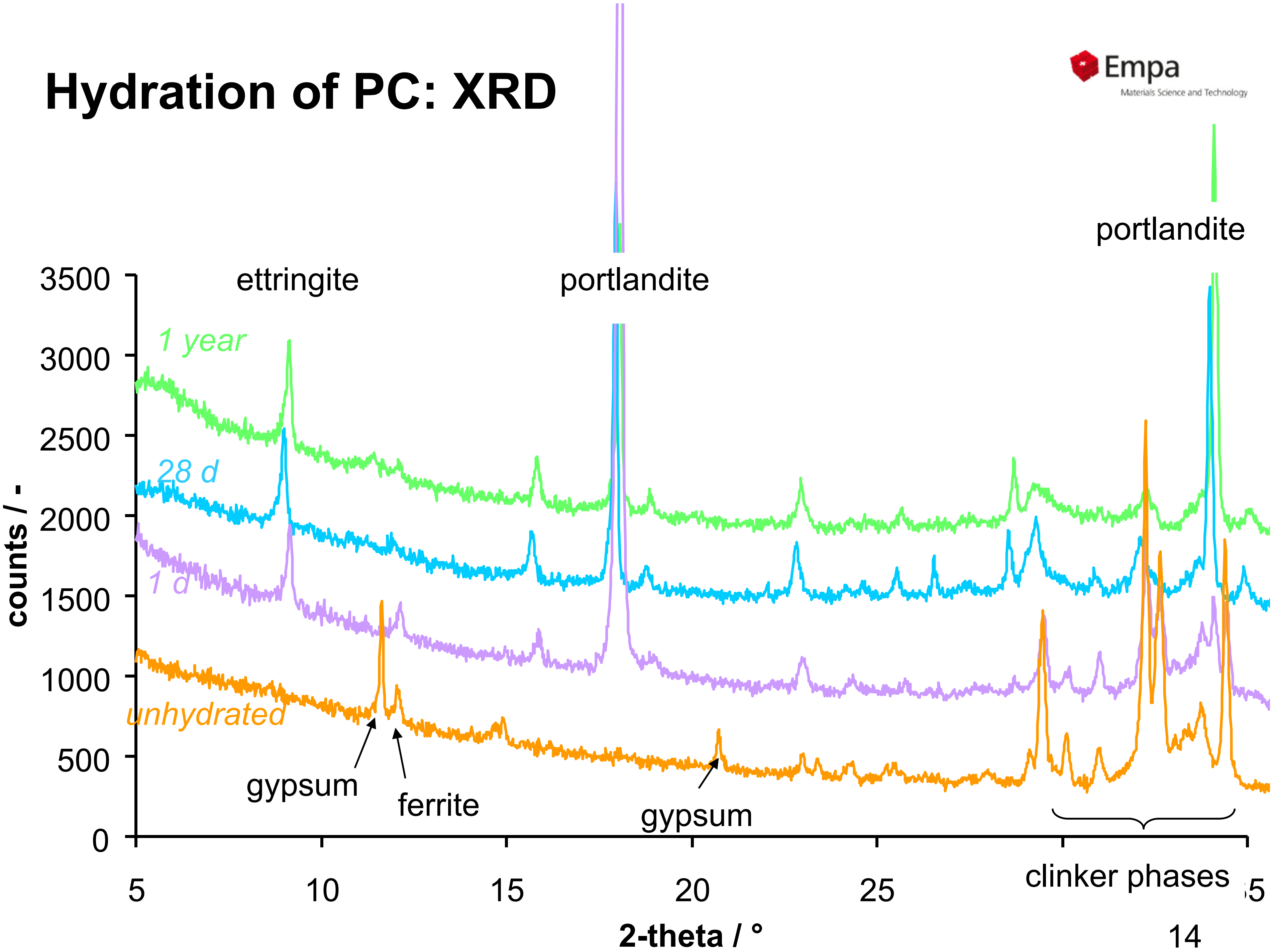
«**Minute Cement**»
Video from John Rossen and Arnaud Muller (EPFL)

https://www.youtube.com/watch?v=L4OLBNXMdHk

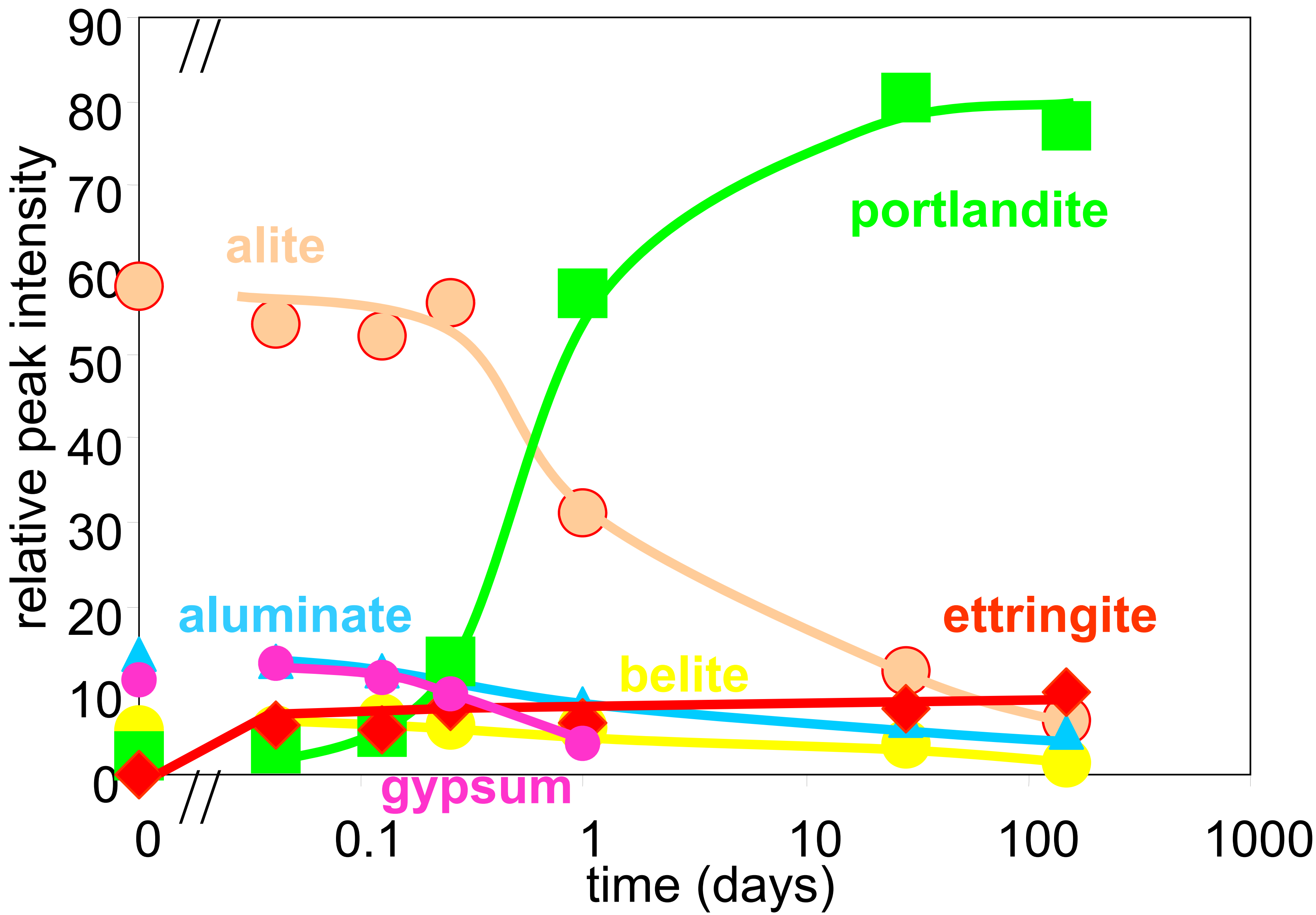
Hydration of PC: TGA

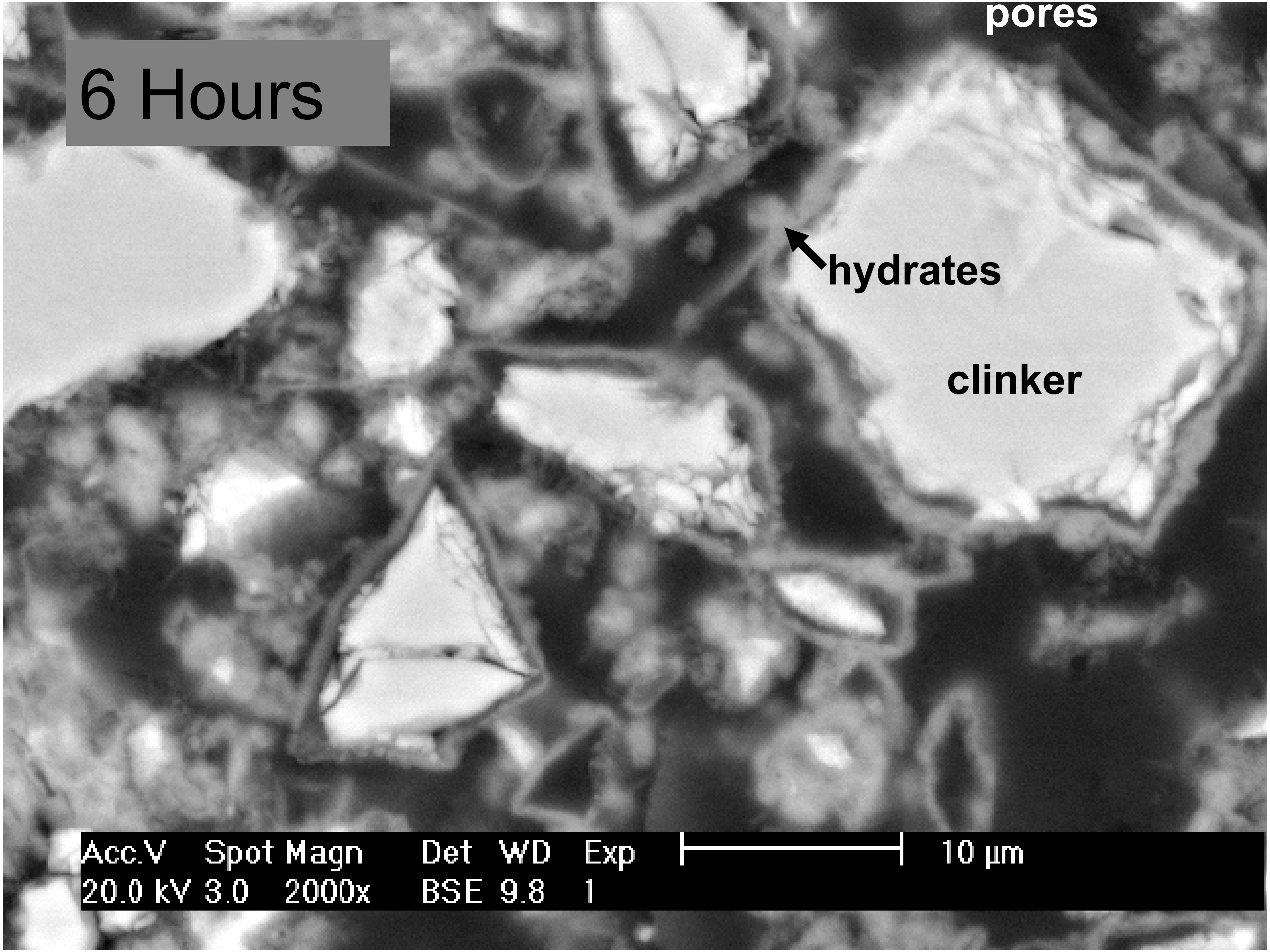


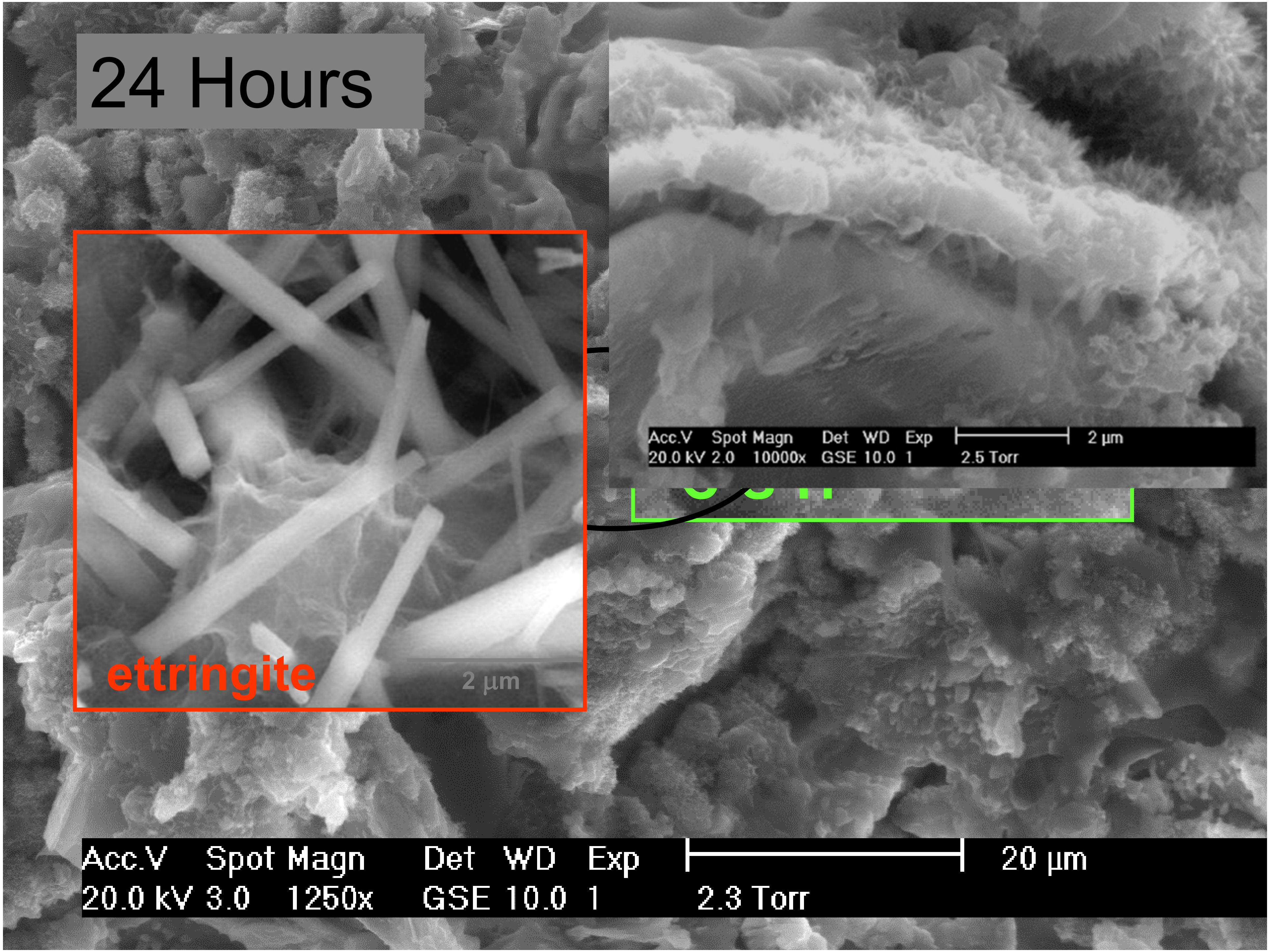
Hydration of PC: XRD



Hydration of PC: XRD




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


24 Hours
ettringite
2 µm
Acc.V Spot Magn Det WD Exp 2 µm
20.0 kV 2.0 10000x GSE 10.0 1 2.5 Torr
Acc.V Spot Magn Det WD Exp 20 µm
20.0 kV 3.0 1250x GSE 10.0 1 2.3 Torr

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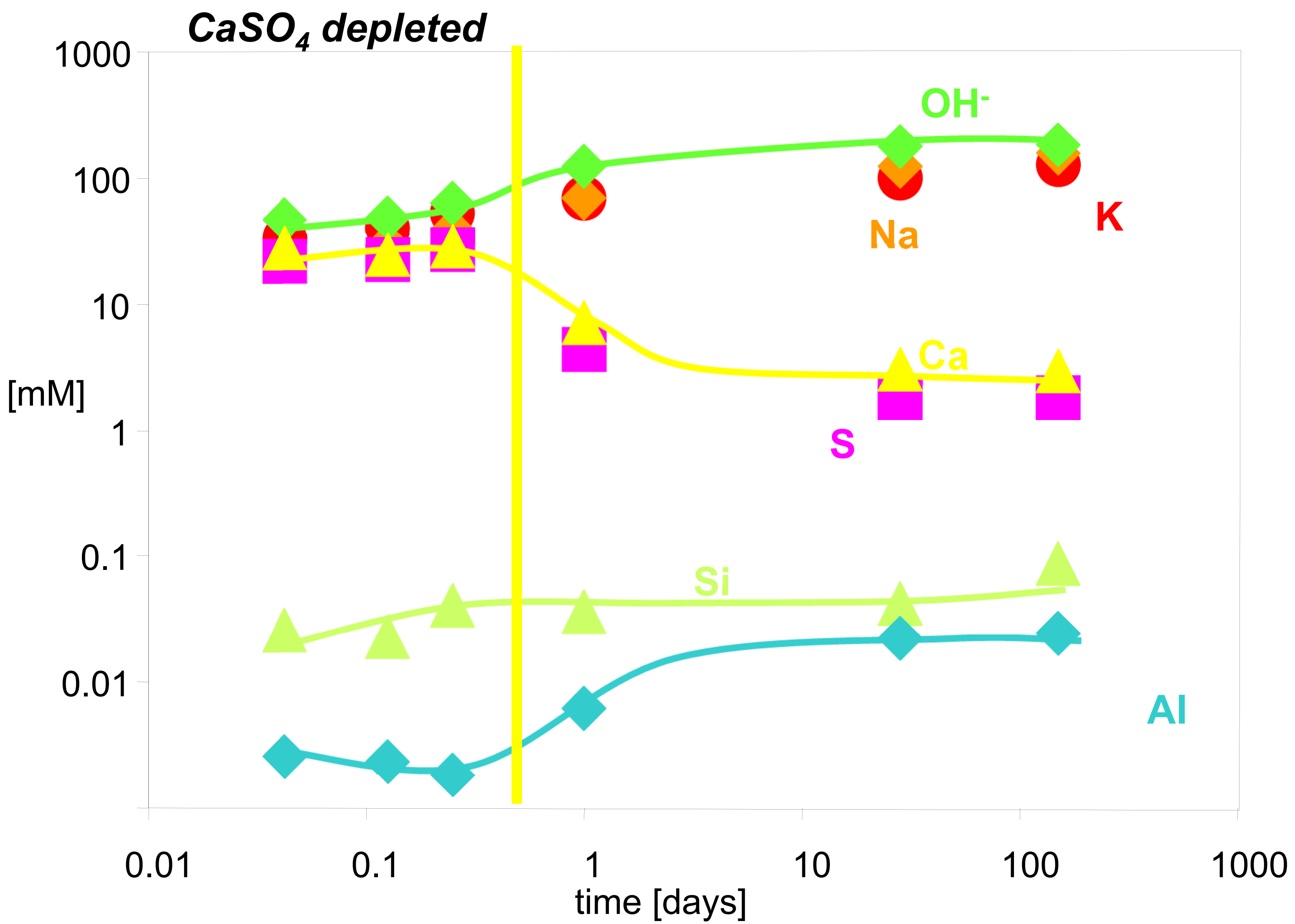
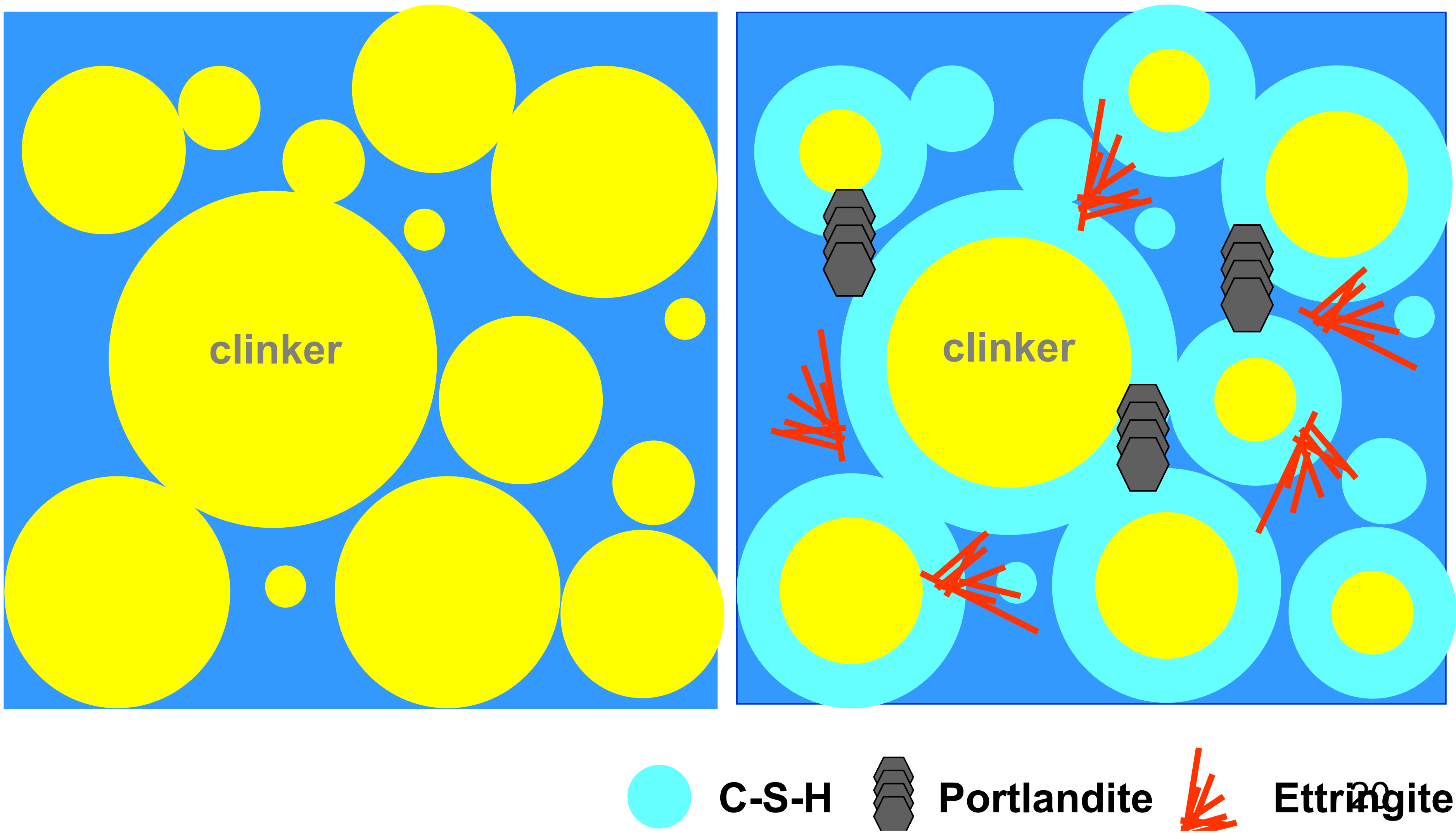
Hydration of PC: Pore solution



Modelling of Hydration



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What is needed to model hydration?

1 Portland cement

Multi-component input

I Clinkers

C_3S C_2S C_3A C_4AF

K_2O
Na_2O
MgO

II Other solids

K_2SO_4
Na_2SO_4
Hemihydrate
CaO

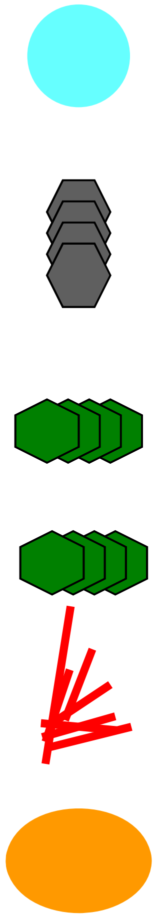
Gypsum
Anhydrite
Calcite

III Water

H_2O

Thermodynamic modeling

Hydrated OPC



C-S-H
portlandite
monosulfate
monocarbonate
ettringite
hydrotalcite

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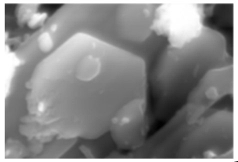
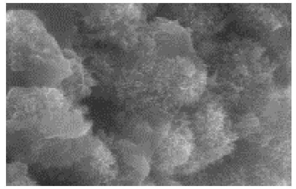
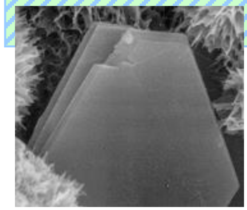
2 Thermodynamic databases







PSI/Nagra TDB

- Aqueous phase (Ca^{2+}, $Ca(OH)^{+}$, …)
- Gaseous phase (e.g. CO_2 (g), …)
- Minerals (calcite, gypsum, portlandite, …)

Cemdata07, 18

AFm

- SO_4-AFm ↔ OH-AFm *solid solution*
- CO_3-AFm
- hemicarb.
- strätlingite
- Al-AFm ↔ Fe-AFm *solid solution*

AFt

- SO_4-AFt ↔ CO_3-AFt *solid solution*
- CO_3-AFt ↔ *thaumasite*
- Fe-AFt ↔ Al-AFt *solid solution*

hydrogarnet

- C_3AH_6
- $C_3FS_{0.84}H_{4.32}$ ↔ $C_3AS_{0.84}H_{4.32}$

C-S-H

- High Ca C-S-H ↔ tobermorite *solid solution*
- SiO_2

Recent additions:
Cl_2, I_2, CrO_4, NO_3, NO_2-AFm, M-S-H, zeolites, C-A-S-H, relative humidity

Data based on solubility measurements at different temperatures + solid phase characterisation

What is needed to model hydration?

3 Reactivity of anhydrous phases

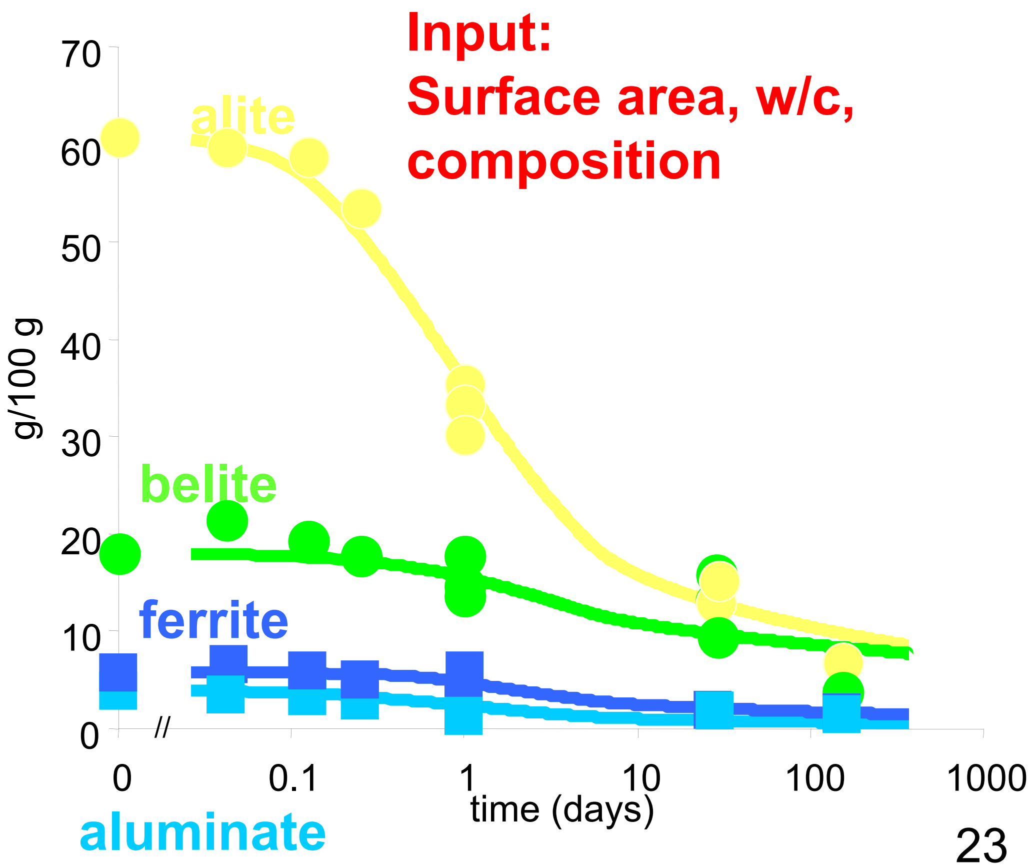
based on empirical data, measured data, dissolution rates,…

$$R_t = \frac{K_1}{N_1}(1-\alpha_t)(-\ln(1-\alpha_t))^{(1-N_1)}$$

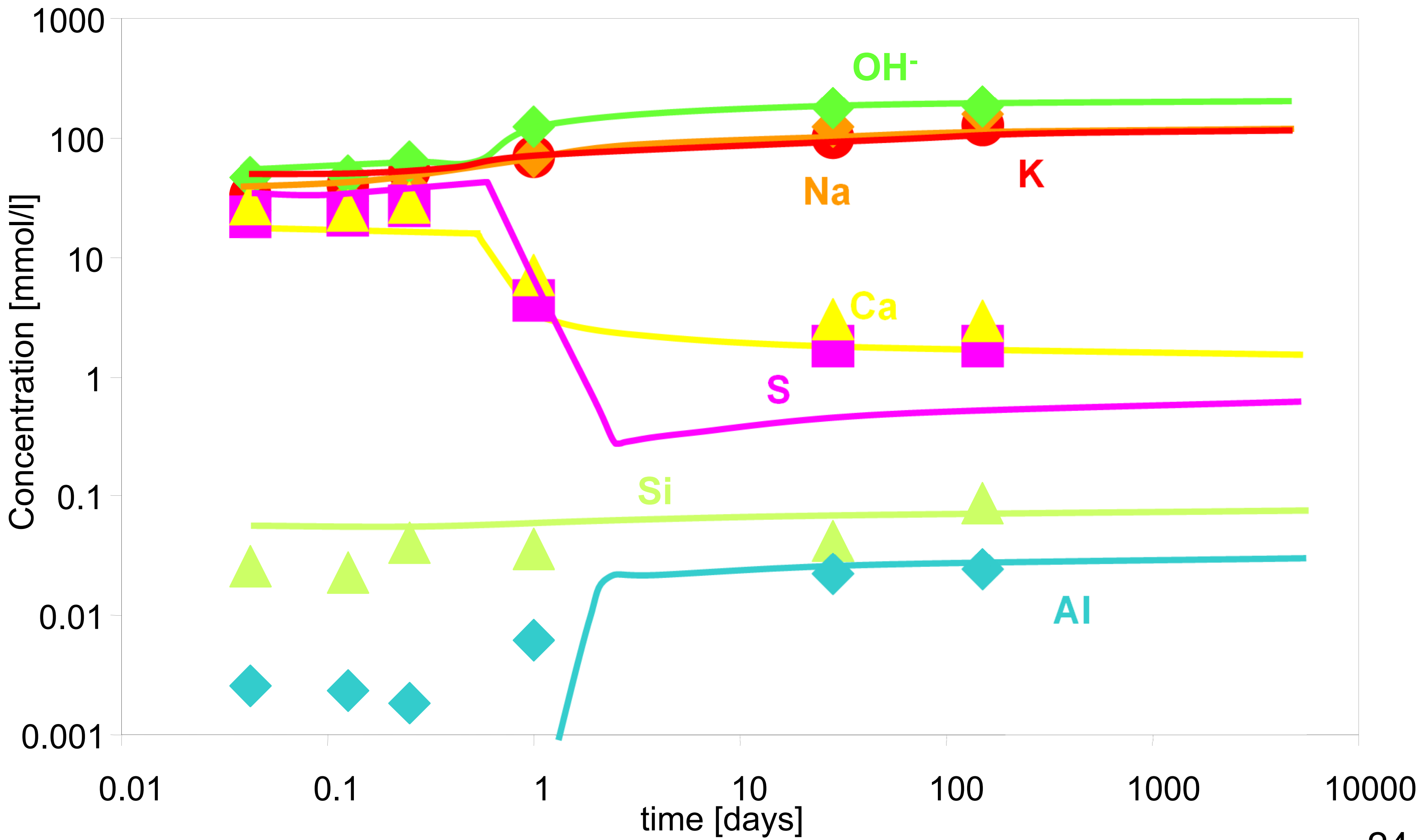
$$R_t = \frac{K_2 \times (1-\alpha_t)^{2/3}}{1-(1-\alpha_t)^{1/3}}$$

$$R_t = K_3 \times (1-\alpha_t)^{N_3}$$

All parameters (K_i, N_i) from Parrot and Killoh (1984)

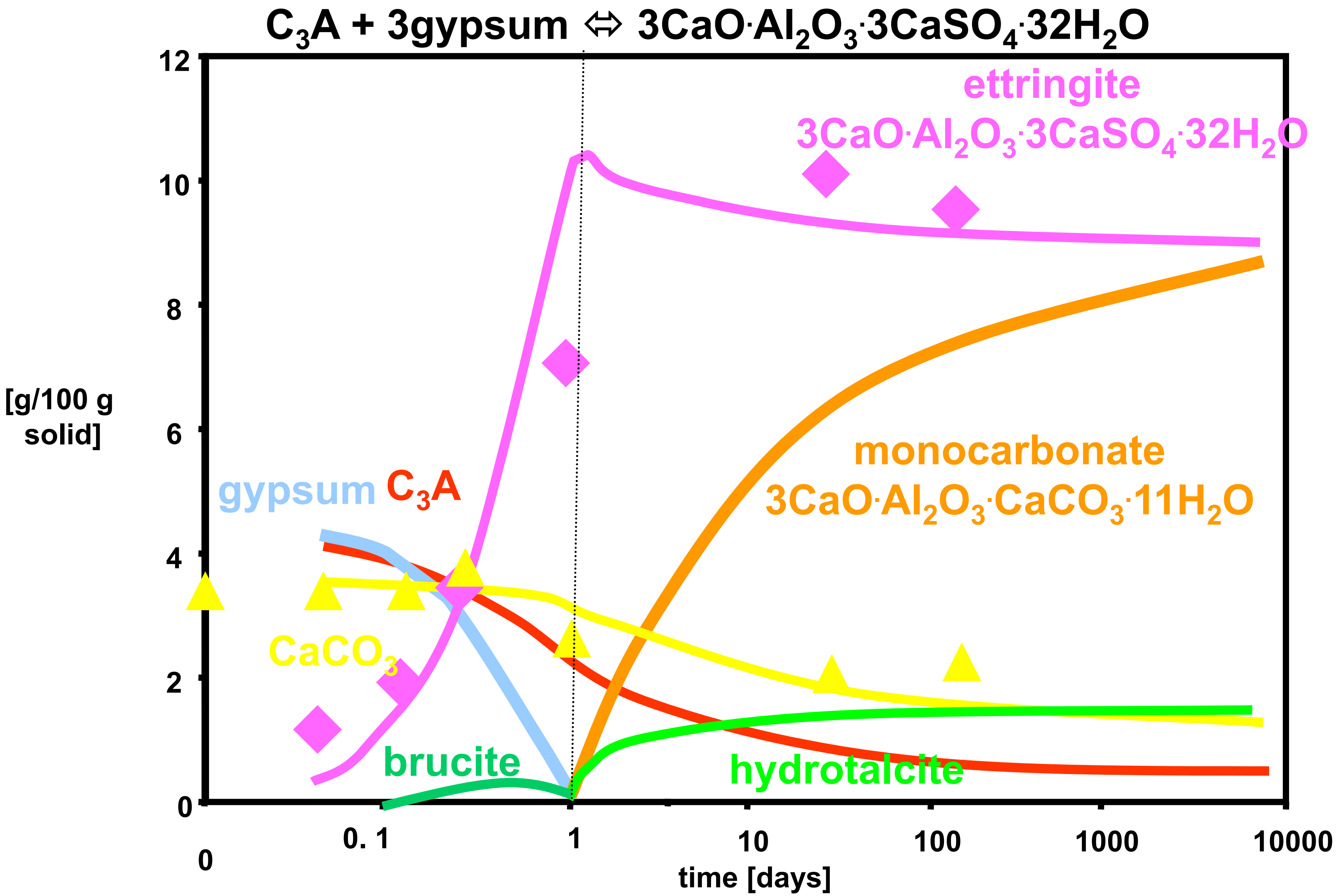


Modelled pore solutions



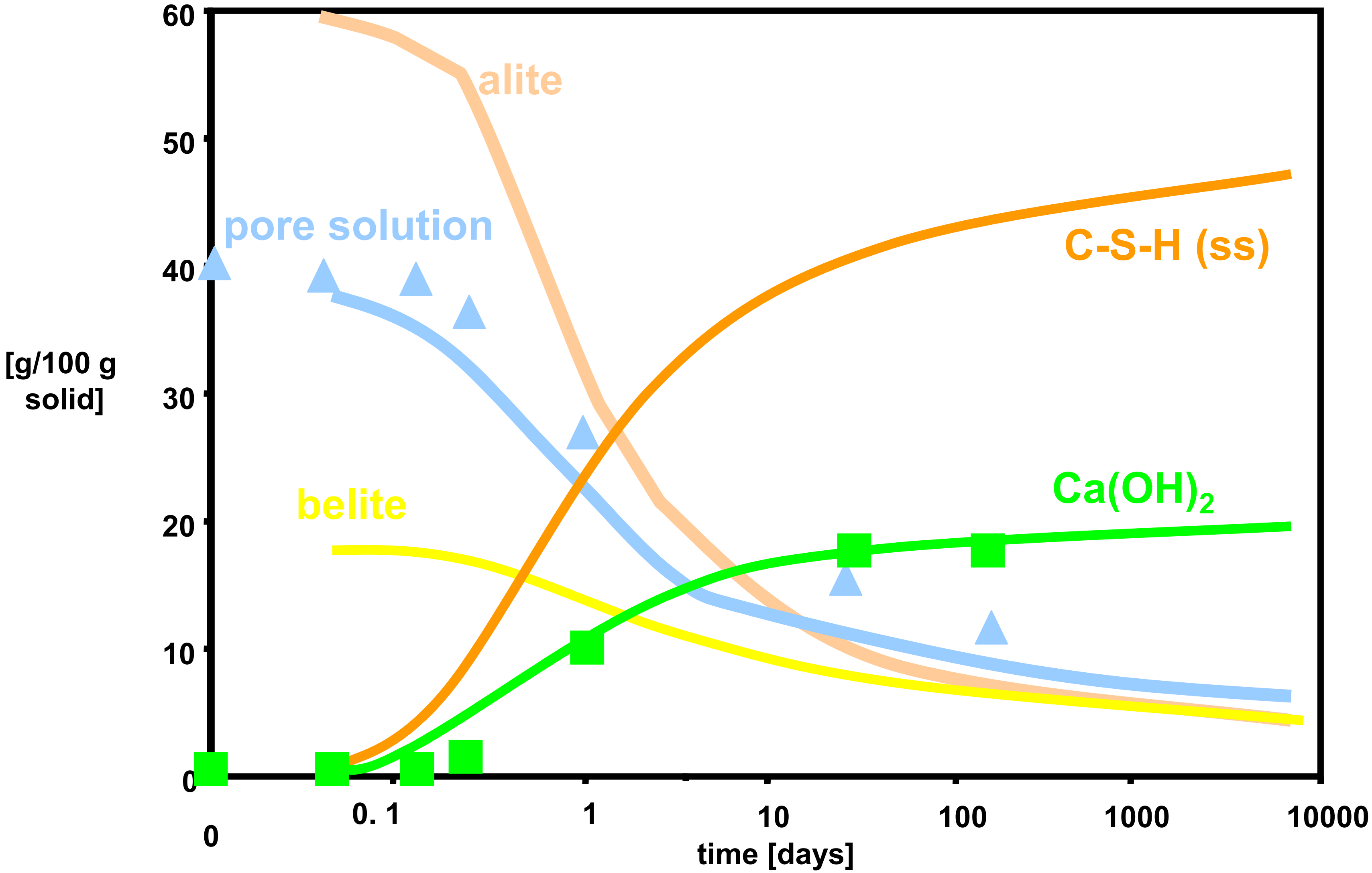
Lothenbach, Winnefeld (2006), CCR 36, 209-226

Al-, SO_4- and CO_3-hydrates



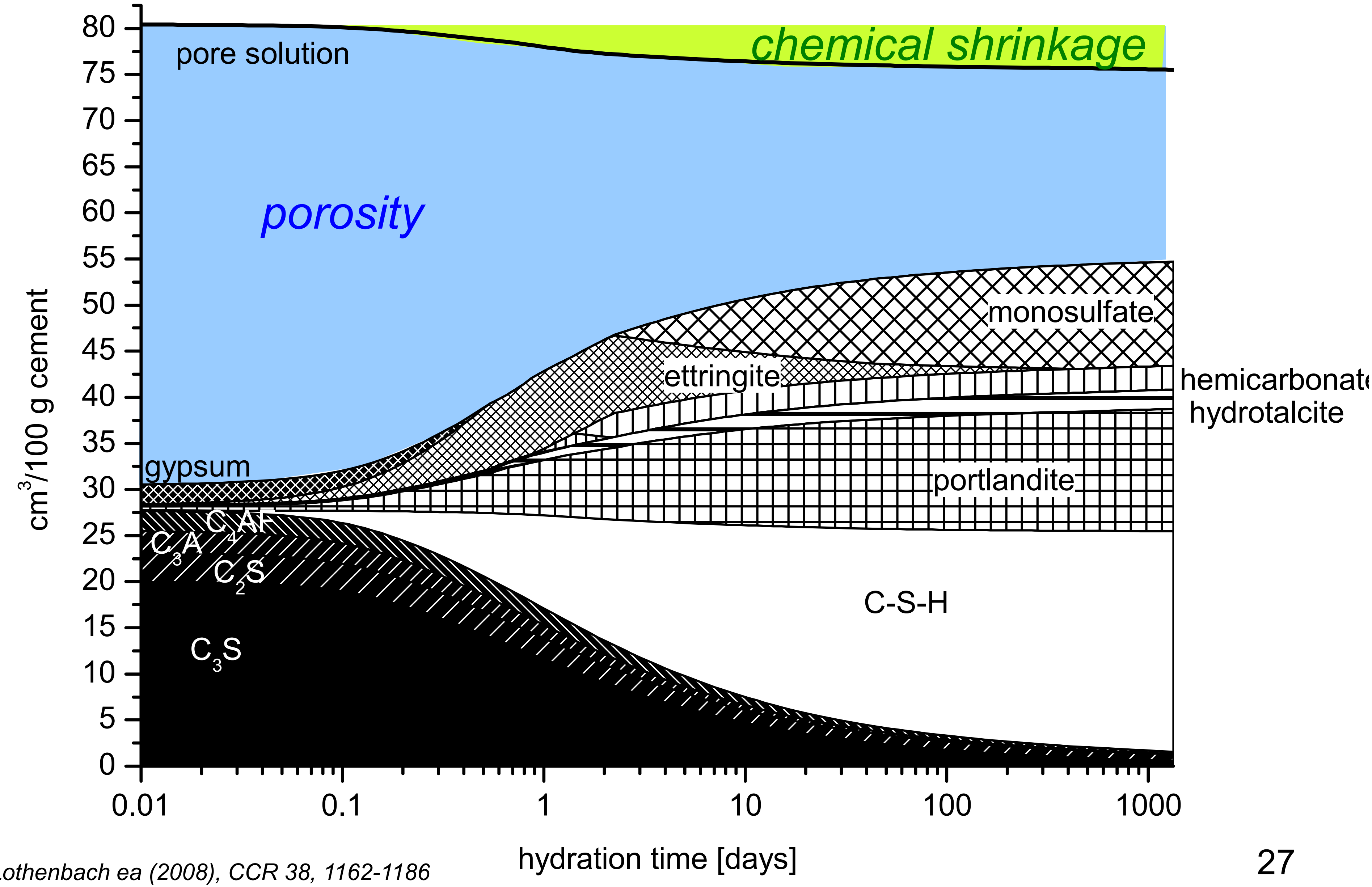
Lothenbach, Winnefeld (2006), CCR 36, 209-226

Modelled Ca- and Si-Hydrates



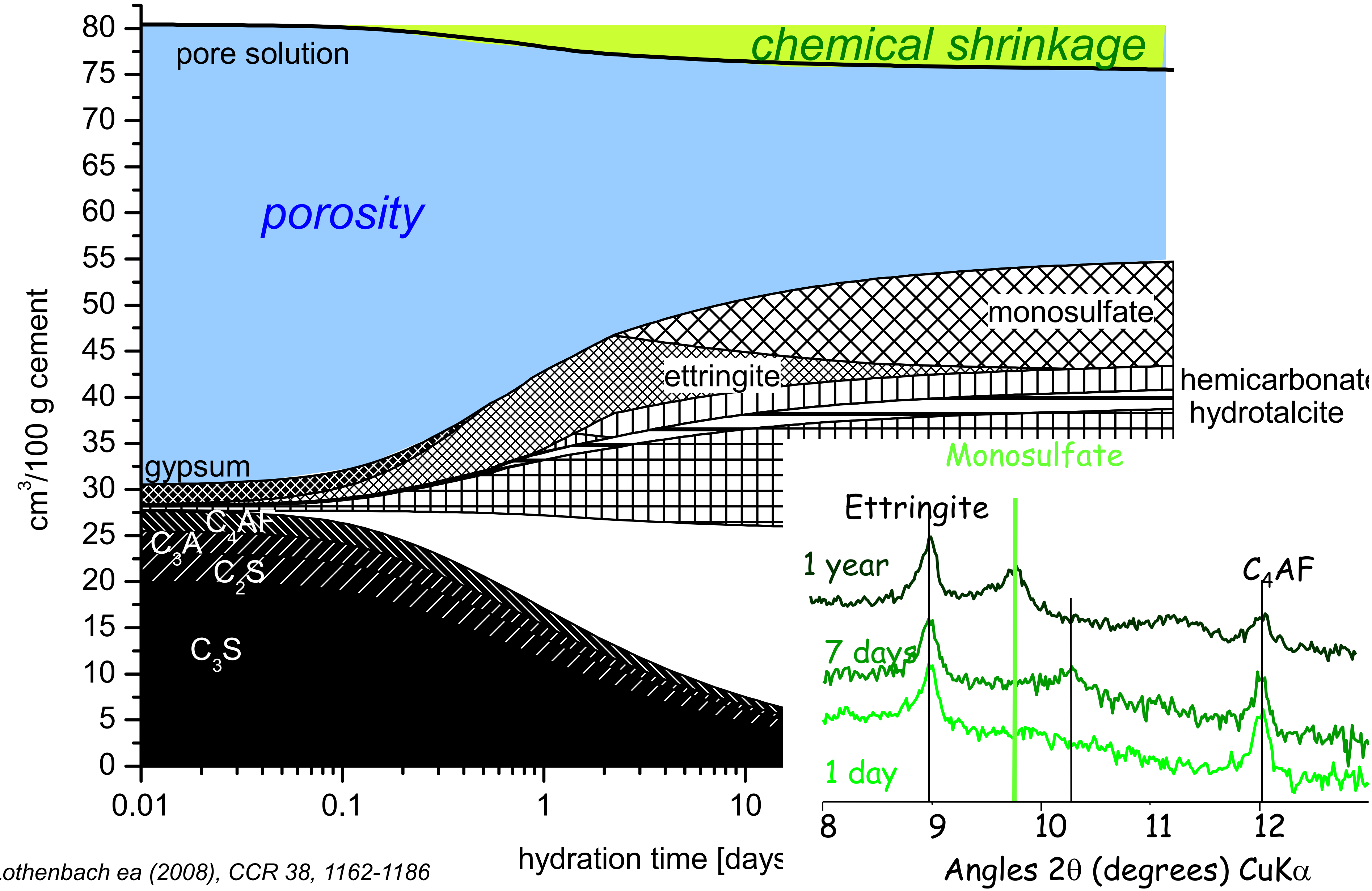
Lothenbach, Winnefeld (2006), CCR 36, 209-226

Portland cement (without calcite)



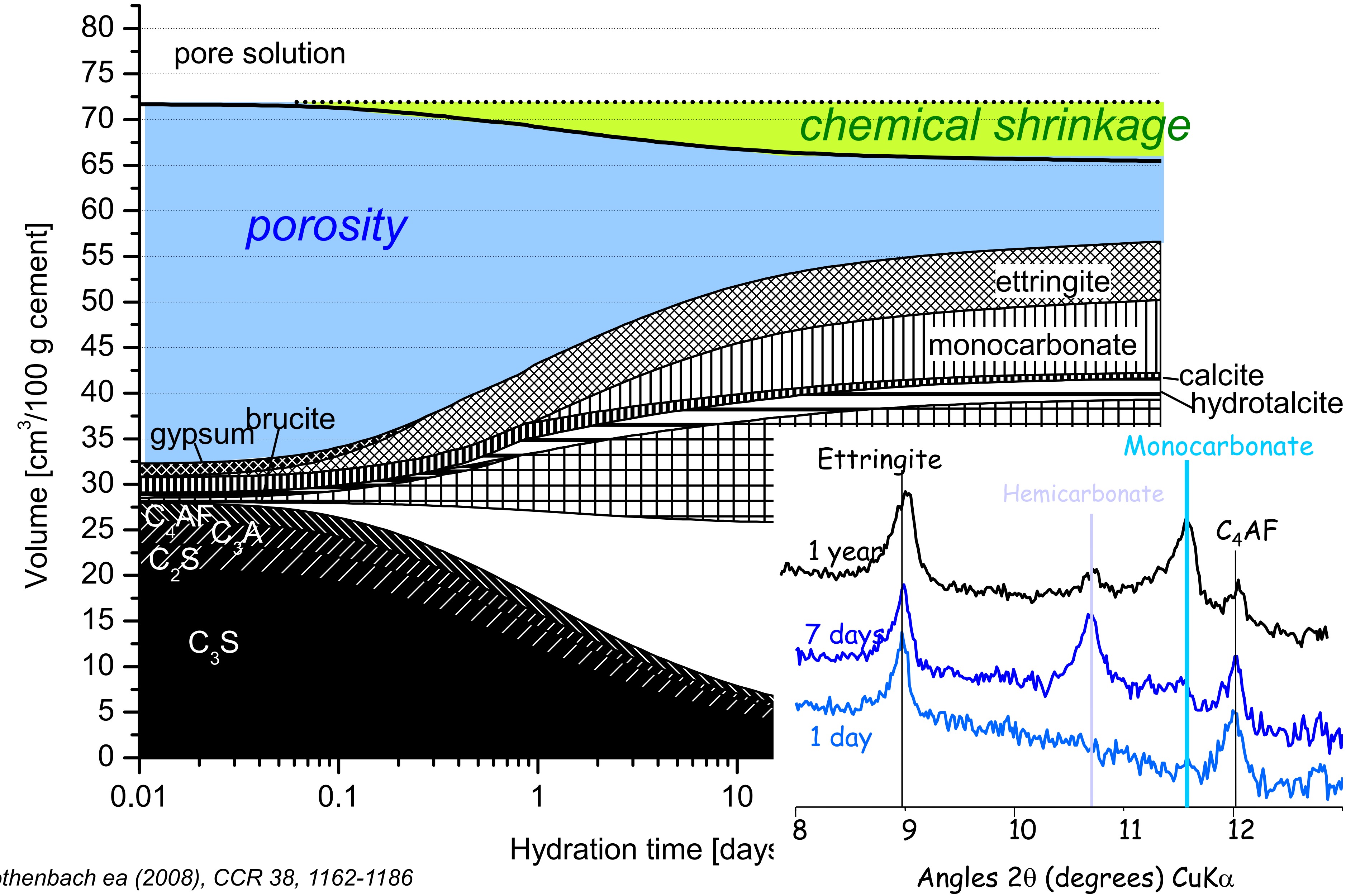
Lothenbach ea (2008), CCR 38, 1162-1186

Portland cement (without calcite)



Lothenbach ea (2008), CCR 38, 1162-1186

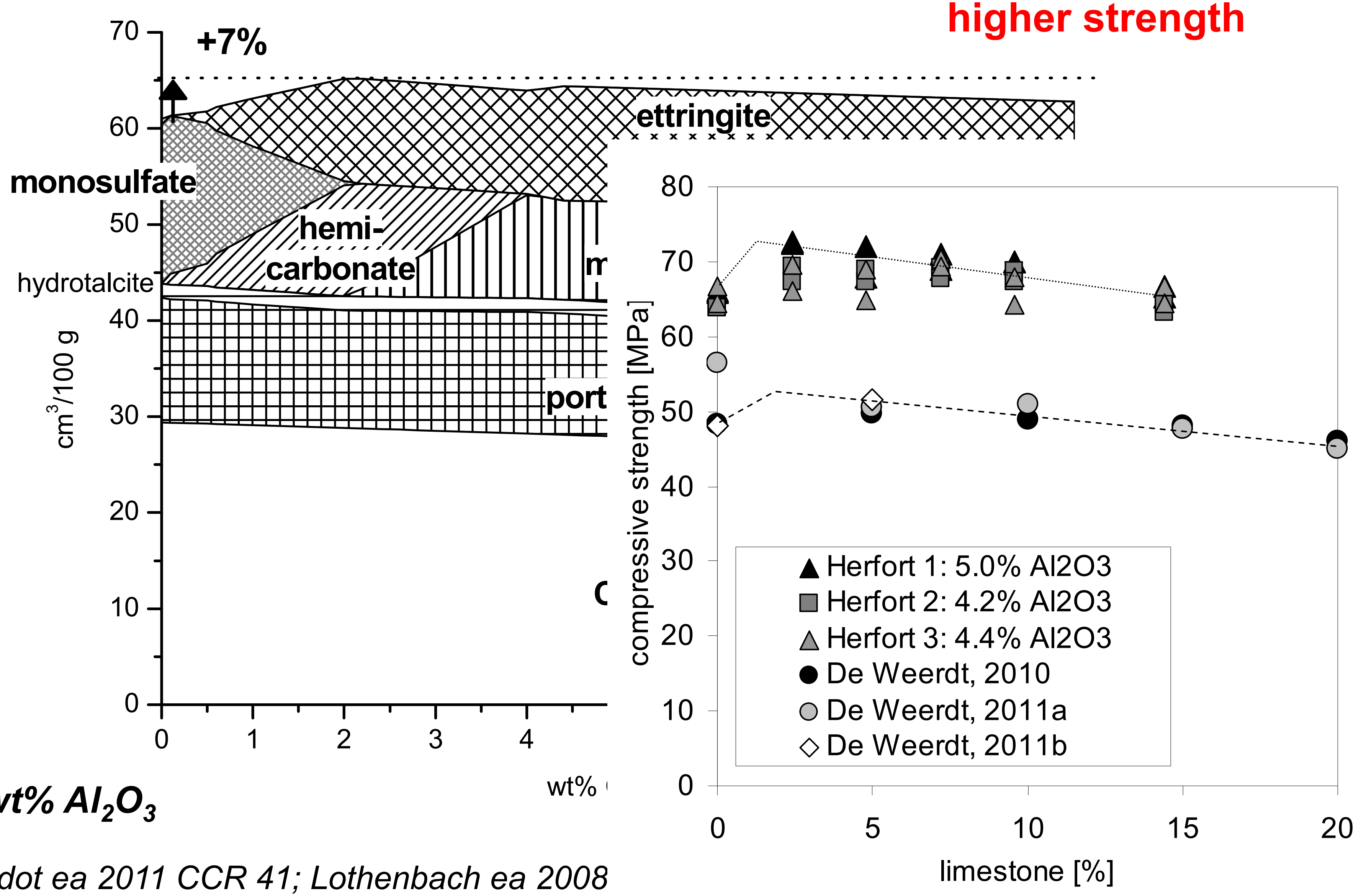
Portland cement (with 4% calcite)



Lothenbach ea (2008), CCR 38, 1162-1186

Influence of limestone on PC

More Volume ⇔ higher strength

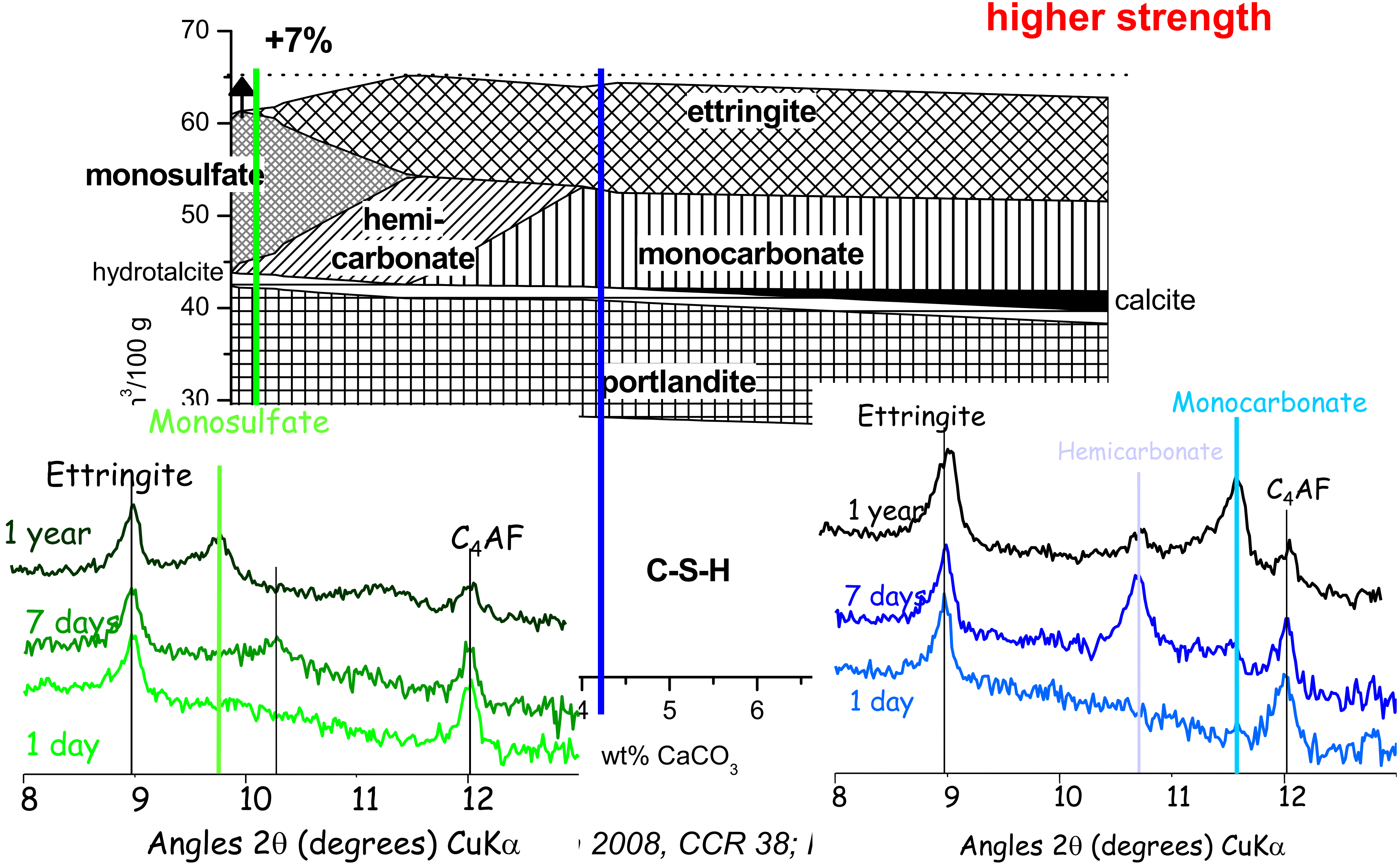


5.3 wt% Al_2O_3

Damidot ea 2011 CCR 41; Lothenbach ea 2008

Influence of limestone on PC

More Volume ⇔ higher strength



Effect of limestone on pore solution

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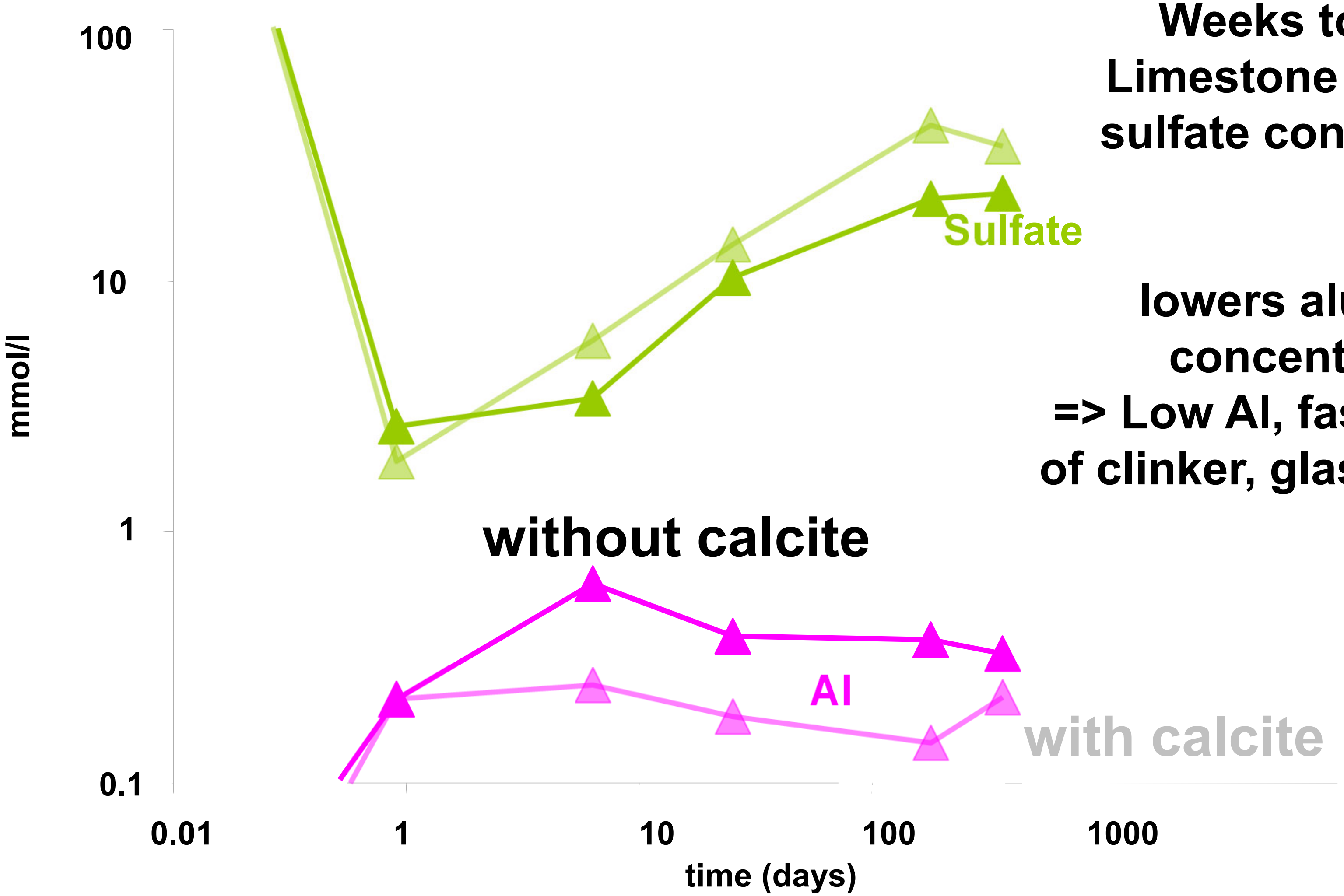


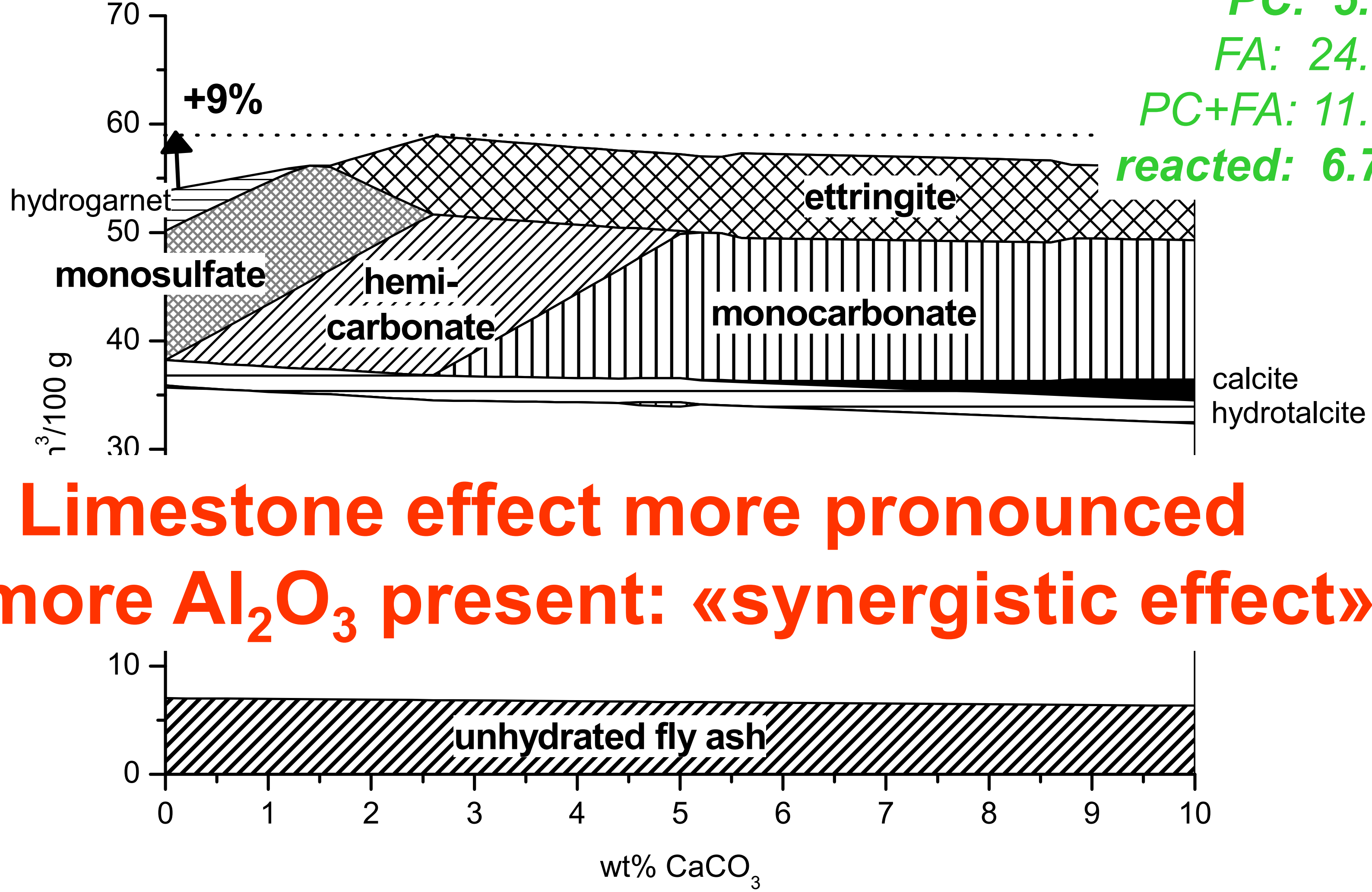
Weeks to years:
Limestone increases sulfate concentration

lowers aluminium concentrations
=> Low Al, faster reaction of clinker, glasses, slag, …

Lothenbach ea 2008, CCR 38

Influence of limestone on PC blended with fly ash (FA): CEM II/B-V

wt% Al_2O_3
PC: 5.3
FA: 24.0
PC+FA: 11.8
reacted: 6.7



Limestone effect more pronounced if more Al_2O_3 present: «synergistic effect»

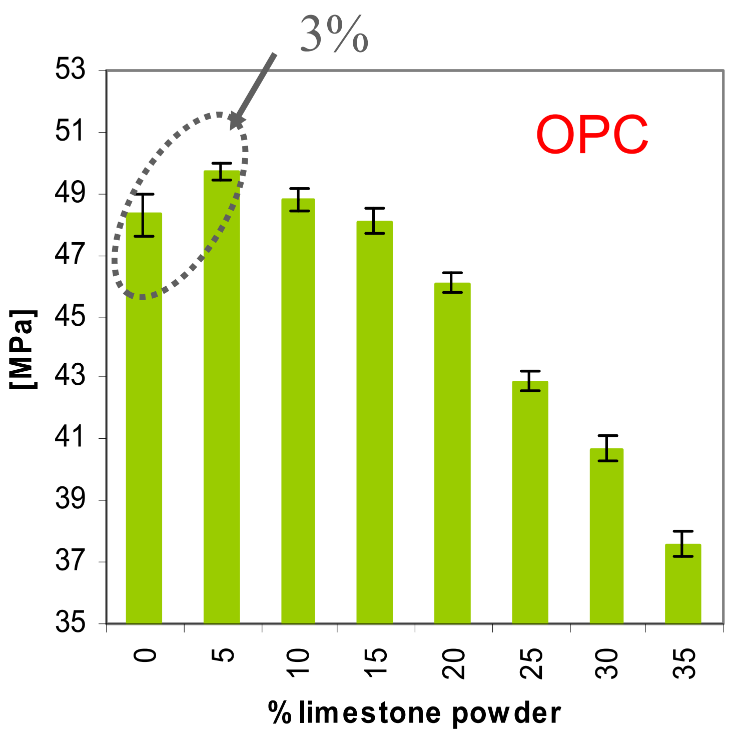
De Weerdt ea 2011, CCR 41; Damidot ea 2011, CCR 41

Influence of limestone on strength

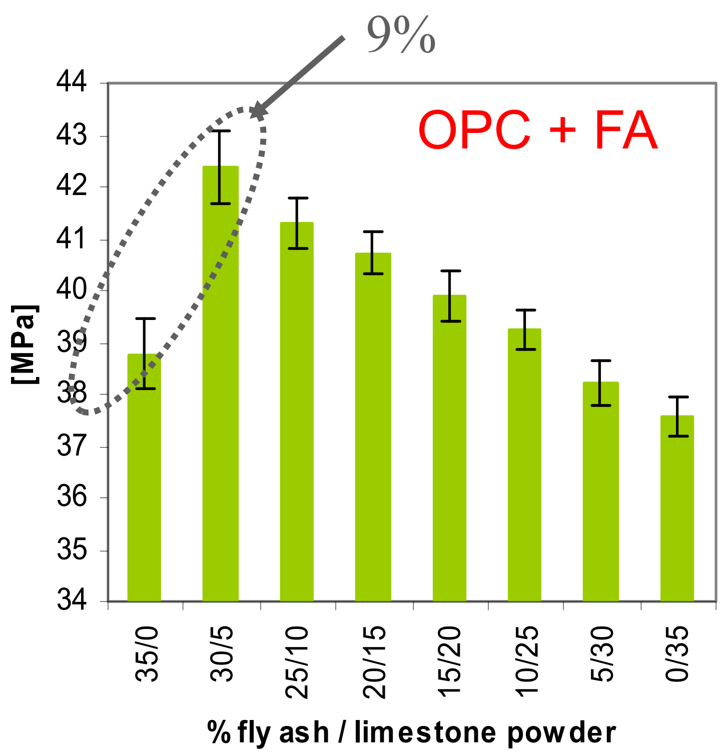
OPC: 6% Al_2O_3

Blending of OPC with fly ash and limestone
Al_2O_3-content: Fly ash 24% ↔ OPC 6%

more Al_2O_3 => «synergistic» effect



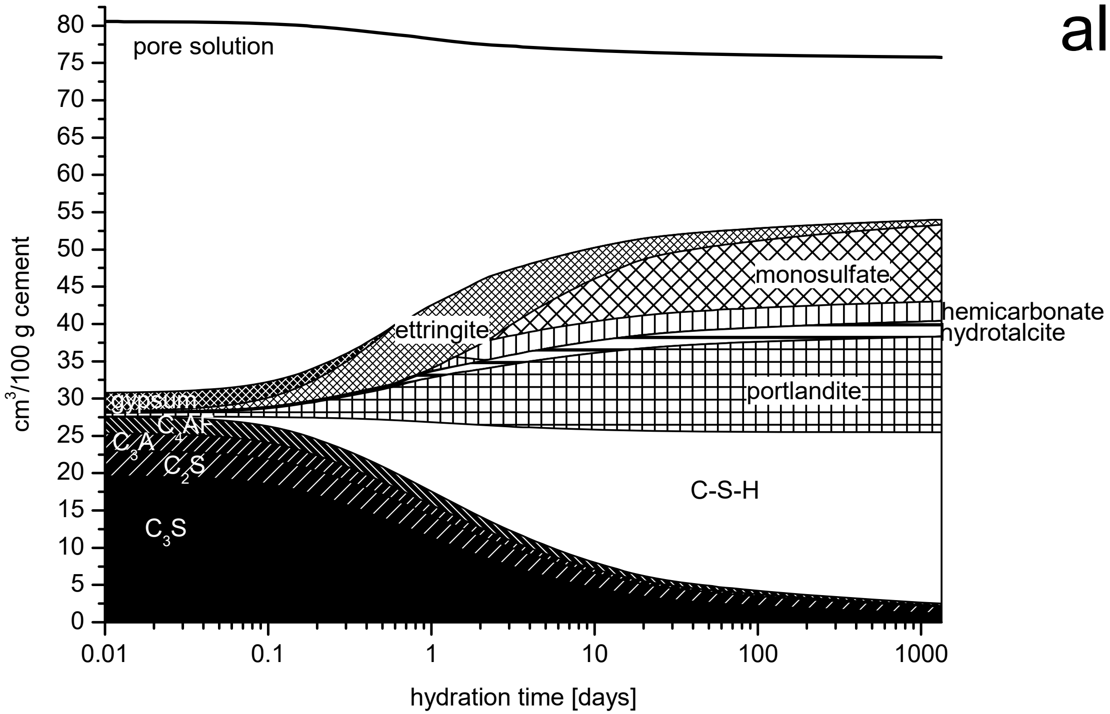
De Weerdt ea, 2010, 2011



=> Calcined clay + limestone

Conclusions

PC
- High pH, portlandite
- High Ca/Si C-S-H



Limestone
- Positive effect
- MS+Cc => AFt+Mc
- Accelerates slag and alite reaction

Questions?