Hydration of “low pH” cements

Barbara Lothenbach[1], Erich Wieland[2], B. Schwyn[3], R. Figi[1] ,D. Rentsch[1]

[1] Empa, Laboratory for Concrete & Construction Chemistry, Switzerland
[2] PSI, Laboratory for Waste Management, Switzerland
[3] Nagra, National Cooperation for the Disposal of Radioactive Waste, Switzerland

EMPA
Materials Science & Technology

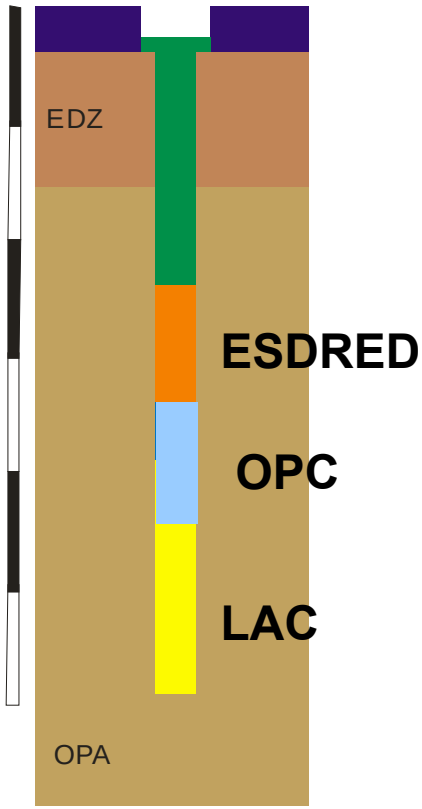
Objectives

- Hydration of
  - OPC: CEM I 42.5 HS
  - ESDRED:
    CEM I 42.5 N + 40% silica fume + accelerator
  - LAC: CEM III/B 42.5 L + 10% nanosilica

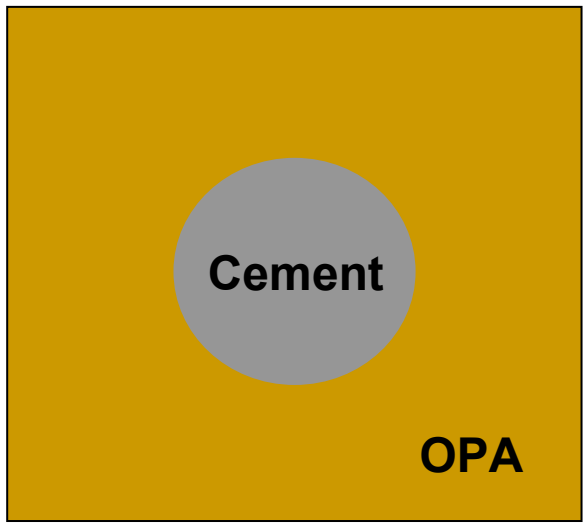
Cementitious materials used in field experiments
- composition of the pore solution
- mineral composition of the cement matrix
- comparison

Cement-Clay interface

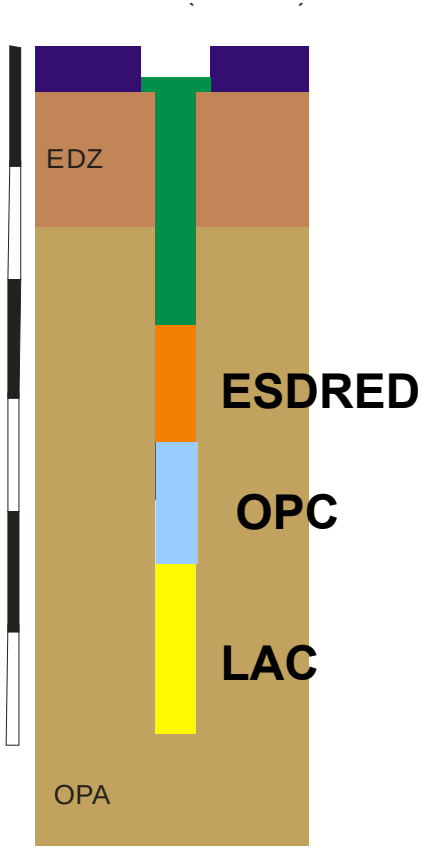
Side view

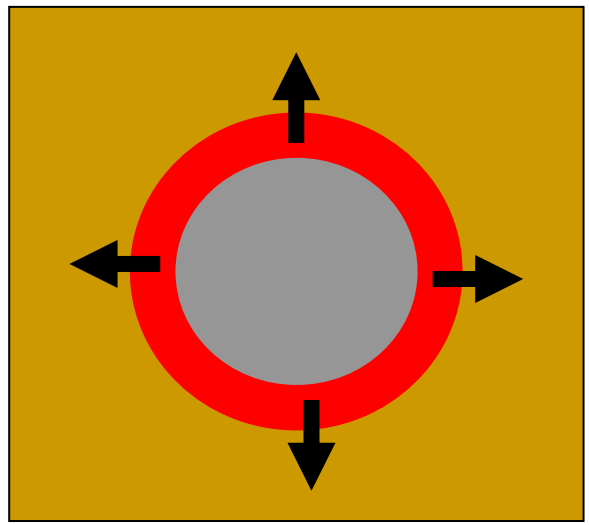


Top view

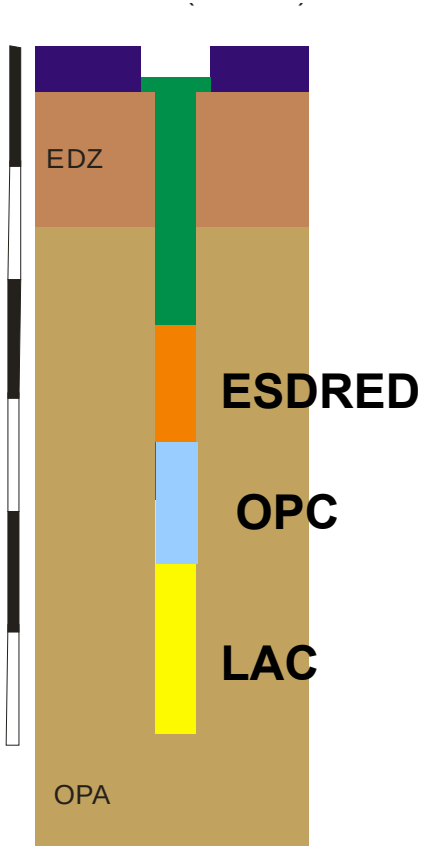


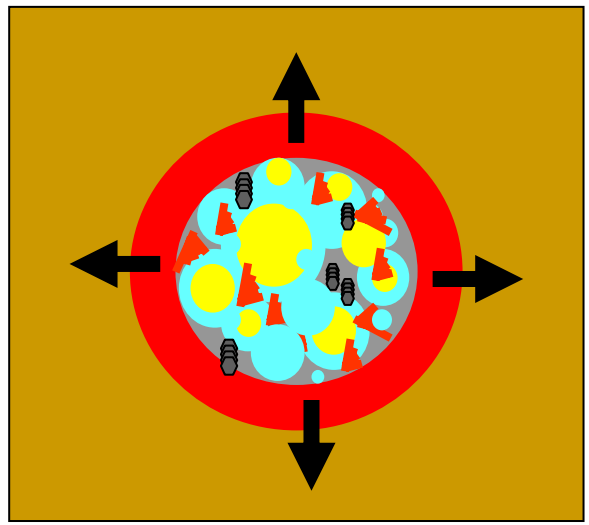
Cement-Clay interface





Cement-Clay interface

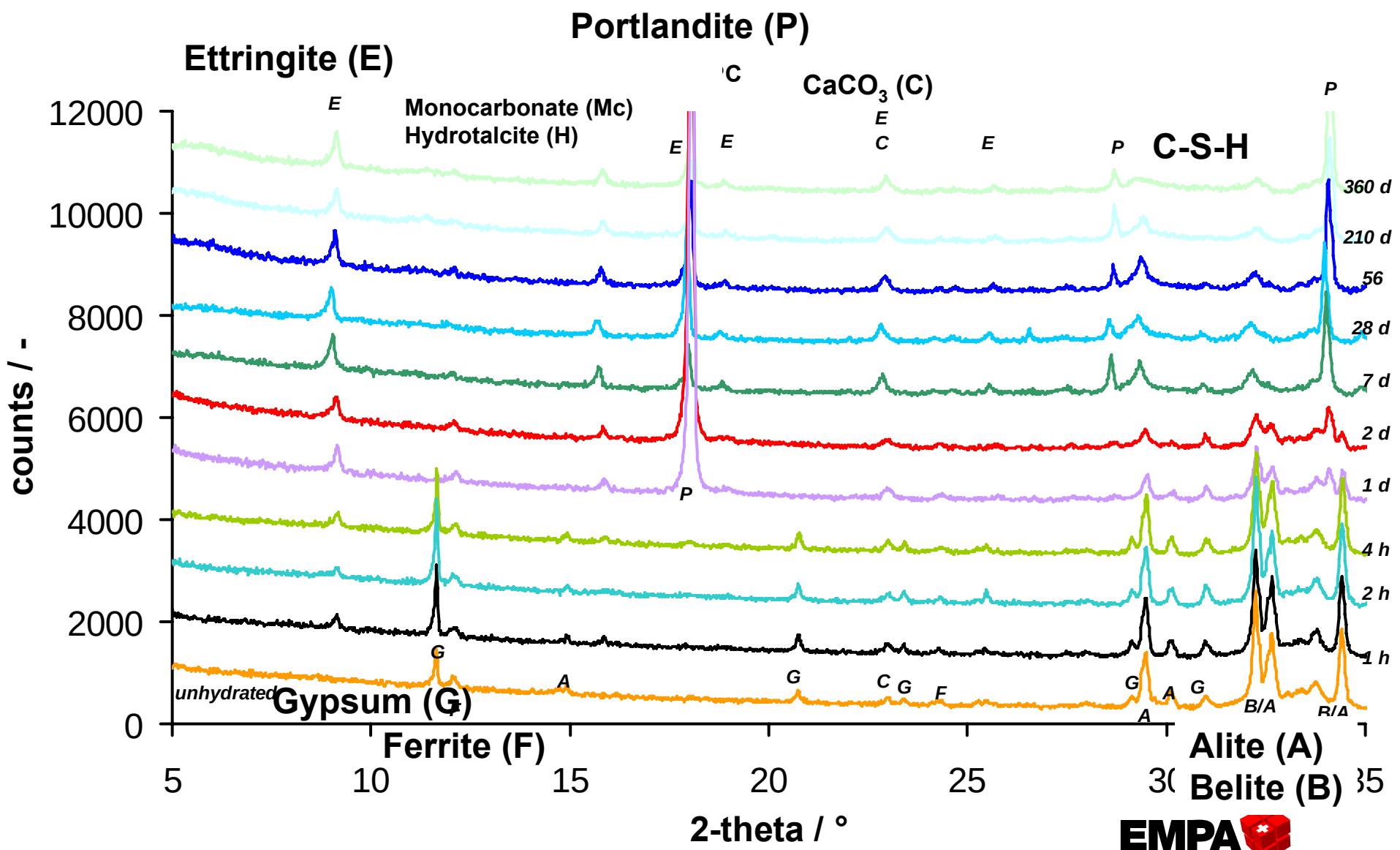




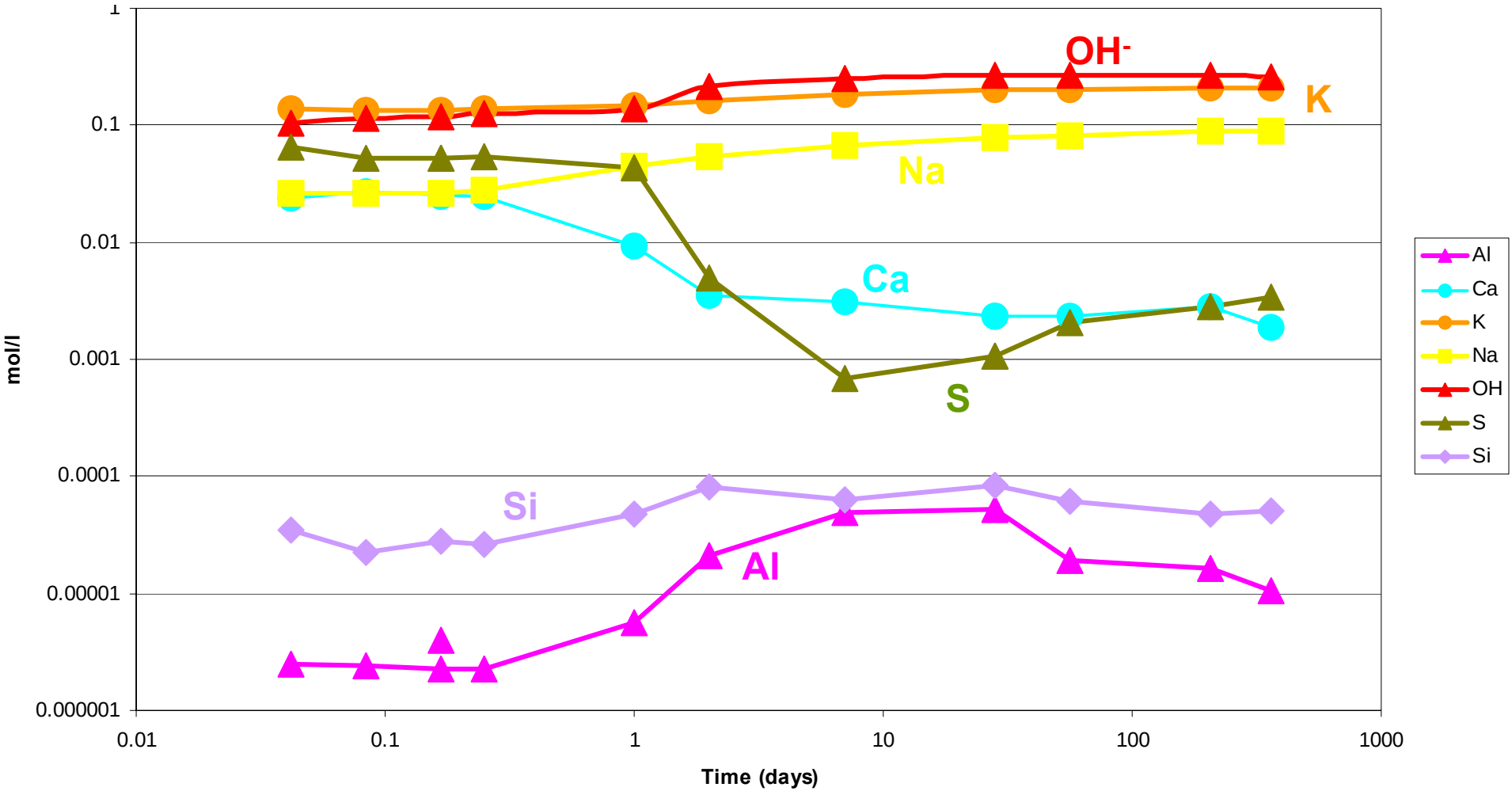
OPC: CEM I 42.5 R HS

	(g/100g)		
CaO	58.8	alite	31
SiO_2	20.6	belite	36
Al_2O_3	3.9	aluminate	1.6
Fe_2O_3	5.2	ferrite	16
MgO	4.6	MgO	4.6
Na_2O	0.27	$CaCO_3$	3.1
K_2O	0.75	$CaSO_4$	5.1
CO_2	1.4	Na_2O	0.22
SO_3	3.5	K_2O	0.27
CaO_{free}	0.71	Na_2SO_4	0.12
LOI	2.3	K_2SO_4	0.89
		w/c = 0.8	

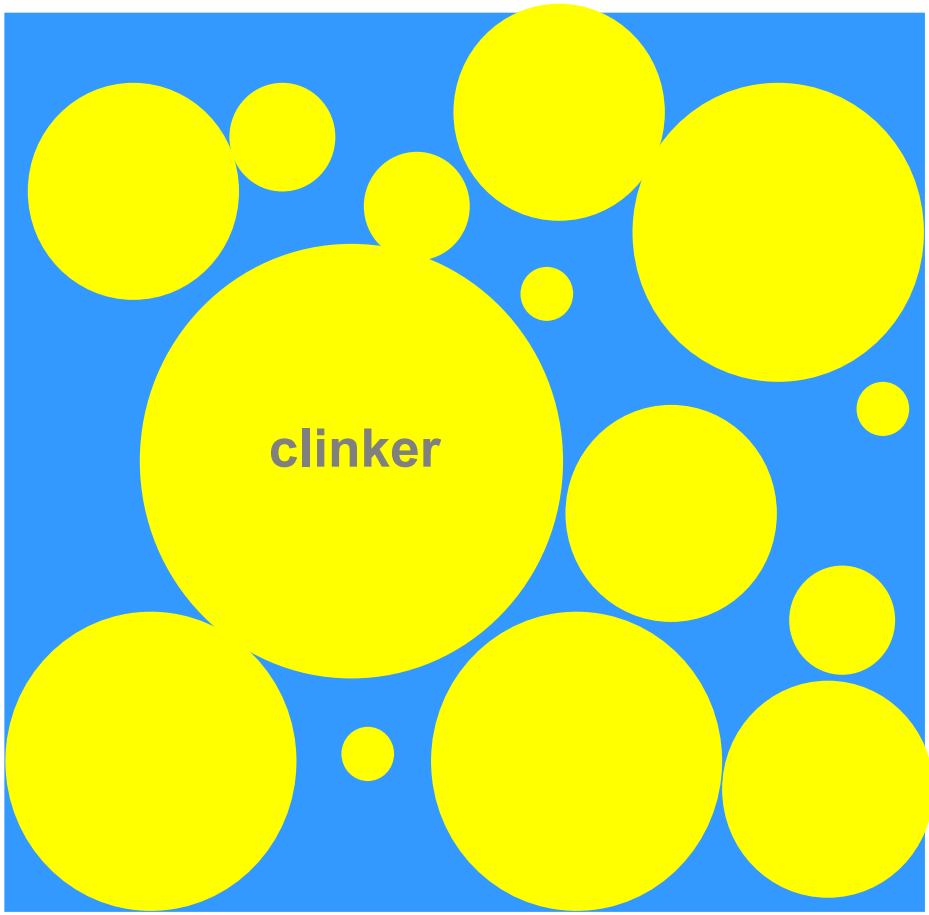
XRD

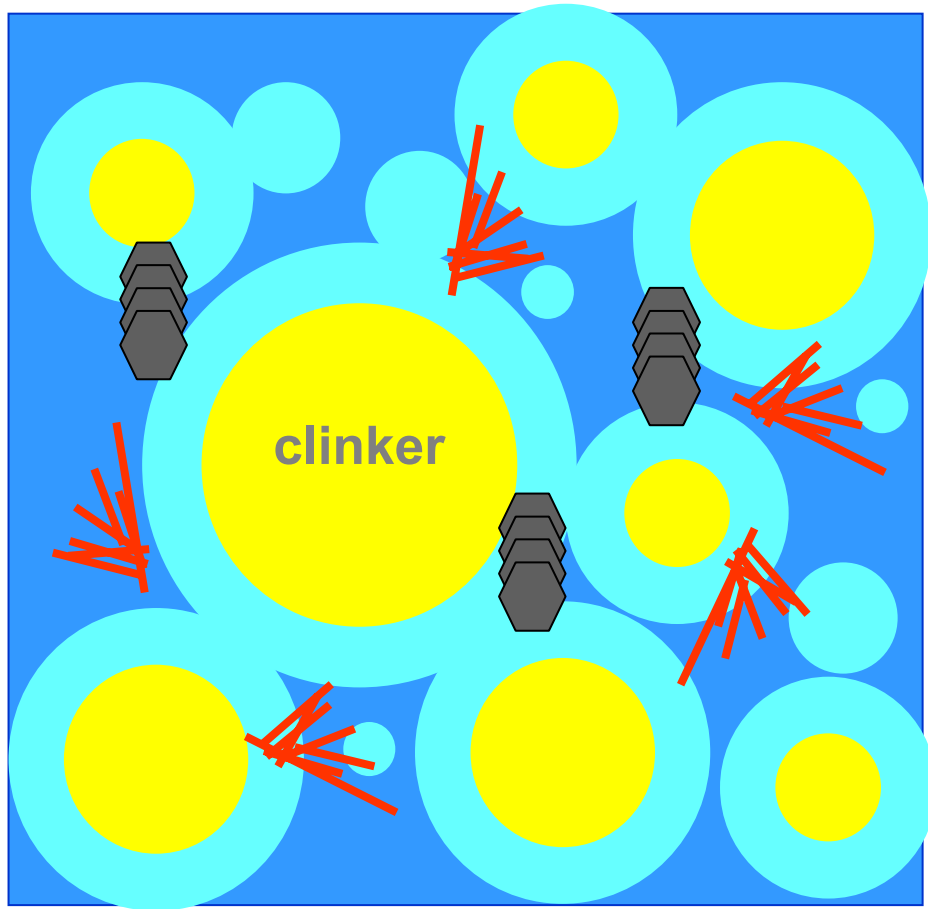

Portlandite (P)
Ettringite (E)
CaCO3 (C)
Monocarbonate (Mc)
Hydrotalcite (H)
C-S-H
360 d
210 d
56
28 d
7 d
2 d
1 d
4 h
2 h
1 h
unhydrated
Gypsum (G)
Ferrite (F)
Alite (A)
Belite (B)
B/A
counts / -
2-theta / °
12000
10000
8000
6000
4000
2000
0
5
10
15
20
25

Composition of the pore solution



Hydration (Lothenbach and Winnefeld, 2006)





alite (C_3S), belite (C_2S)
aluminate(C_3A), ferrite C_4AF)

C-S-H

Portlandite

Ettringite

EMPA

Modeling - Dissolution

Empirical Approach: Parrot and Killoh (1984)

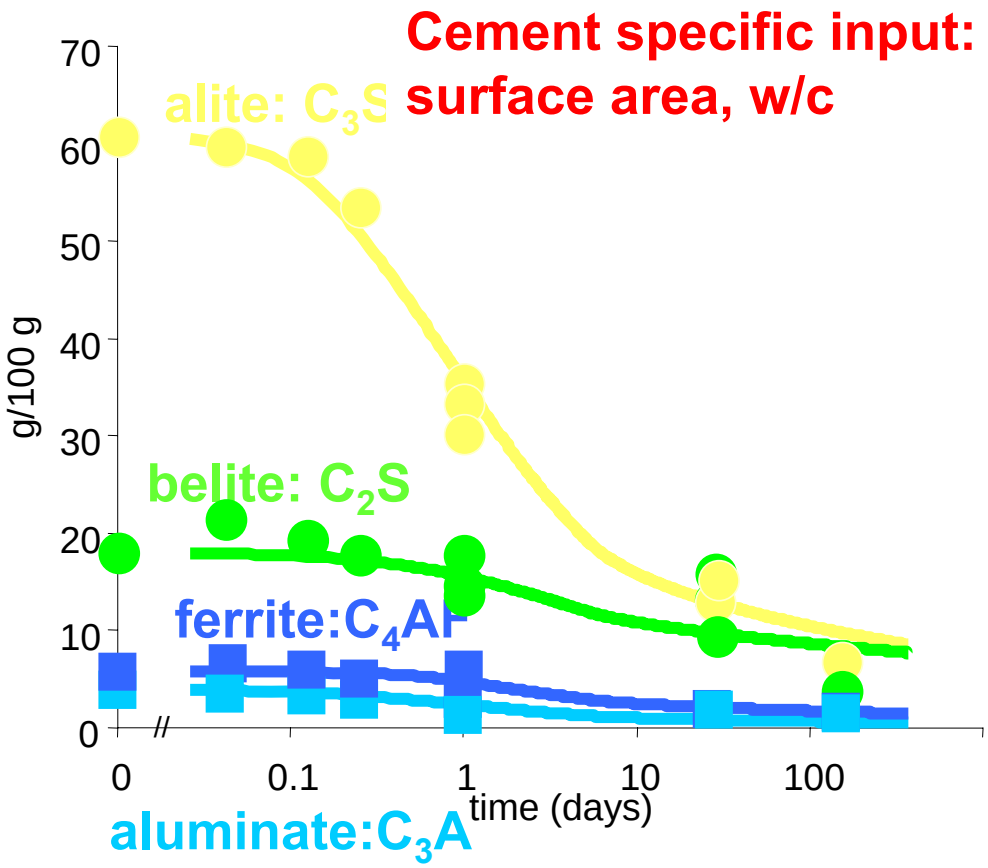
$$R_t = \frac{K_1}{N_1}(1-\alpha_t)(-\ln(1-\alpha_t))^{(1-N_1)}$$

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

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

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

α: degree of hydration



Thermodynamic Modeling

Cements

I clinkers (slowly soluble)

C_3S C_2S
C_3A C_4AF

K_2O
Na_2O
MgO

II soluble solids

K_2SO_4
Na_2SO_4
hemihydrate

gypsum
anhydrite
calcite

CaO

III water

H_2O

Thermodynamic modeling

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

Portlandite

C-S-H

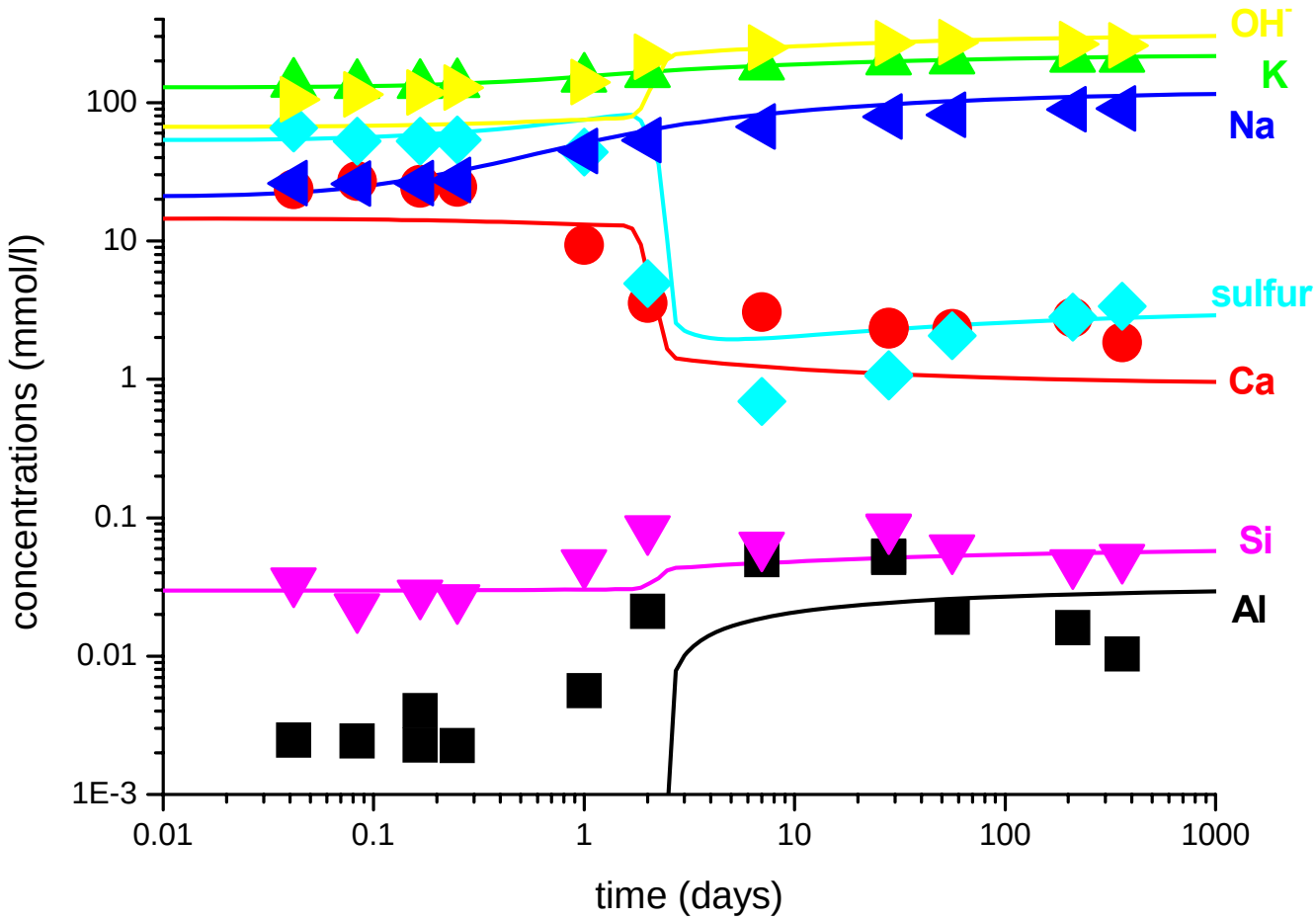
Ettringite

AFm

Hydrotalcites, ...

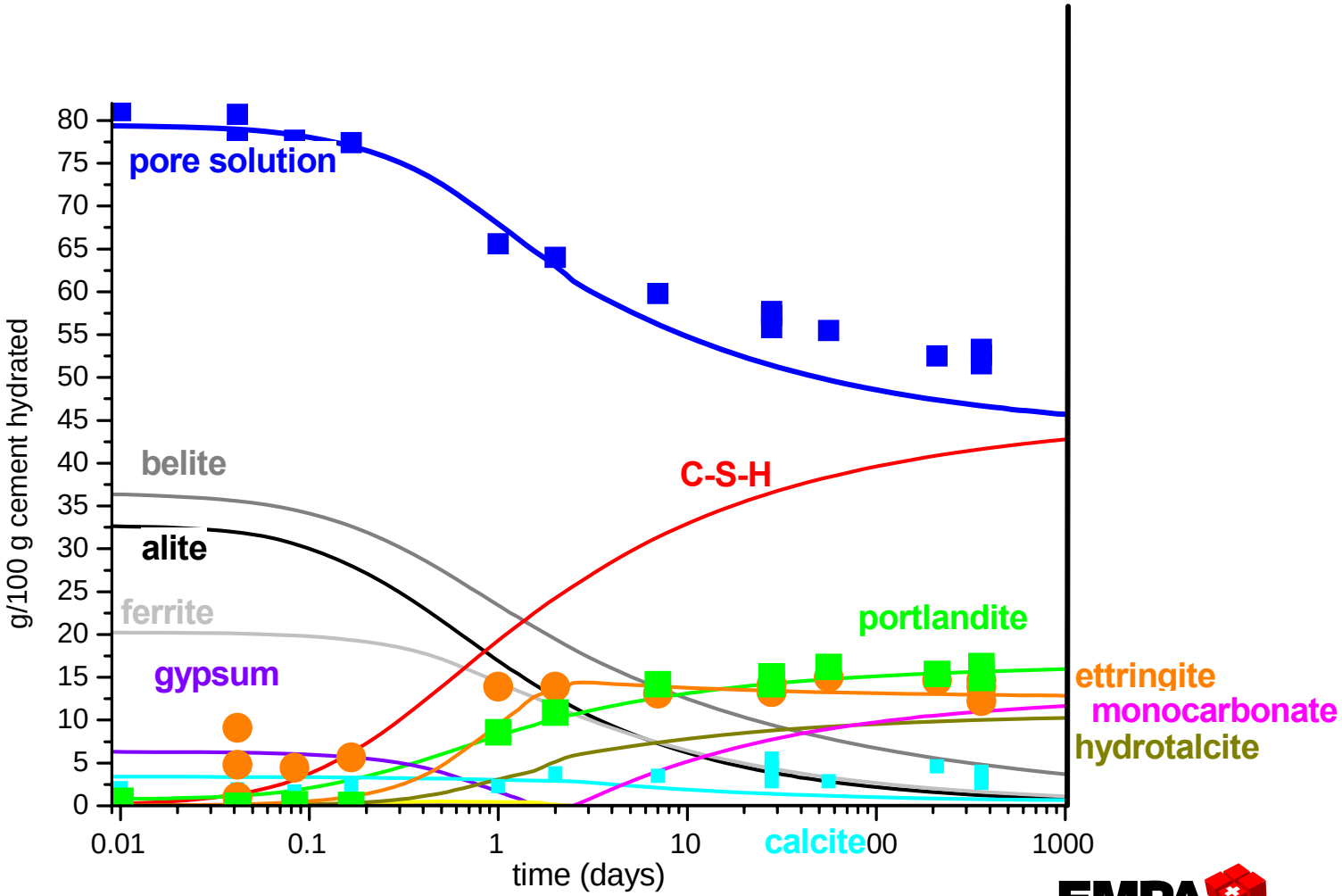
Modeling – Concentrations in solution

pH (360 days)
13.3

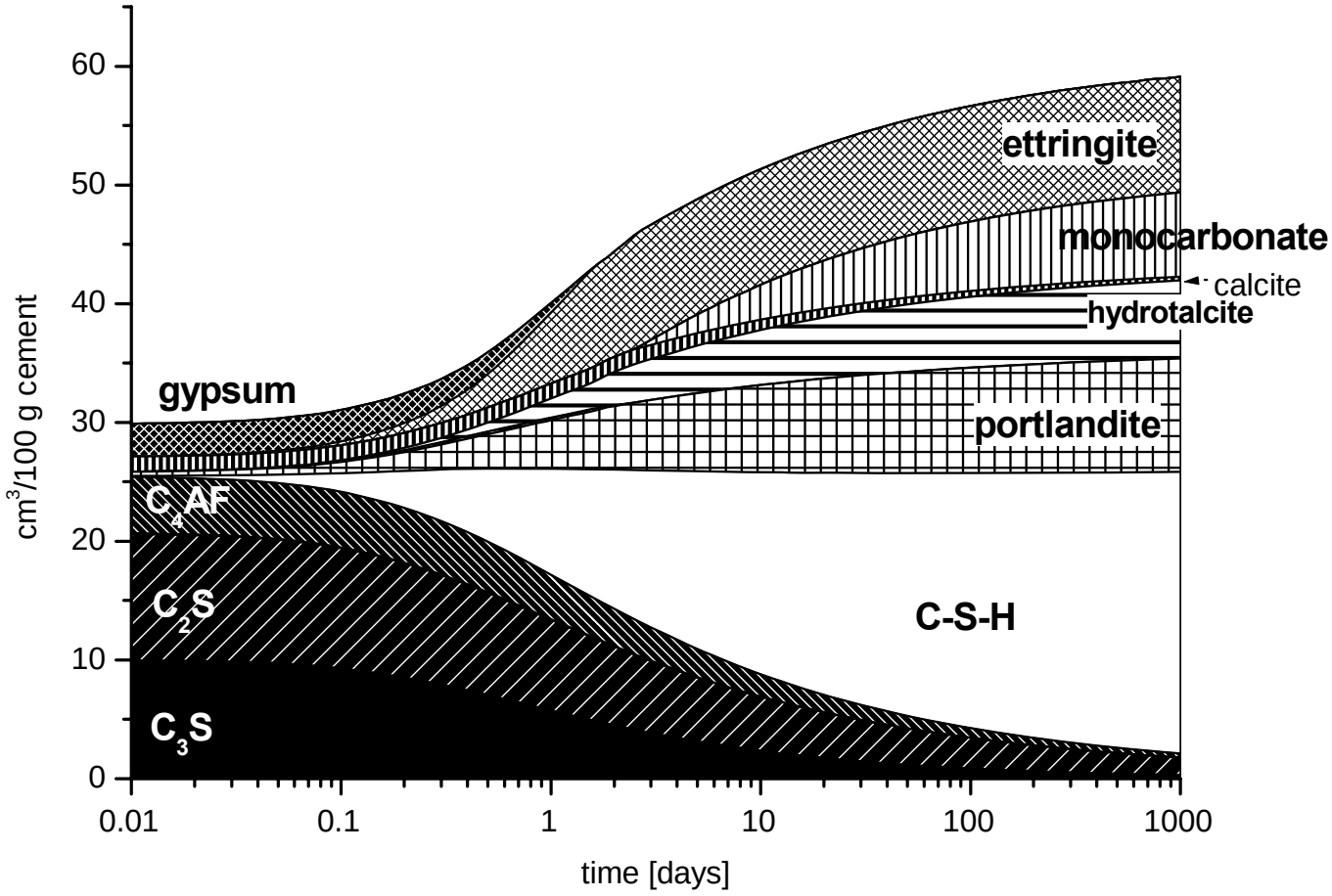


Modeling - relative mass of solids

(mass refers to total solid, including hydrated)



Modeling – Volume of solids



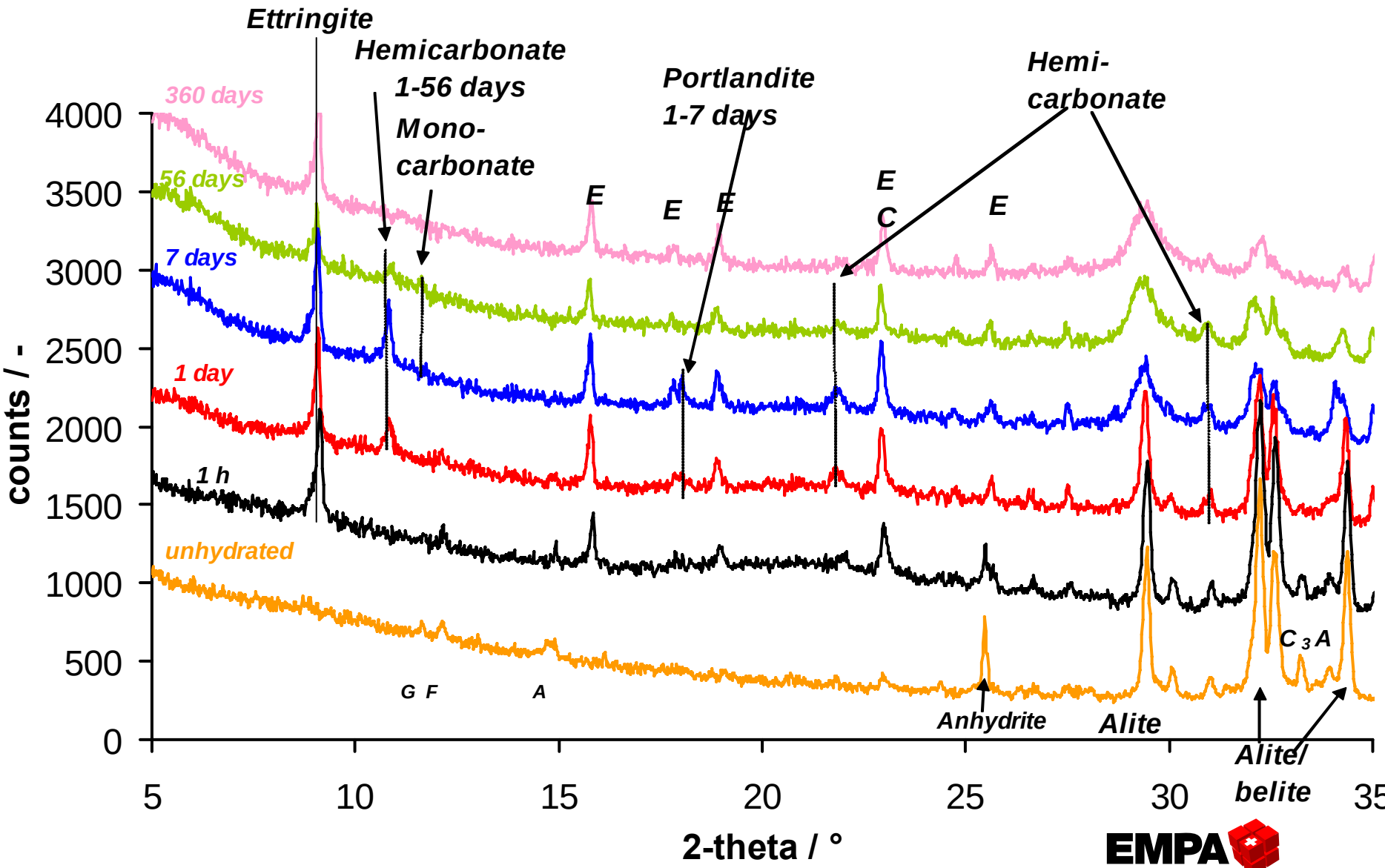
Summary - OPC

- Comparable to other OPC systems investigated
- Main hydration products
  - C-S-H, portlandite, ettringite
  - hydrotalcite, monocarbonate, calcite
- pH increases with time
- Solution dominated by OH, K, Na

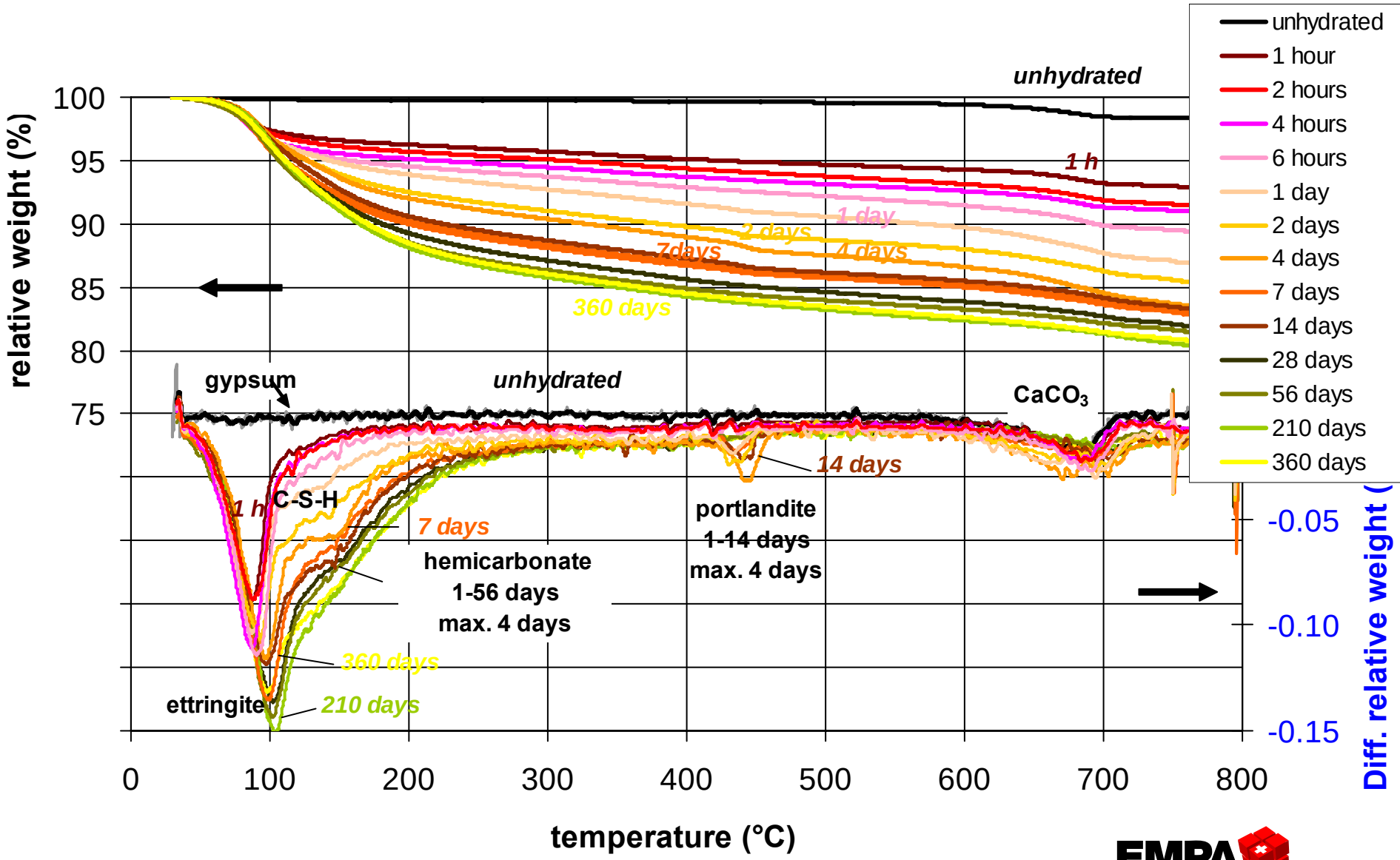
ESDRED: 60% CEM I + 40% silica fume 5% alkali free accelerator

	CEM I 42.5 N	silica fume (g/100g)	alkali-free accelerator	
CaO	61.6	2.1	<	
SiO_2	21.9	93.3	<	
Al_2O_3	4.8	0.2	16	→ 0.16 mmol
Fe_2O_3	2.5	0.1	<	
MgO	1.9	0.4	0.7	+ $CaSO_4$ (0.32)
Na_2O	0.25	<0.01	0.2	+ CaO (0.64) → $C_6A\$_3H_{32}$
K_2O	0.99	0.5	0.5	
CO_2	2.0	--	--	
SO_3	3.4	0.02	15	→ 0.18 mmol
LOI	2.3	3.1		
dissolved organic carbon			2.5	

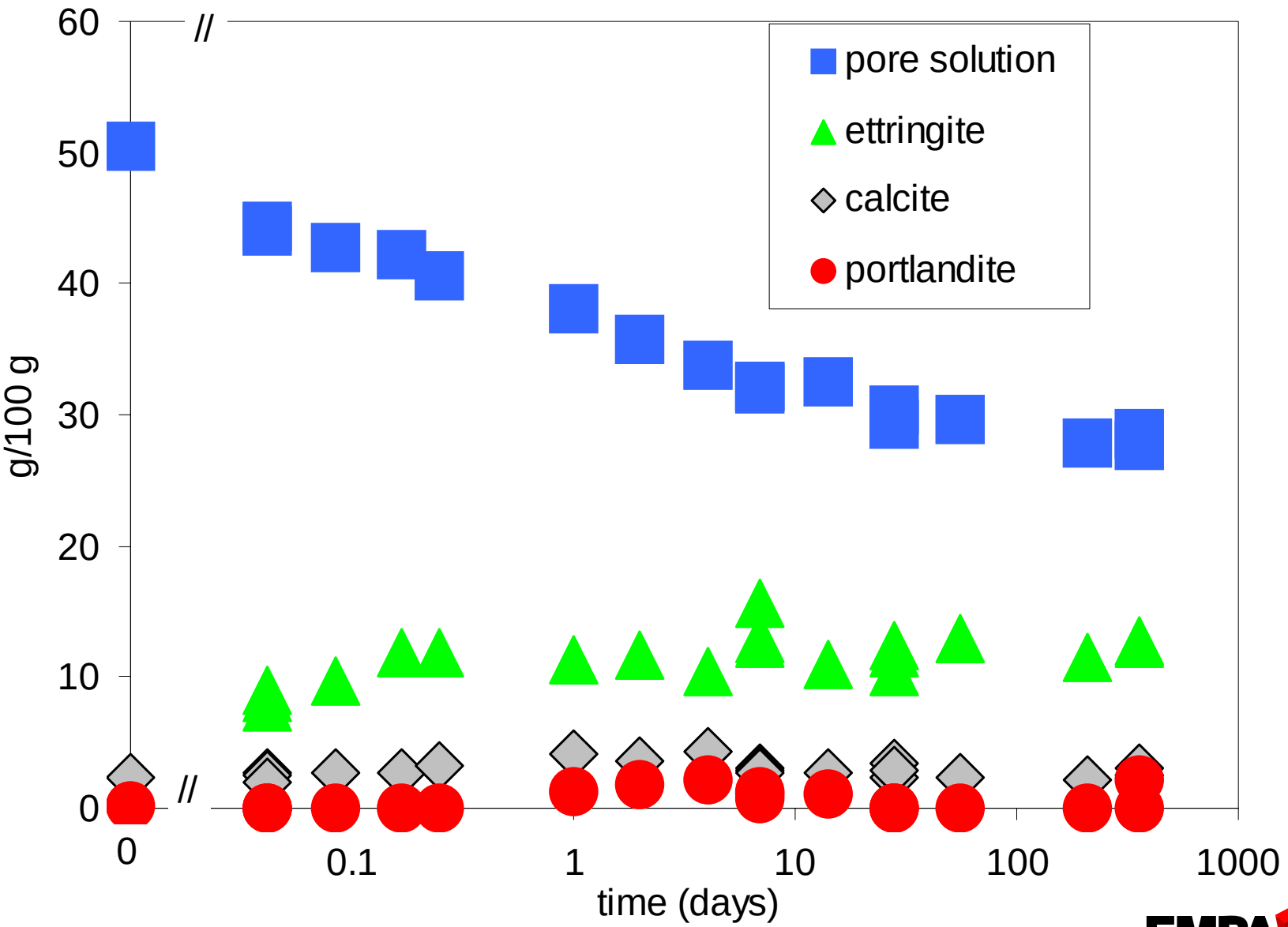
XRD


Ettringite
Hemicarbonate
1-56 days
Mono-
carbonate
Portlandite
1-7 days
Hemi-
carbonate
360 days
56 days
7 days
1 day
1 h
unhydrated
E
E
E
E
C
E
G F
A
C 3 A
Anhydrite
Alite
Alite/
belite
counts / -
2-theta / °
0
500
1000
1500
2000
2500
3000
3500
4000
5
10
15
20
25
30
35

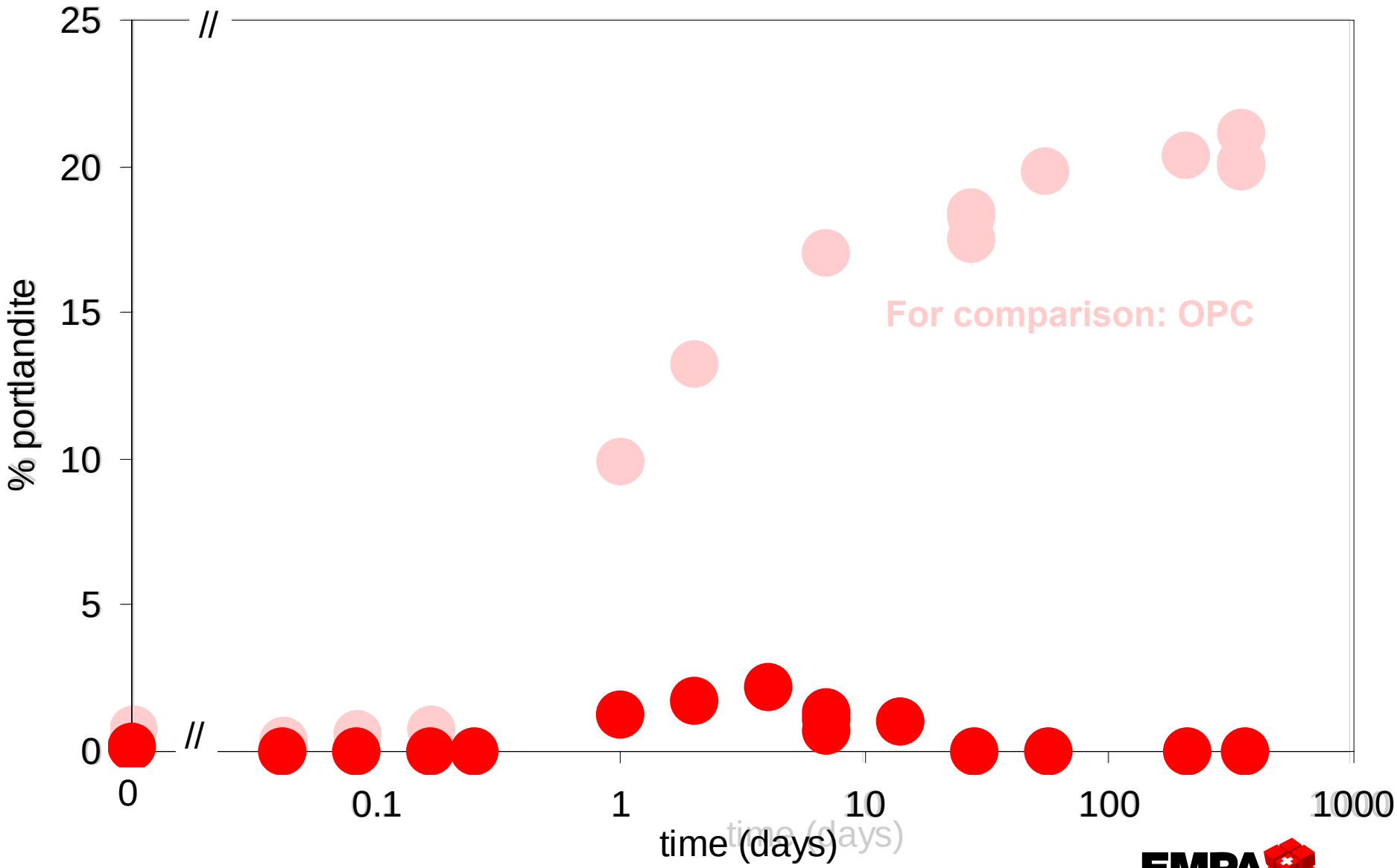
TGA


unhydrated
1 hour
2 hours
4 hours
6 hours
1 day
2 days
4 days
7 days
14 days
28 days
56 days
210 days
360 days
relative weight (%)
100
95
90
85
80
75
unhydrated
1 h
1 day
2 days
7days
4 days
360 days
gypsum
unhydrated
CaCO3
14 days
1 h
C-S-H
7 days
hemicarbonate
1-56 days
max. 4 days
portlandite
1-14 days
max. 4 days
360 days
ettringite
210 days
-0.05
-0.10
-0.15
Diff. relative weight (
0
100
200
300
400
500
600
700
800
temperature (°C)

TGA – Quantification of solution and solids

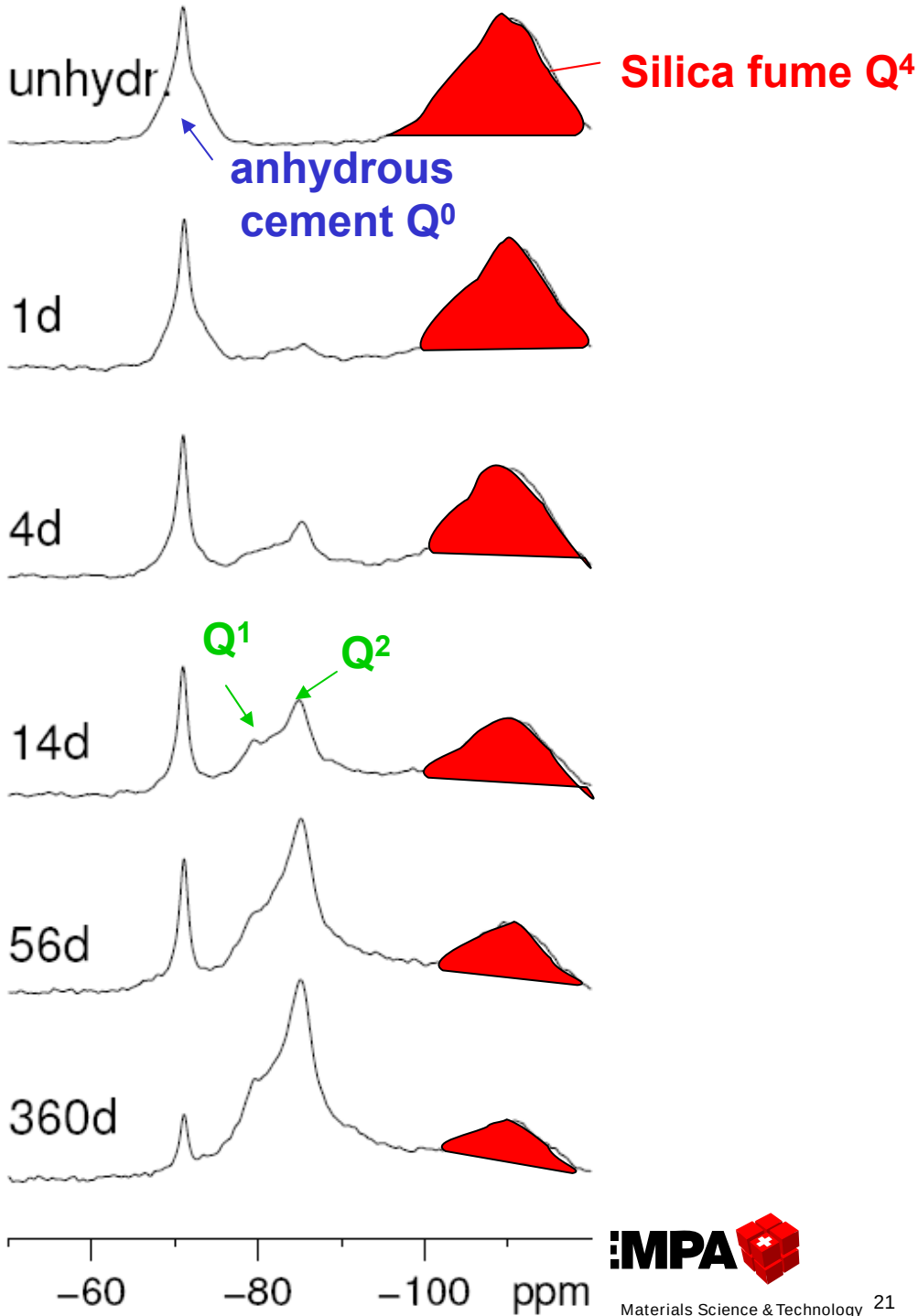


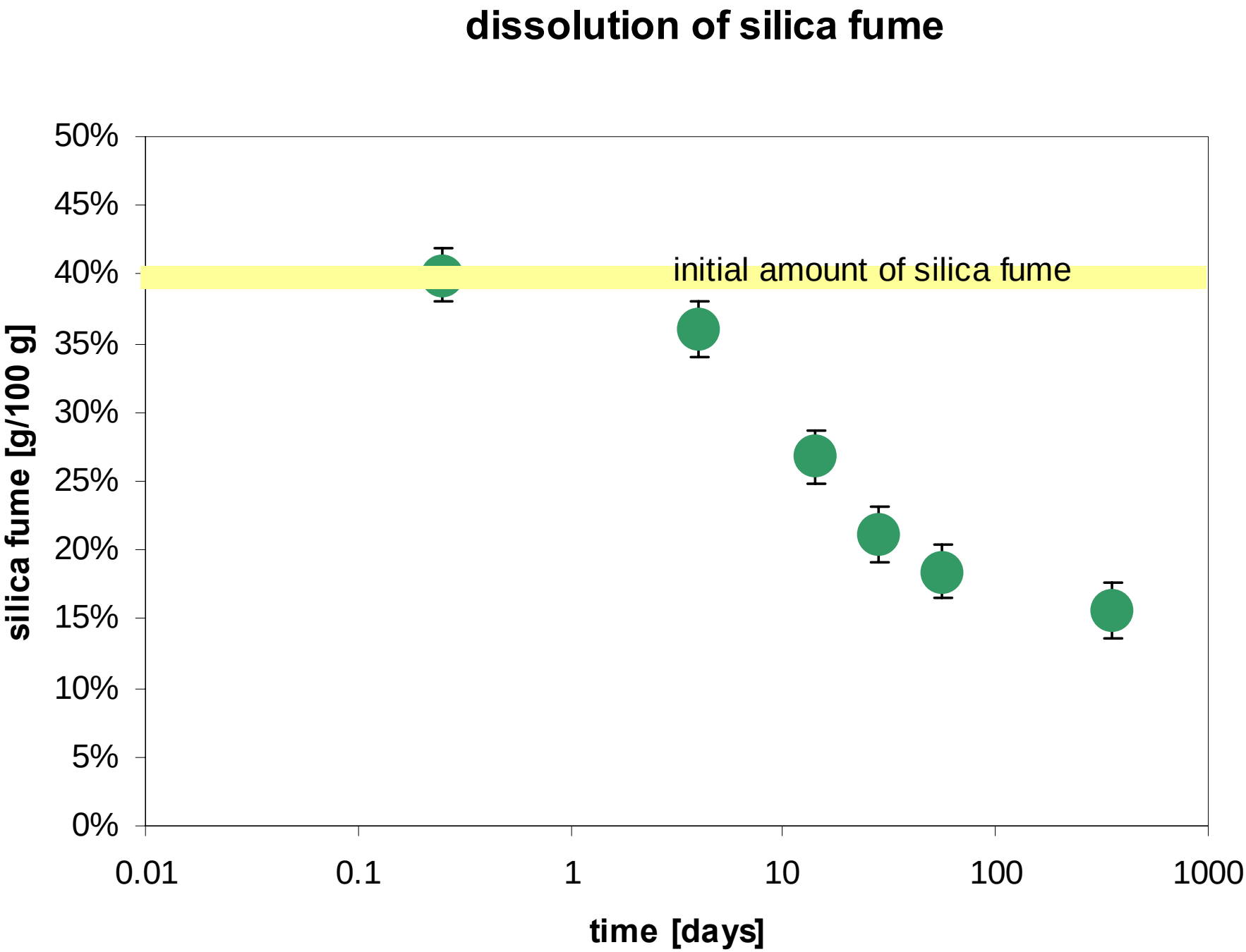
ESDRED - Portlandite

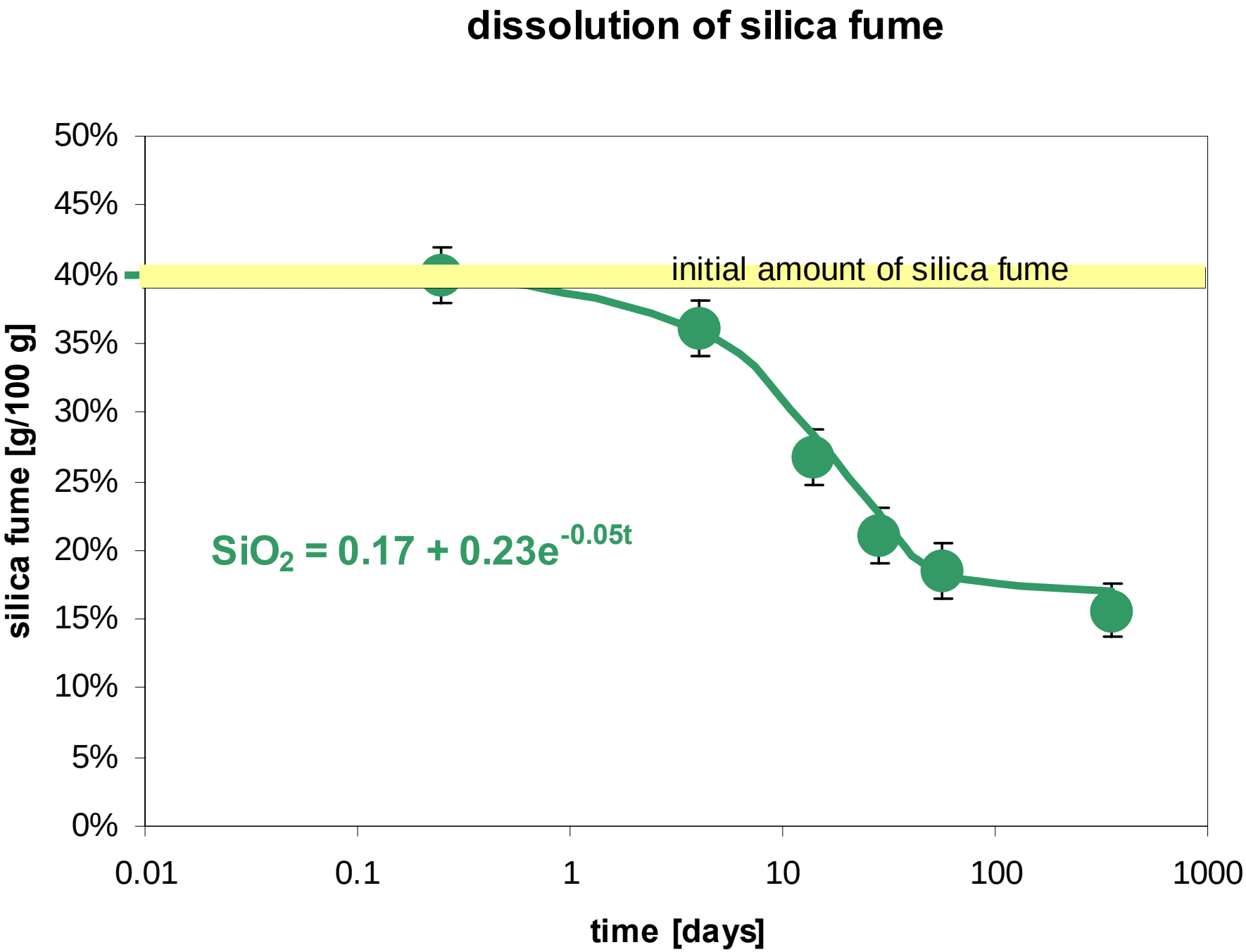


Reactivity of SiO_2

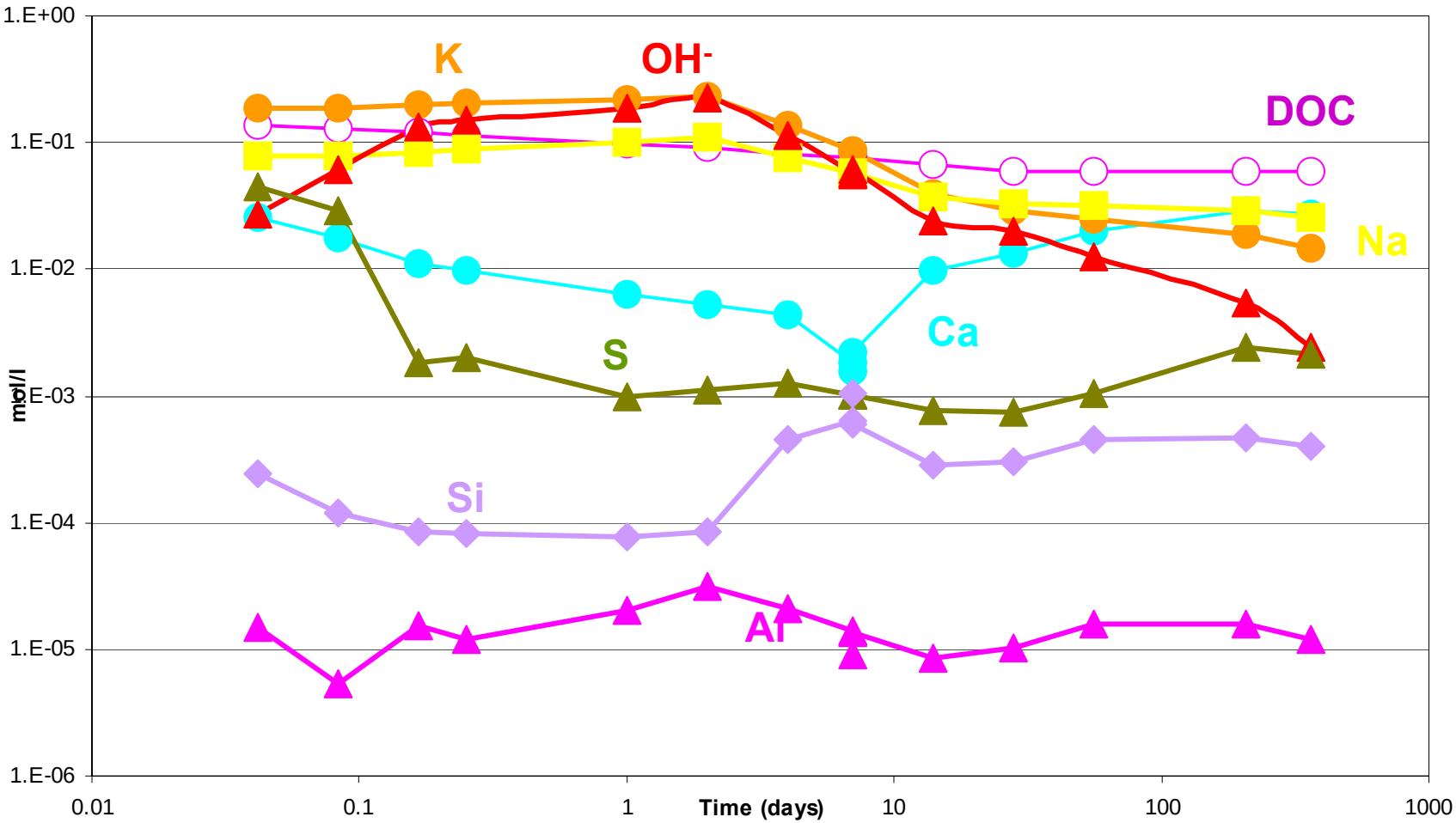
- Si-NMR



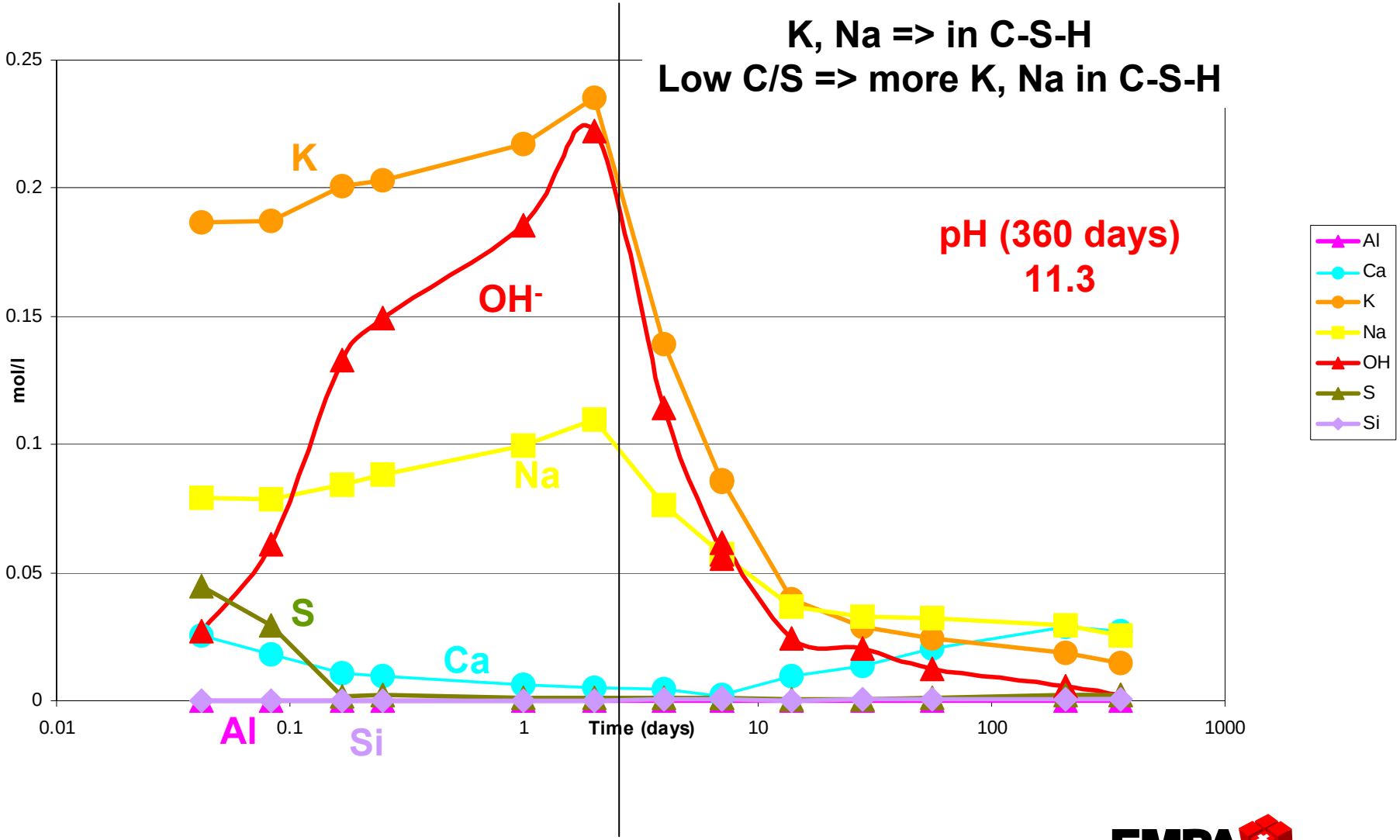

dissolution of silica fume
50%
45%
40%
35%
30%
25%
20%
15%
10%
5%
0%
silica fume [g/100 g]
initial amount of silica fume
0.01
0.1
1
10
100
1000
time [days]


dissolution of silica fume
50%
45%
40%
35%
30%
25%
20%
15%
10%
5%
0%
silica fume [g/100 g]
initial amount of silica fume
$SiO_2 = 0.17 + 0.23e^{-0.05t}$
0.01
0.1
1
10
100
1000
time [days]

Composition of the pore solution



Composition of the pore solution



Modeling ESDRED hydration

Portland cement hydration

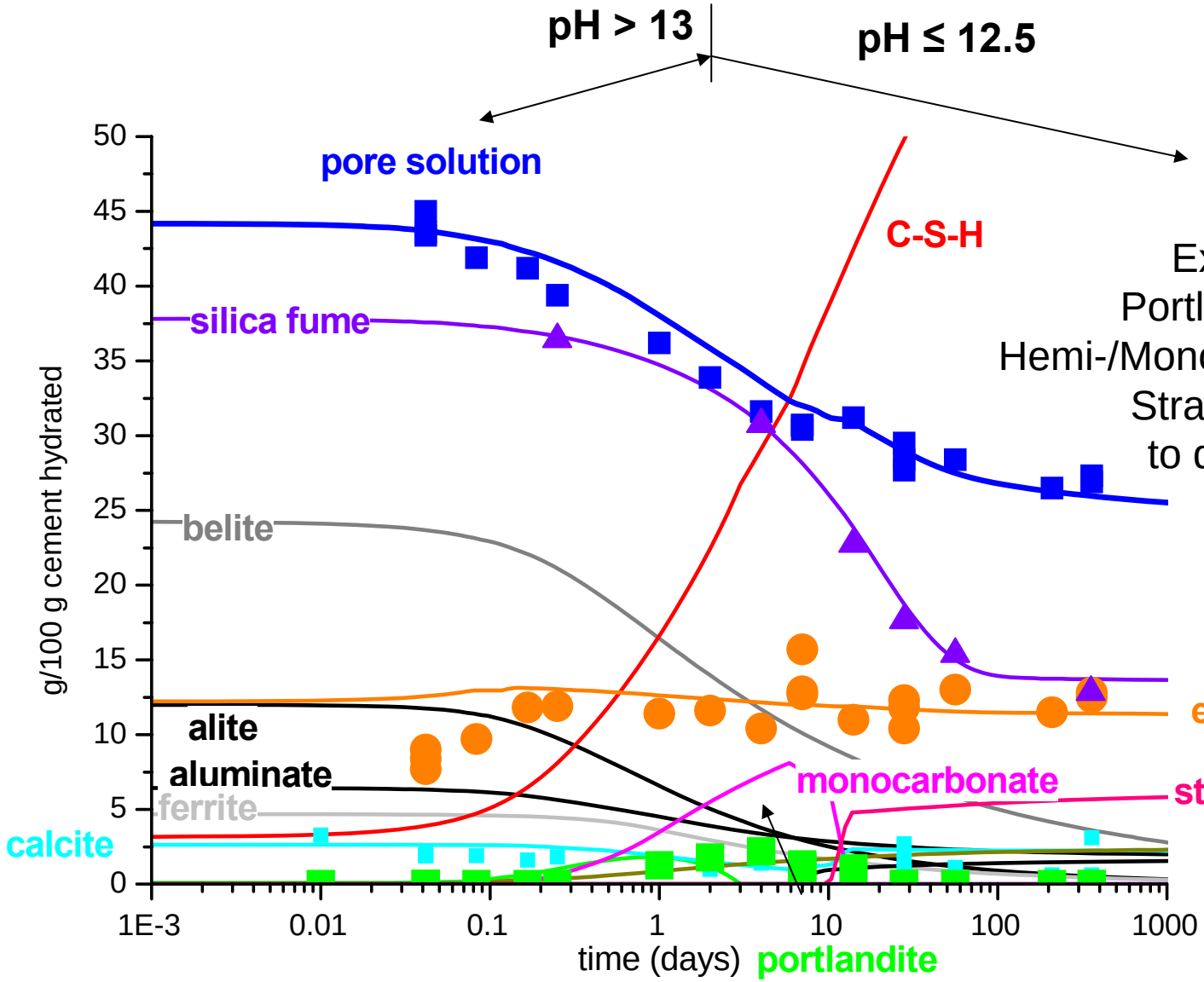
- similar to OPC system
- 1st hour increased dissolution of clinker (Paglia et al., 2004)
- silica fume dissolution according to NMR data

Problems

- Alkali (K) and Al-uptake in C-S-H not well known
- strätlingite or Al-in C-S-H?

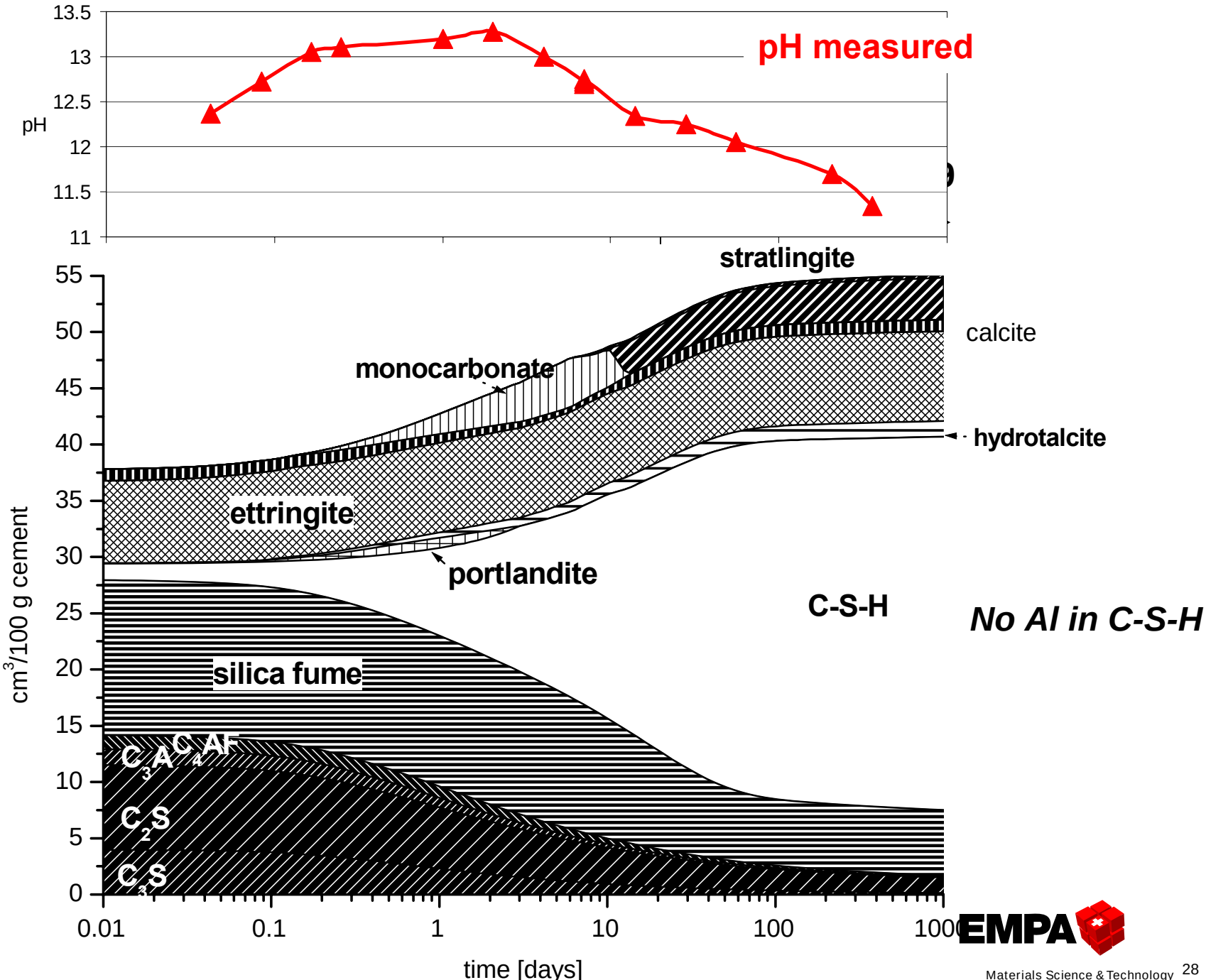
Modeling - relative mass of solids

(mass refers to total solid, including hydrated)

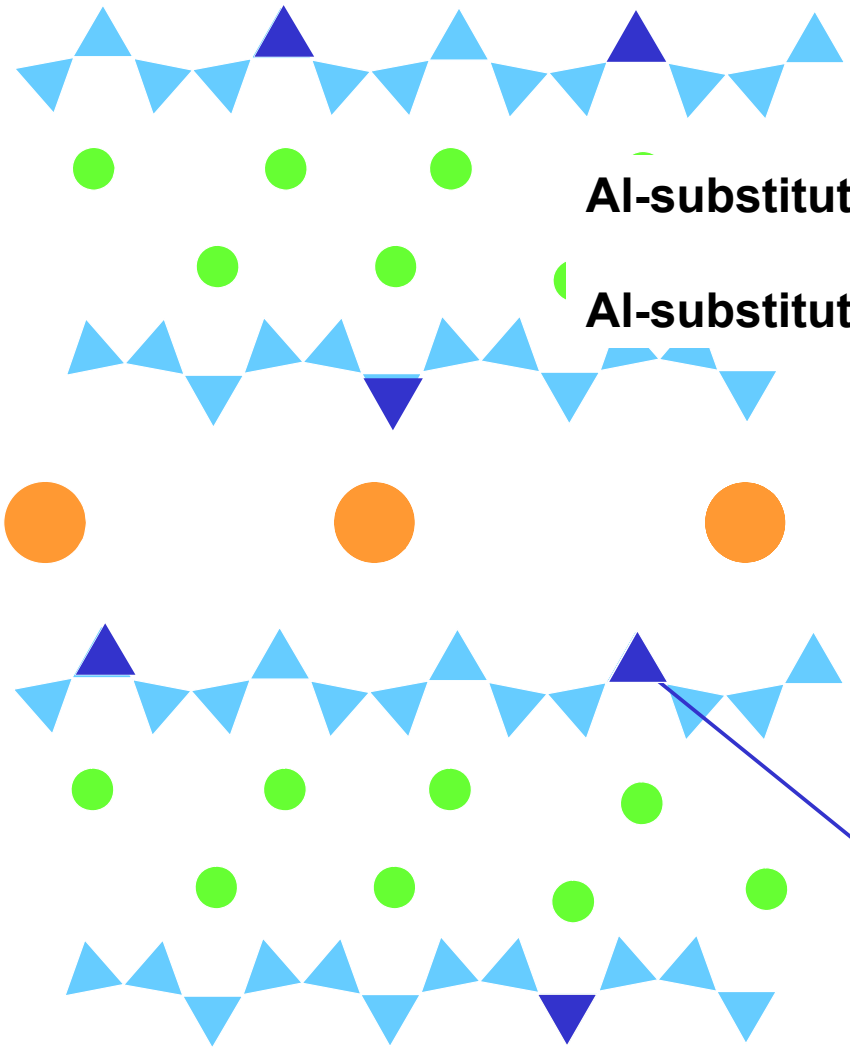


Experimental:
Portlandite 1-7 days
Hemi-/Monocarbonate: 1-28 da
Stratlingite difficult
to detect by XRD

EMPA


pH measured
pH
13.5
13
12.5
12
11.5
11
stratlingite
calcite
monocarbonate
hydrotalcite
ettringite
portlandite
C-S-H
No Al in C-S-H
silica fume
C_3A C_4AF
C_2S
C_3S
cm³/100 g cement
55
50
45
40
35
30
25
20
15
10
5
0
0.01
0.1
1
10
100
time [days]

Tobermorite structure



SiO_2 - Dreierketten

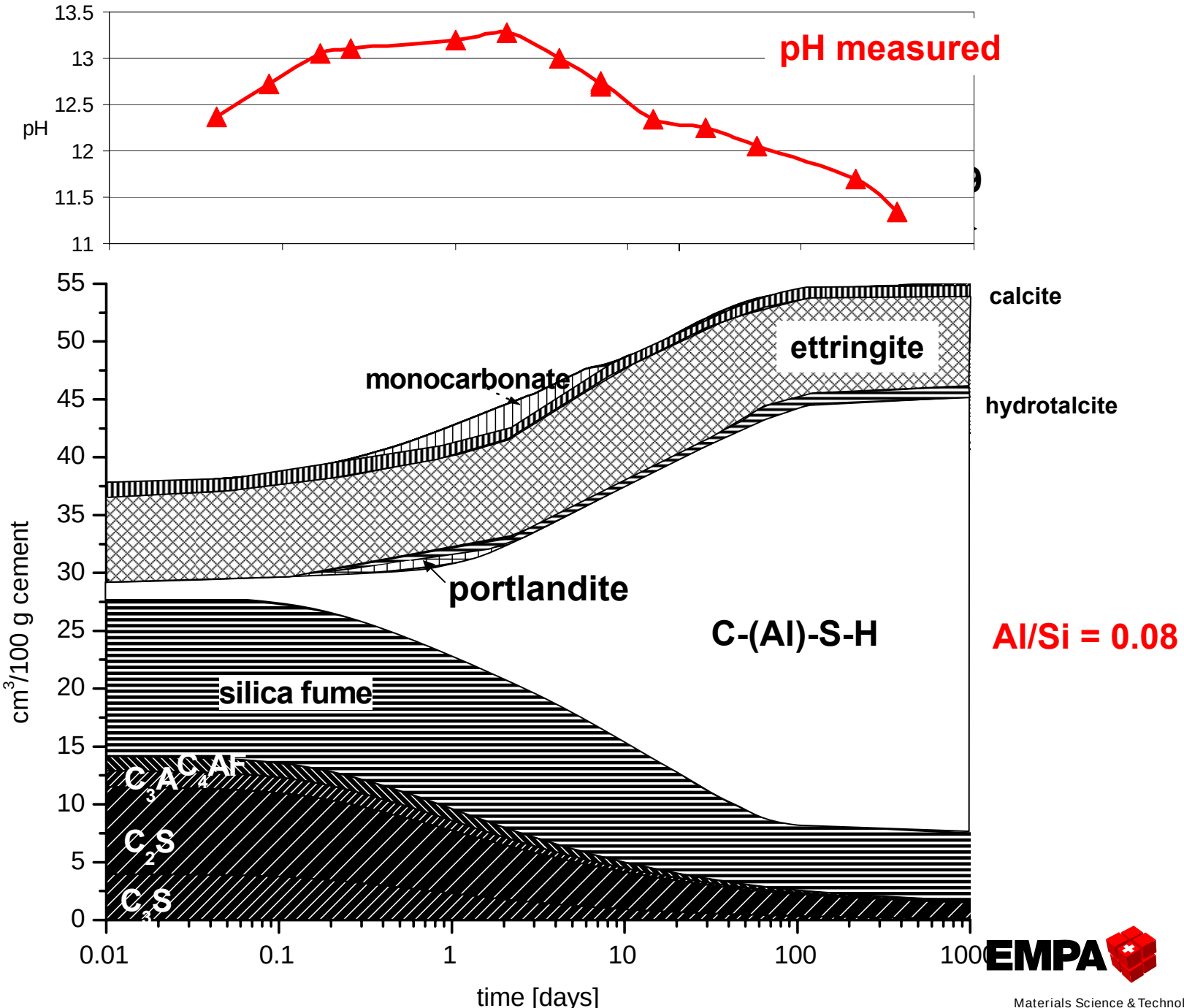
Al-substitution increase at low C/S ratios

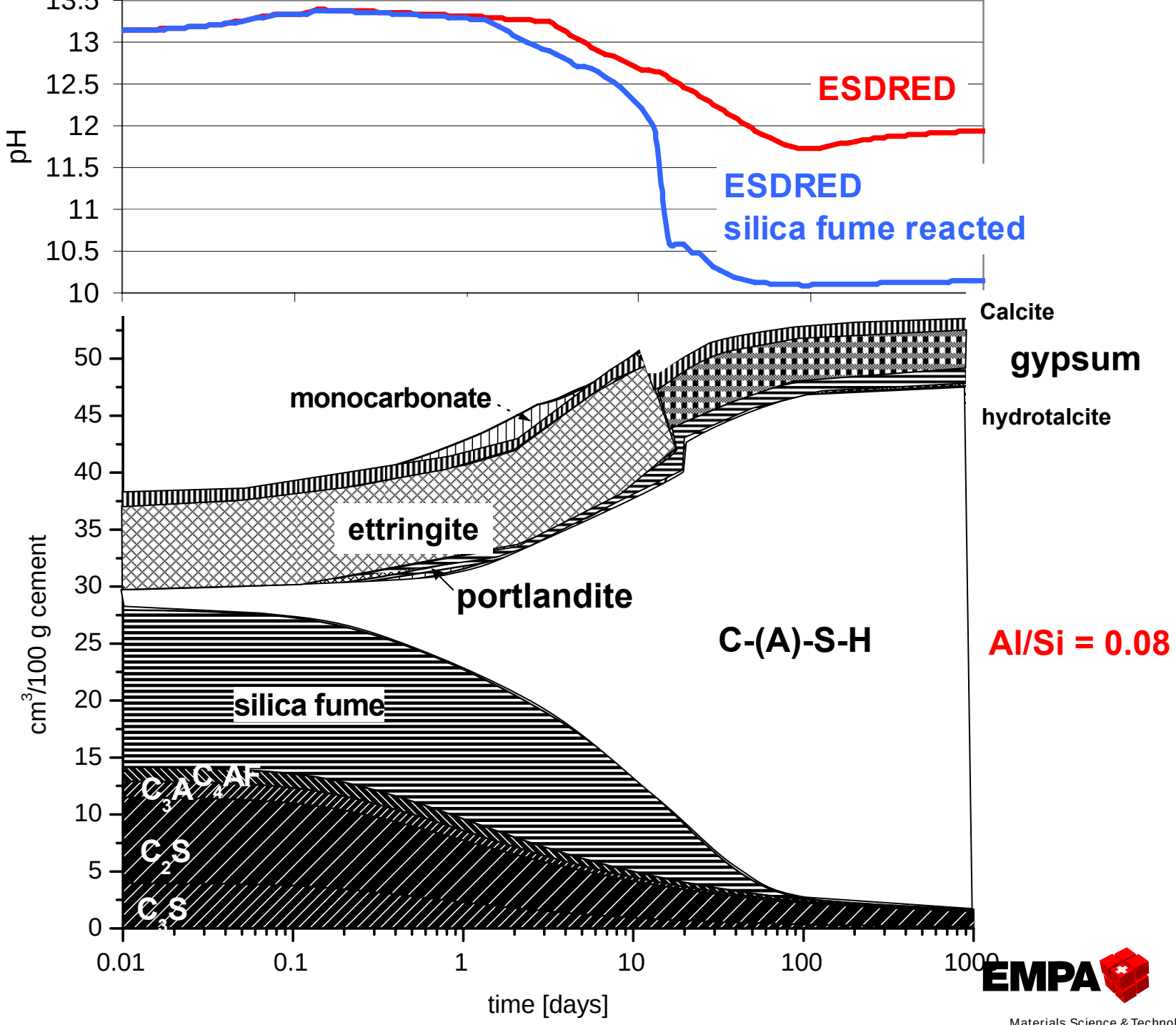
Al-substitution increases uptake of alkalis

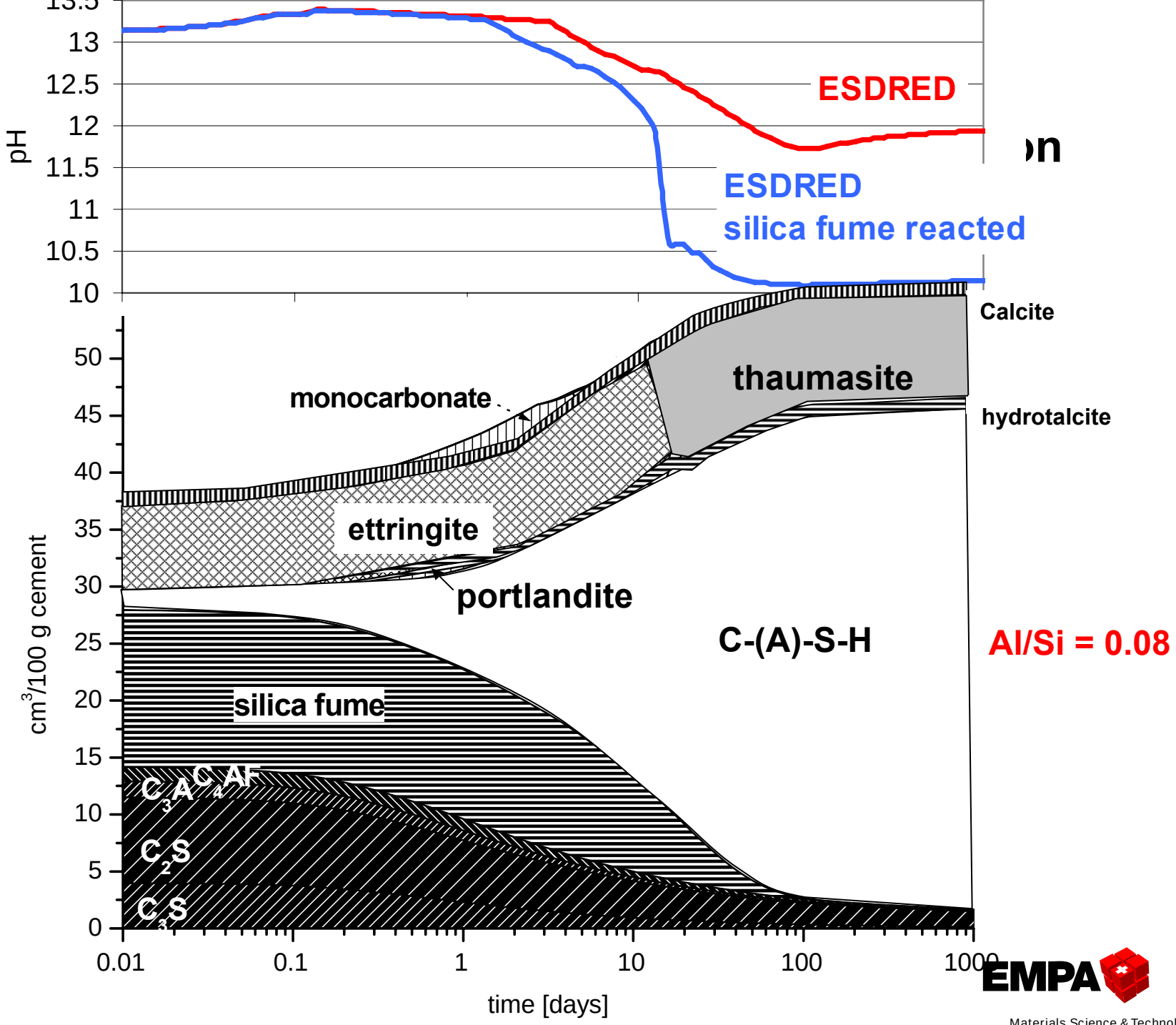
alkalis

Al-substitution

Richardson, 1999


pH measured
pH
13.5
13
12.5
12
11.5
11
cm3/100 g cement
55
50
45
40
35
30
25
20
15
10
5
0
calcite
ettringite
monocarbonate
hydrotalcite
portlandite
C-(Al)-S-H
Al/Si = 0.08
silica fume
C3AC4AF
C2S
C3S
0.01
0.1
1
10
100
1000
time [days]


pH
13.5
13
12.5
12
11.5
11
10.5
10
ESDRED
ESDRED
silica fume reacted
Calcite
gypsum
hydrotalcite
monocarbonate
ettringite
portlandite
C-(A)-S-H
Al/Si = 0.08
silica fume
C3AC4AF
C2S
C3S
cm3/100 g cement
50
45
40
35
30
25
20
15
10
5
0
0.01
0.1
1
10
100
1000
time [days]


pH
13.5
13
12.5
12
11.5
11
10.5
10
ESDRED
ESDRED
silica fume reacted
Calcite
thaumasite
monocarbonate
hydrotalcite
ettringite
portlandite
C-(A)-S-H
Al/Si = 0.08
silica fume
C3A C4AF
C2S
C3S
cm3/100 g cement
50
45
40
35
30
25
20
15
10
5
0
0.01
0.1
1
10
100
1000
time [days]

Summary - ESDRED

- Mix of OPC with SiO_2
- 0-2 days: similar to OPC
- >2 days: SiO_2:
  - no (temporary small amount) portlandite
    – low pH buffering capacity
  - pH decreases
- Hydration products
  - C-S-H (low C/S), ettringite
  - hydrotalcite, calcite, hemi-/monocarbonate
- pH decreases with time (11.3 after 1 year)
- Solution dominated by Ca, K, Na, OH, DOC
- Longterm unclear (ettringite <-> thaumasite ?)
  - potential for stratlingite, Si-hydrogarnet or thaumasite

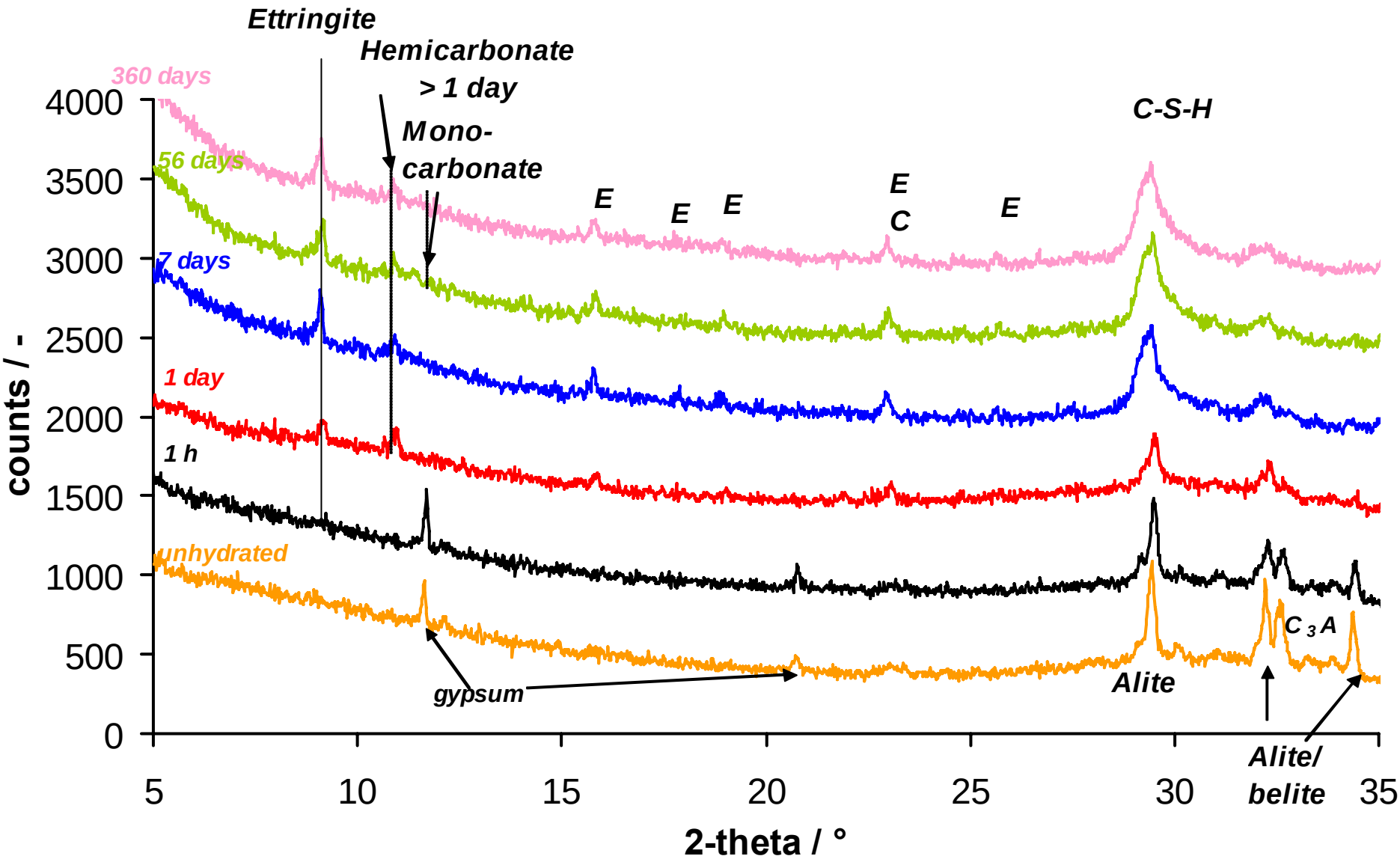
(contains ~74% slag)

LAC: 90% CEM III/B + 10% Nanosilica

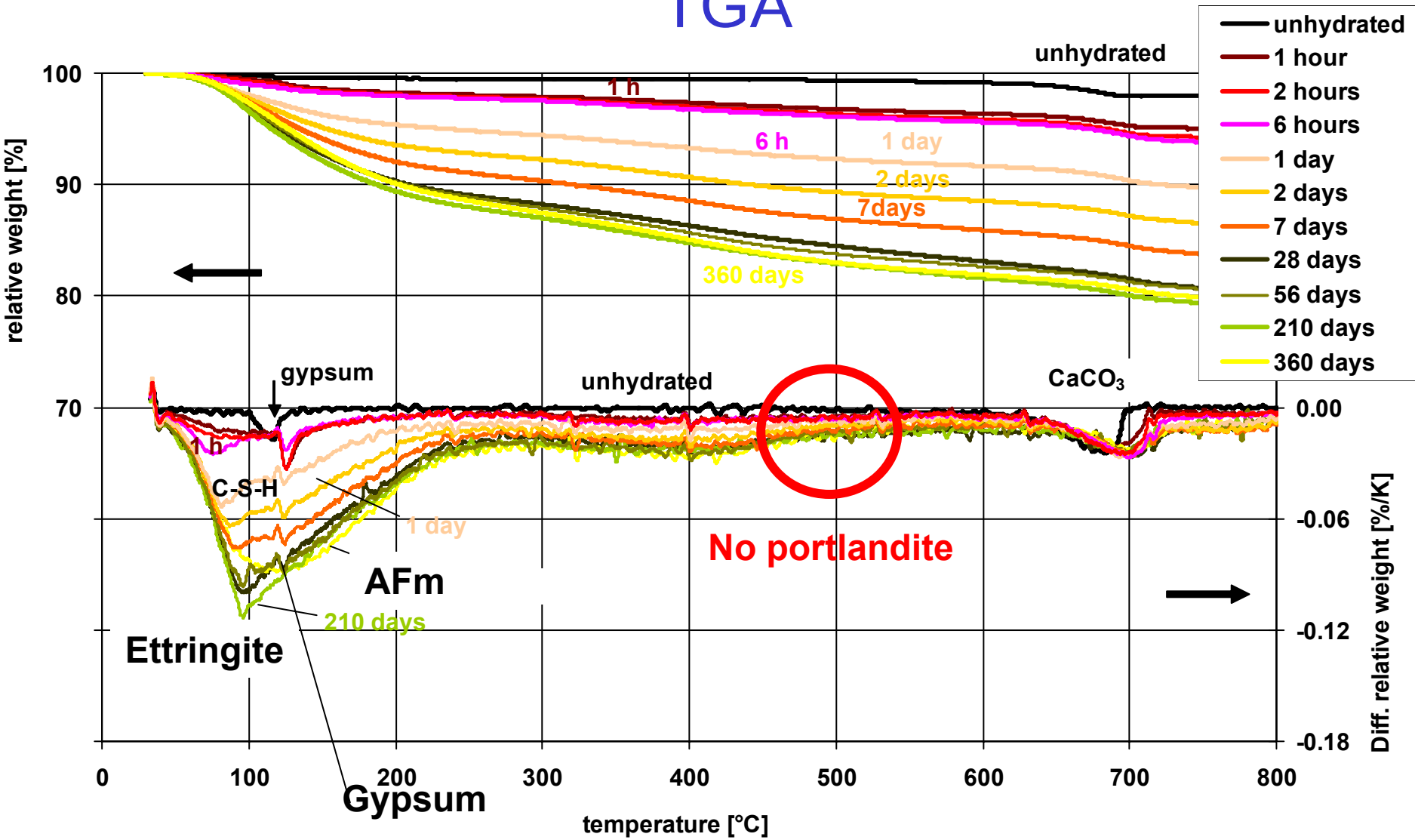
	Portland cement	slag (g/100g)	Nanosilica
CaO	66	41	
SiO_2	17	36	>99.8
Al_2O_3	4	12	
Fe_2O_3	3	0.3	
MgO	5	7	
Na_2O	0.1	0.3	
K_2O	1	0.3	
CO_2	1.7	0.01	
SO_3	3.2	0.8 (as S(-II))	
LOI	0.7		

w/b = 1.1

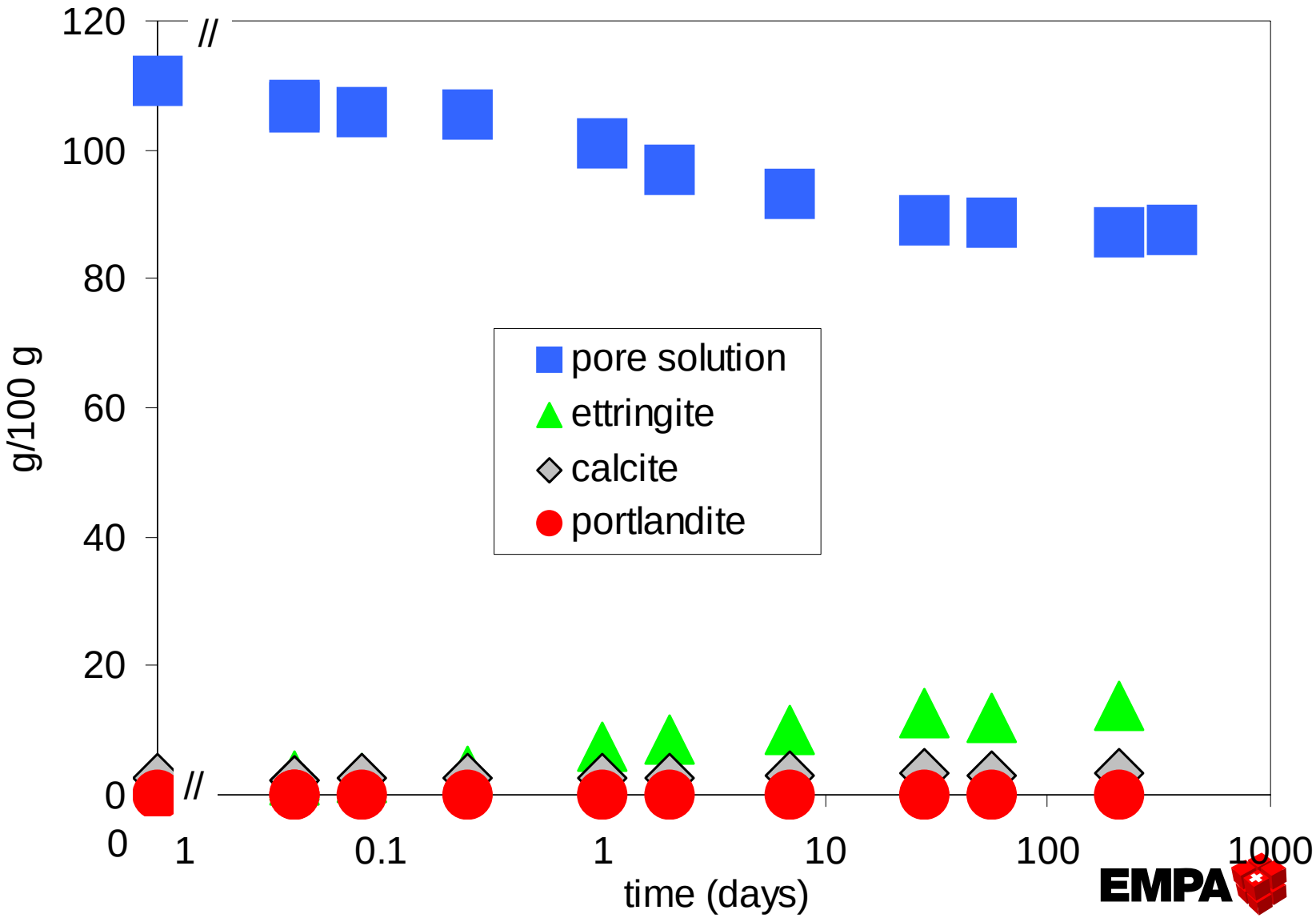
XRD

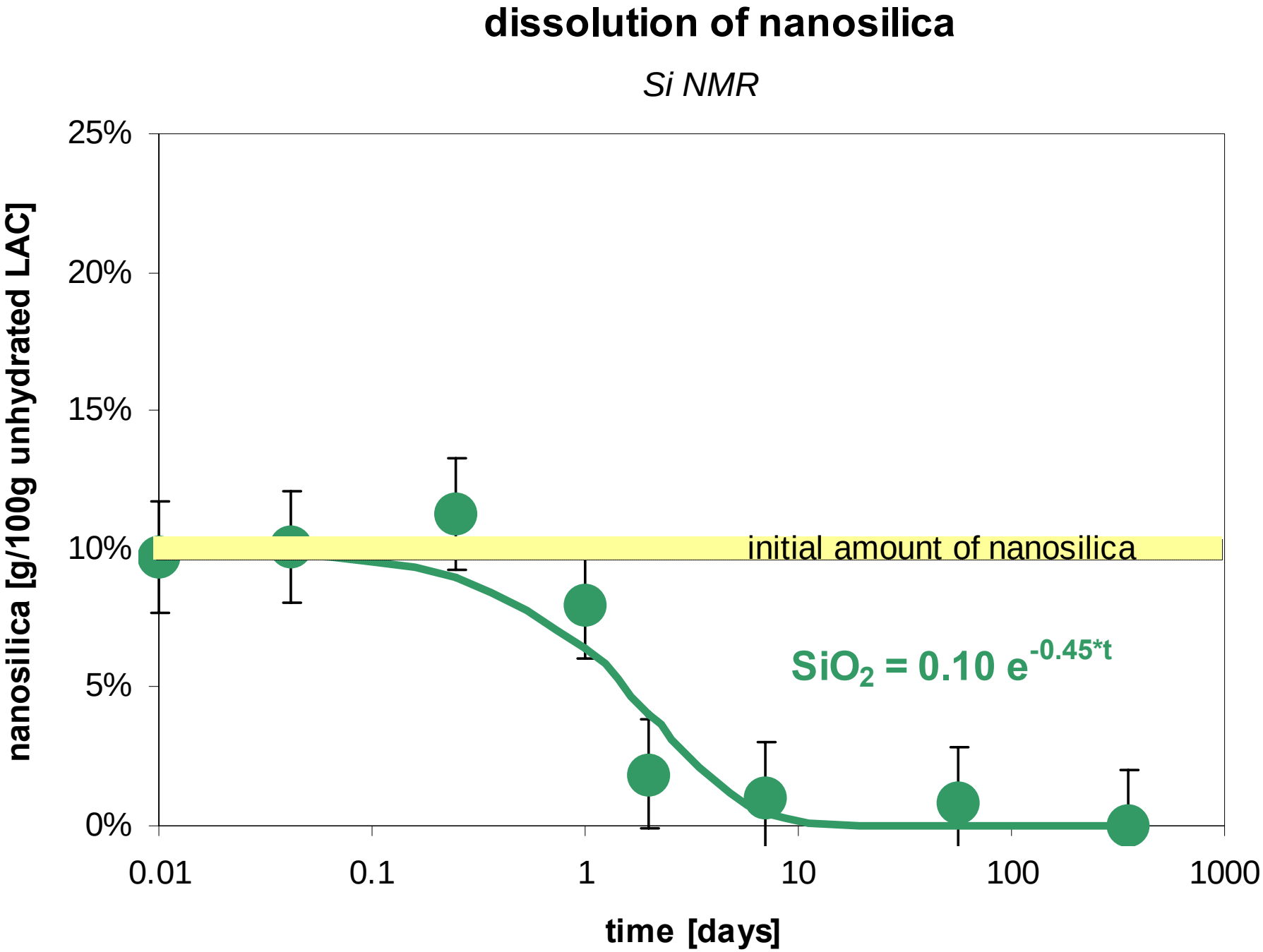

Ettringite
Hemicarbonate
> 1 day
Mono-
carbonate
C-S-H
360 days
56 days
7 days
1 day
1 h
unhydrated
E
E
E
E
C
E
gypsum
Alite
C 3 A
Alite/
belite
counts / -
2-theta / °
0
500
1000
1500
2000
2500
3000
3500
4000
5
10
15
20
25
30
35

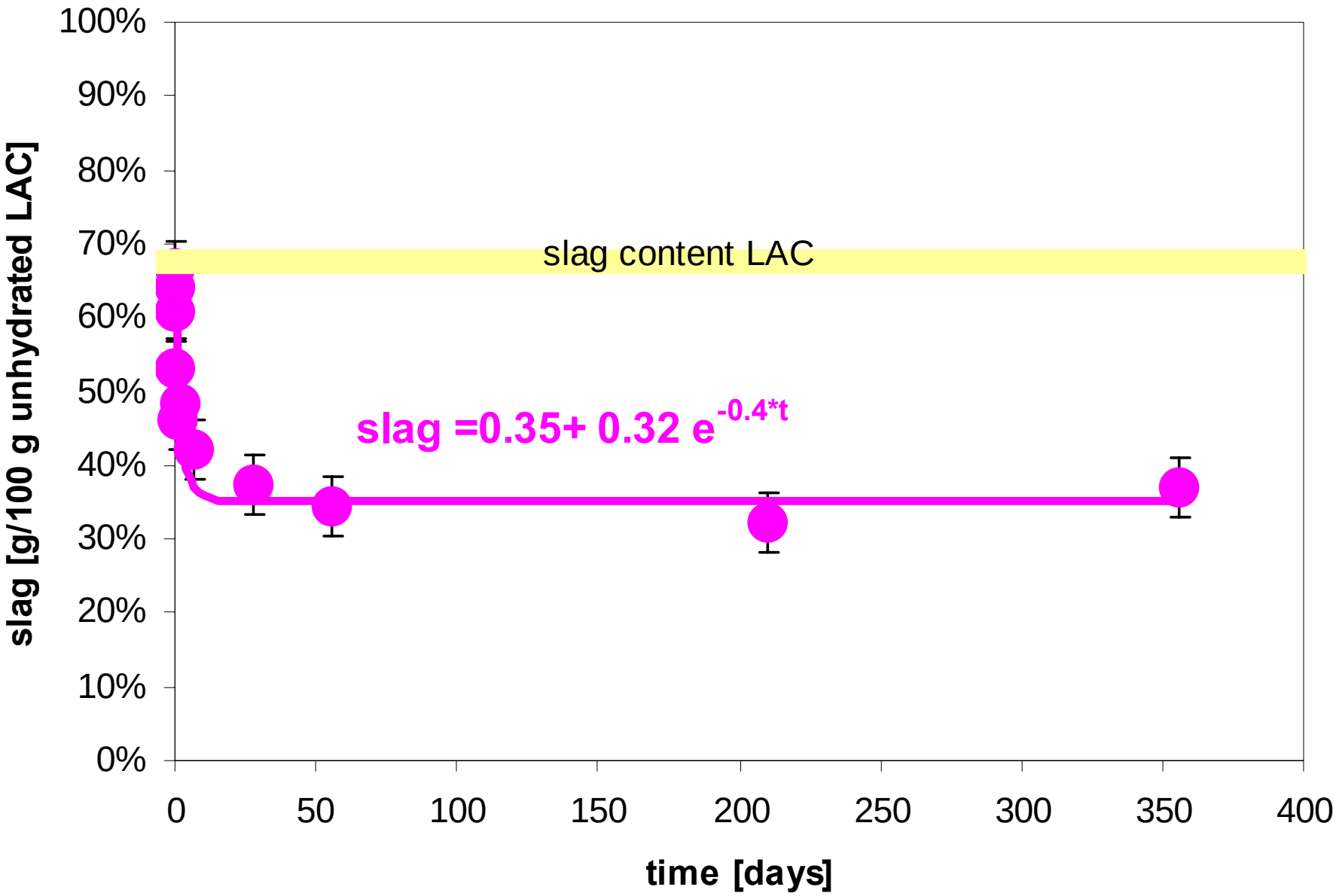
TGA


unhydrated
1 hour
2 hours
6 hours
1 day
2 days
7 days
28 days
56 days
210 days
360 days
relative weight [%]
100
90
80
70
1 h
6 h
1 day
2 days
7days
360 days
gypsum
unhydrated
CaCO3
1 h
C-S-H
1 day
No portlandite
AFm
210 days
Ettringite
Gypsum
0.00
-0.06
-0.12
-0.18
Diff. relative weight [%/K]
0
100
200
300
400
500
600
700
800
temperature [°C]

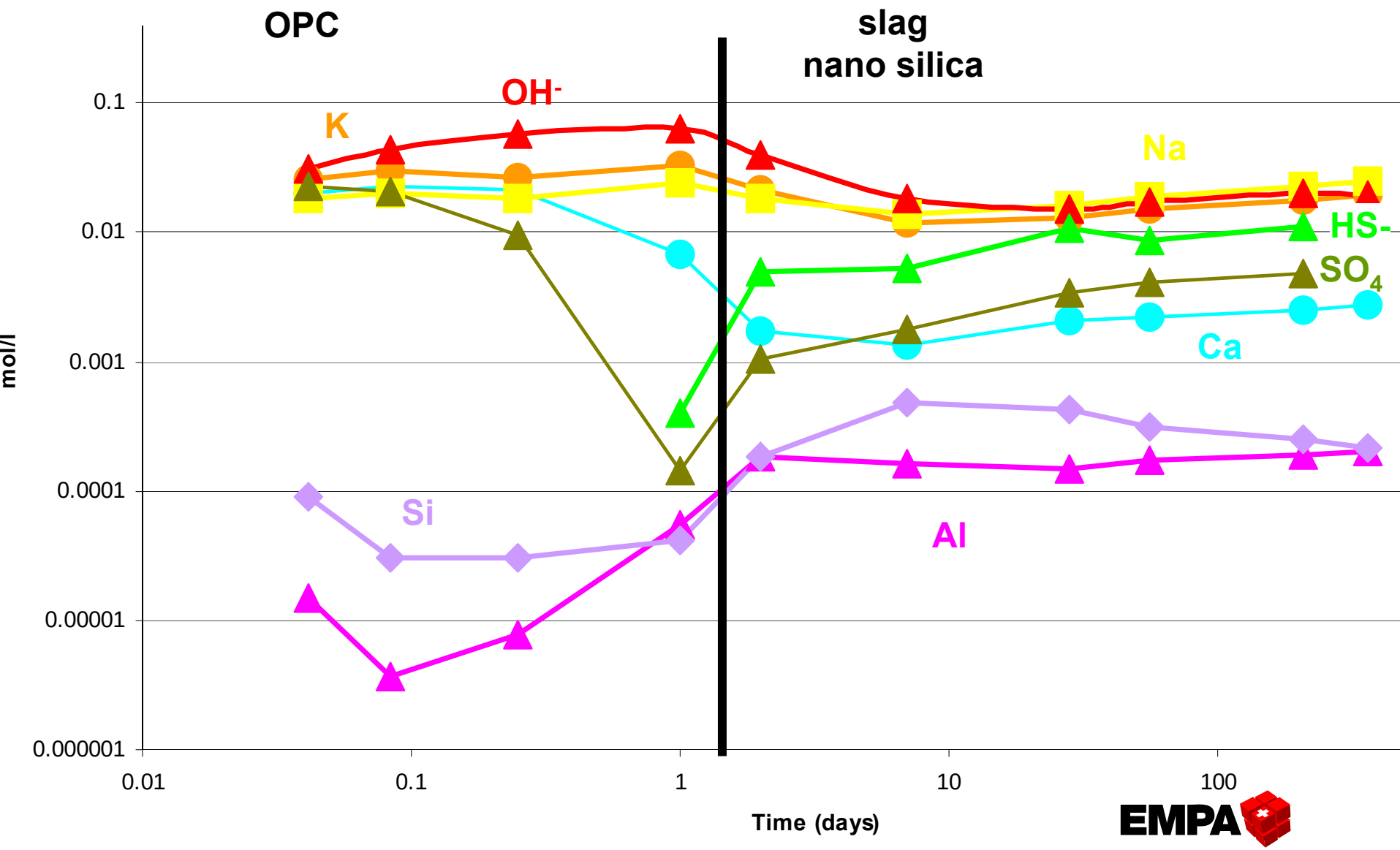
TGA – Quantification of solution and solids



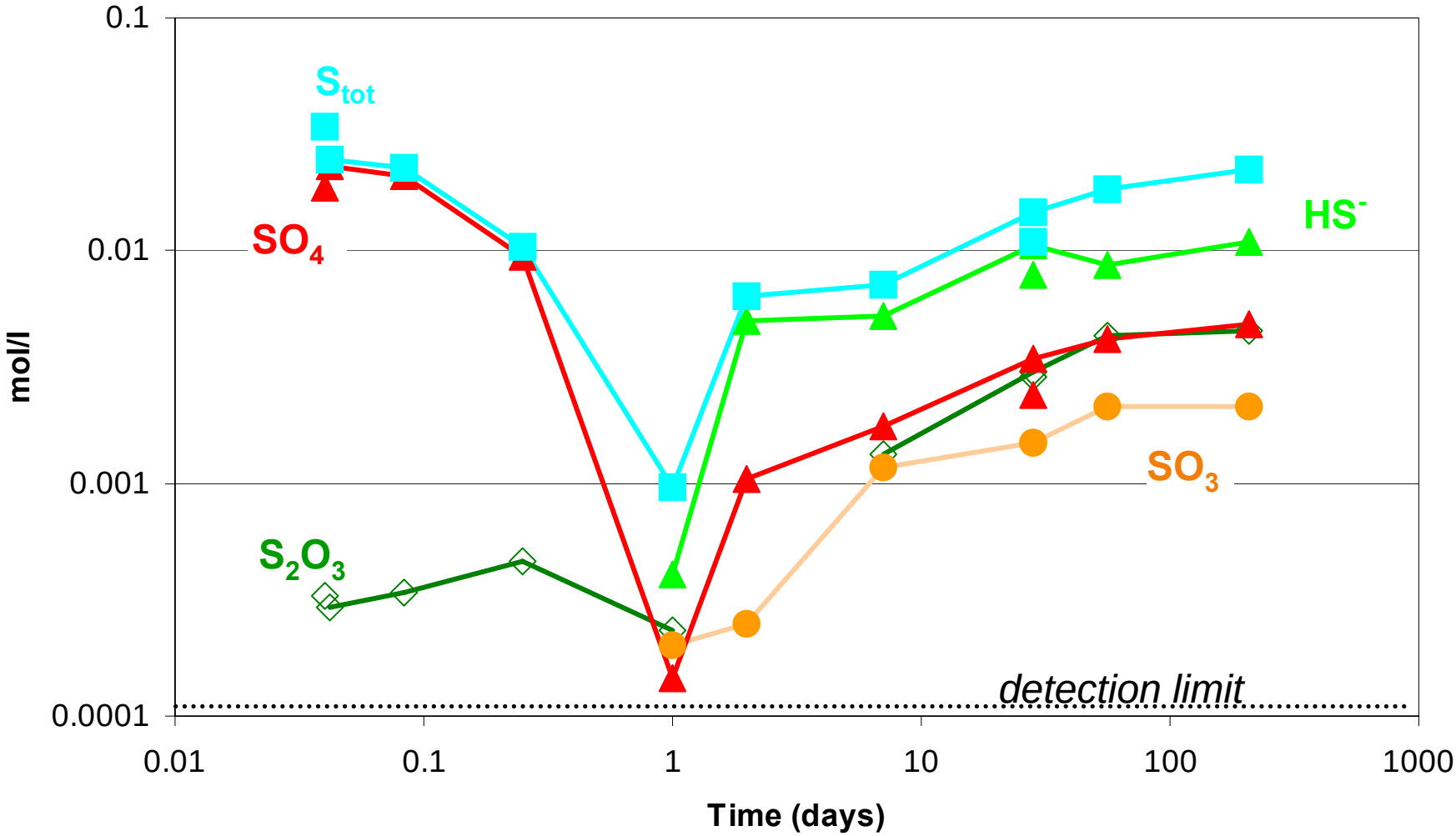

dissolution of nanosilica
Si NMR
nanosilica [g/100g unhydrated LAC]
25%
20%
15%
10%
5%
0%
initial amount of nanosilica
SiO2 = 0.10 e-0.45*t
0.01
0.1
1
10
100
1000
time [days]


dissolution of slag
Selective dissolution with EDTA
slag [g/100 g unhydrated LAC]
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
slag content LAC
slag =0.35+ 0.32 e-0.4*t
0
50
100
150
200
250
300
350
400
time [days]

Composition of the pore solution



Sulfur speciation

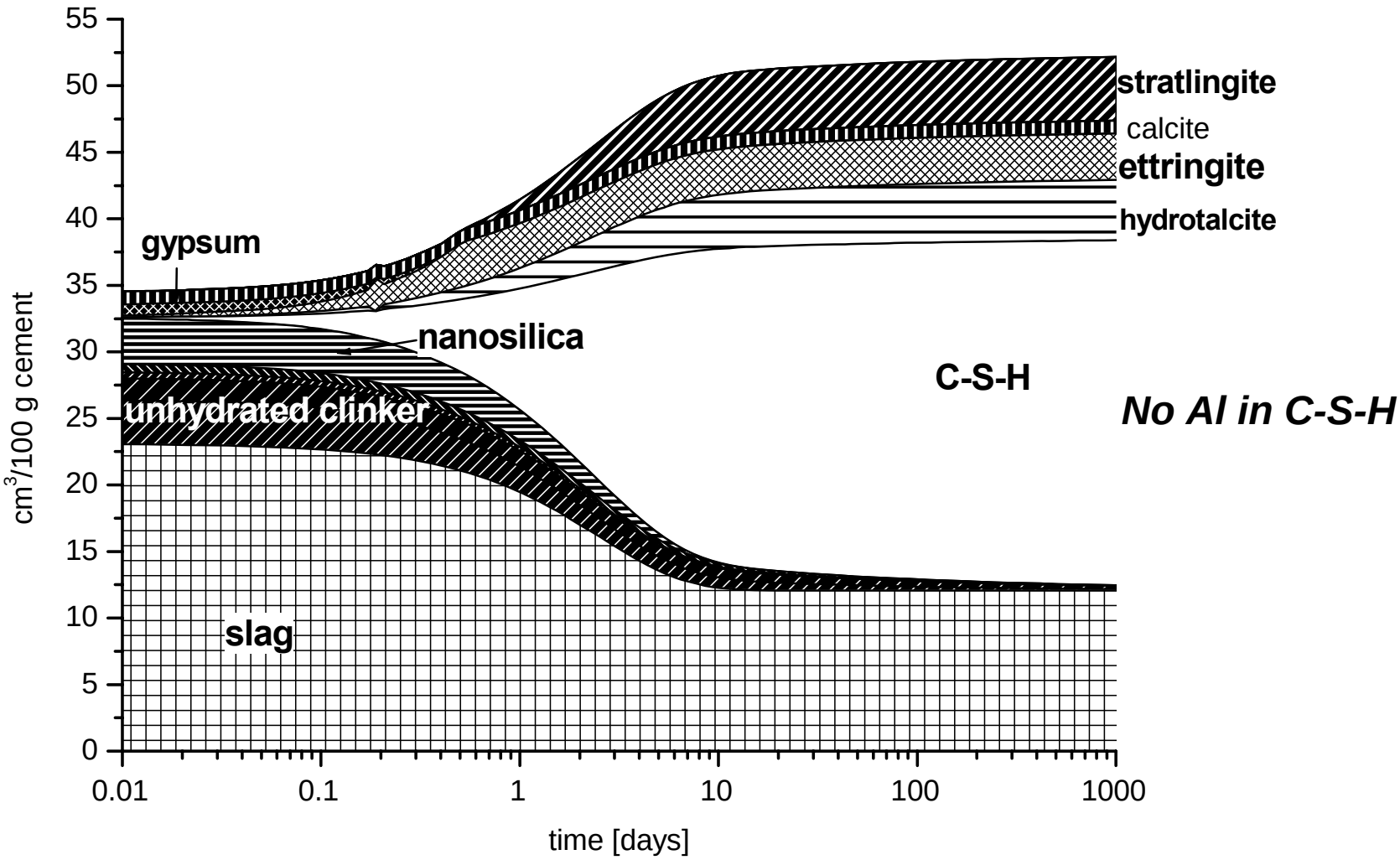


Modeling LAC hydration

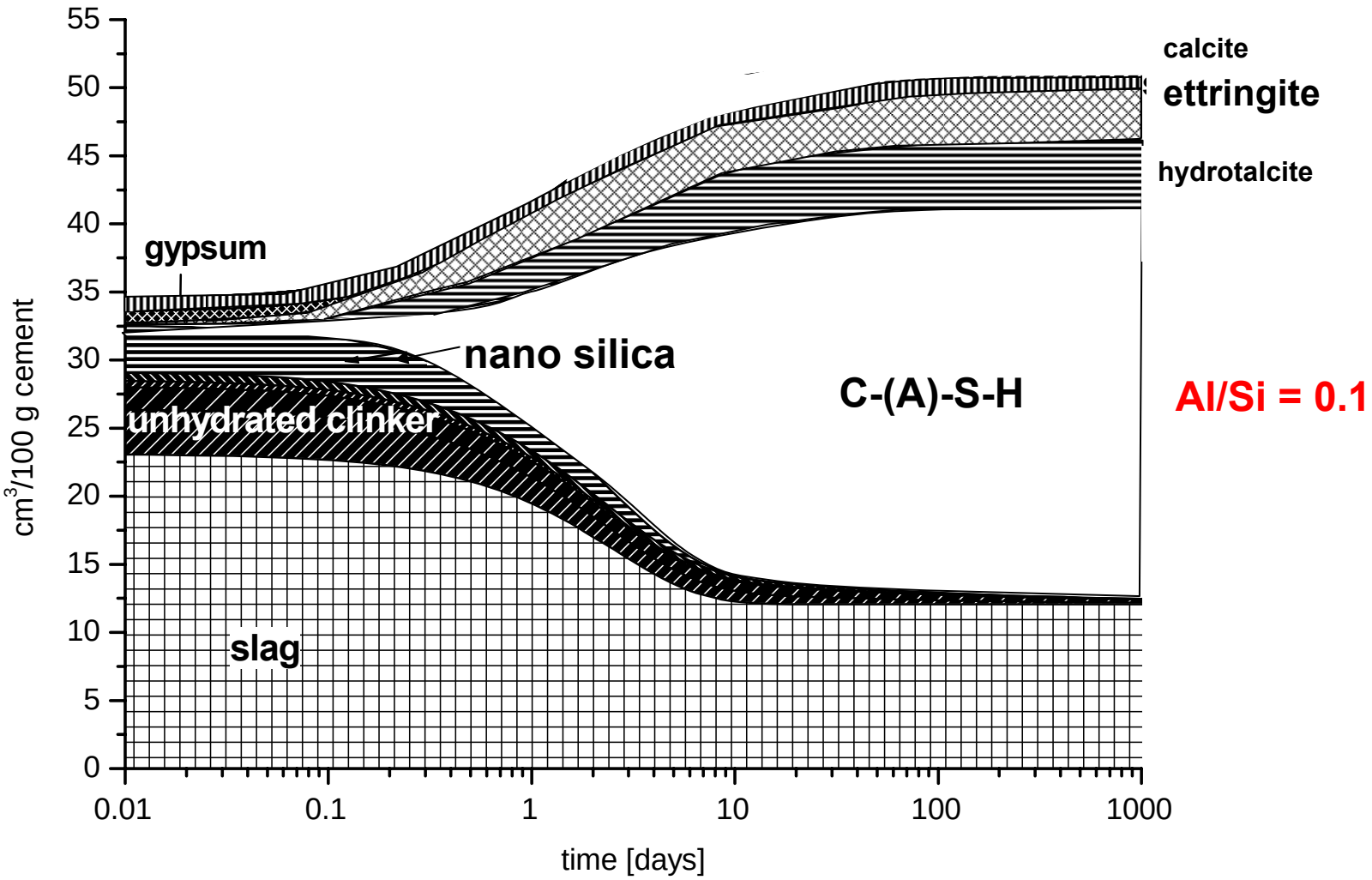
Portland cement hydration
- according to OPC system
- nanosilica dissolution according to NMR data
- slag dissolution according to selective dissolution

Problems
- Alkali (K) and Al-uptake in C-S-H not well known
- strätlingite or Al-in C-S-H?

LAC modelled



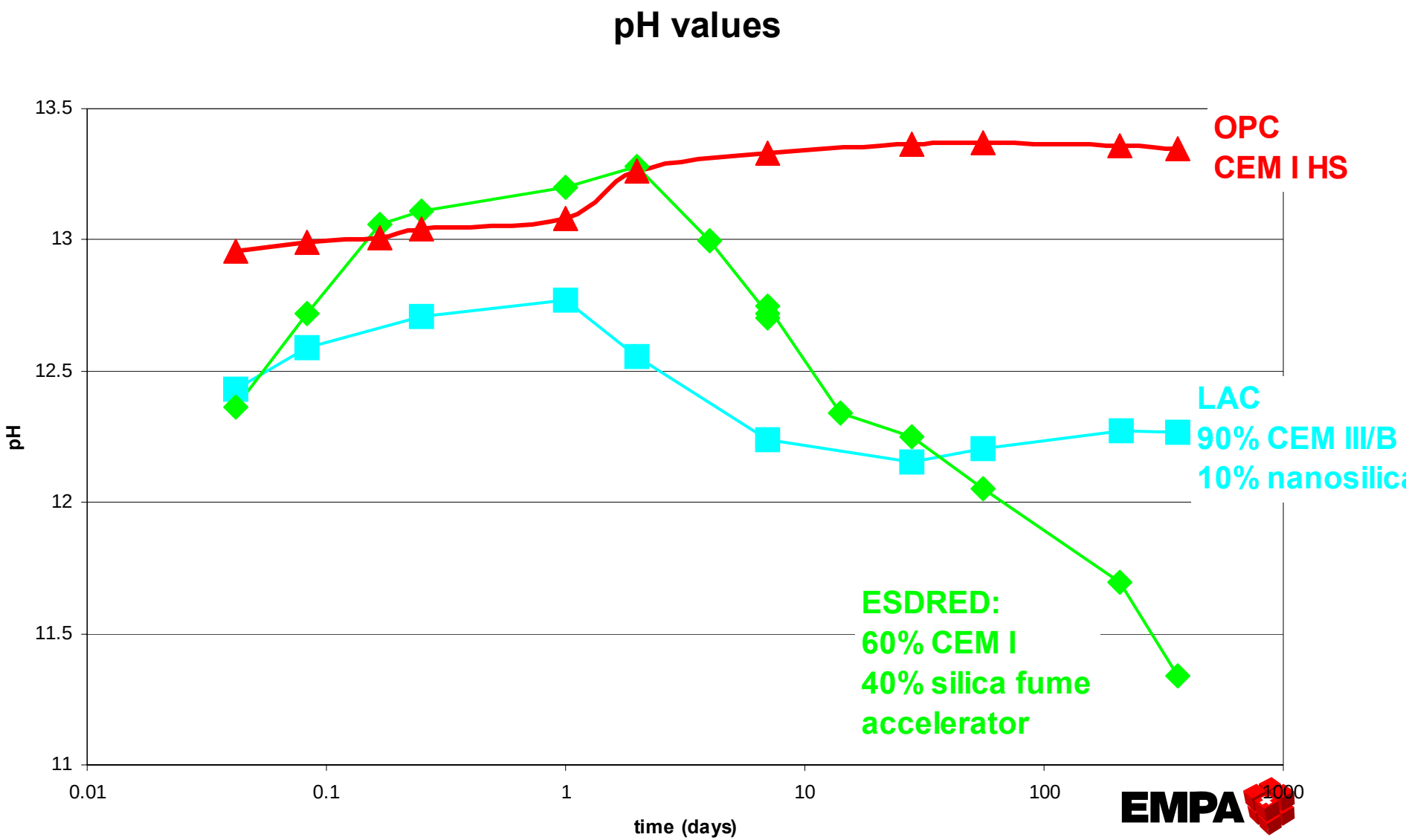
LAC modelled



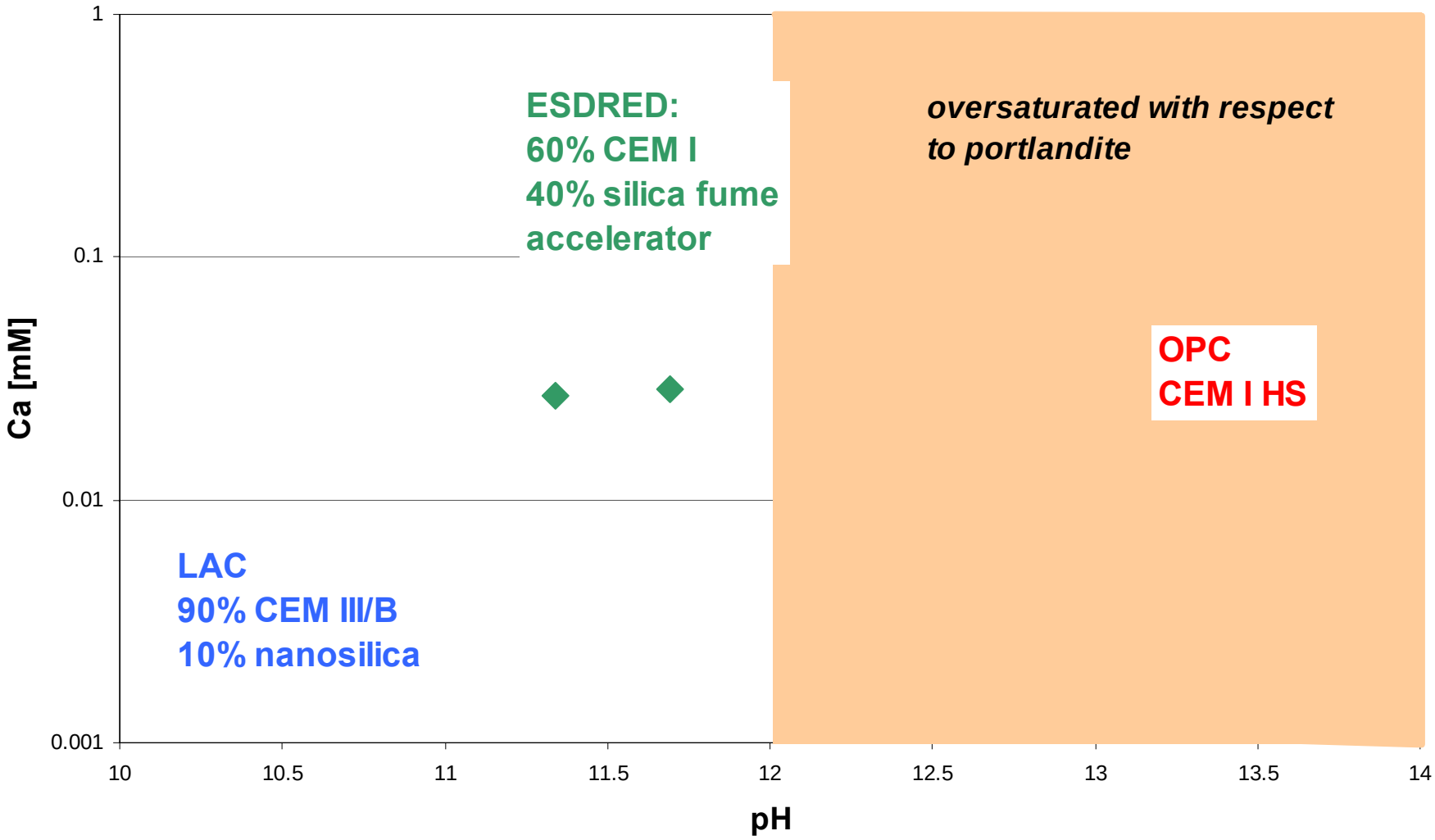
Summary - LAC

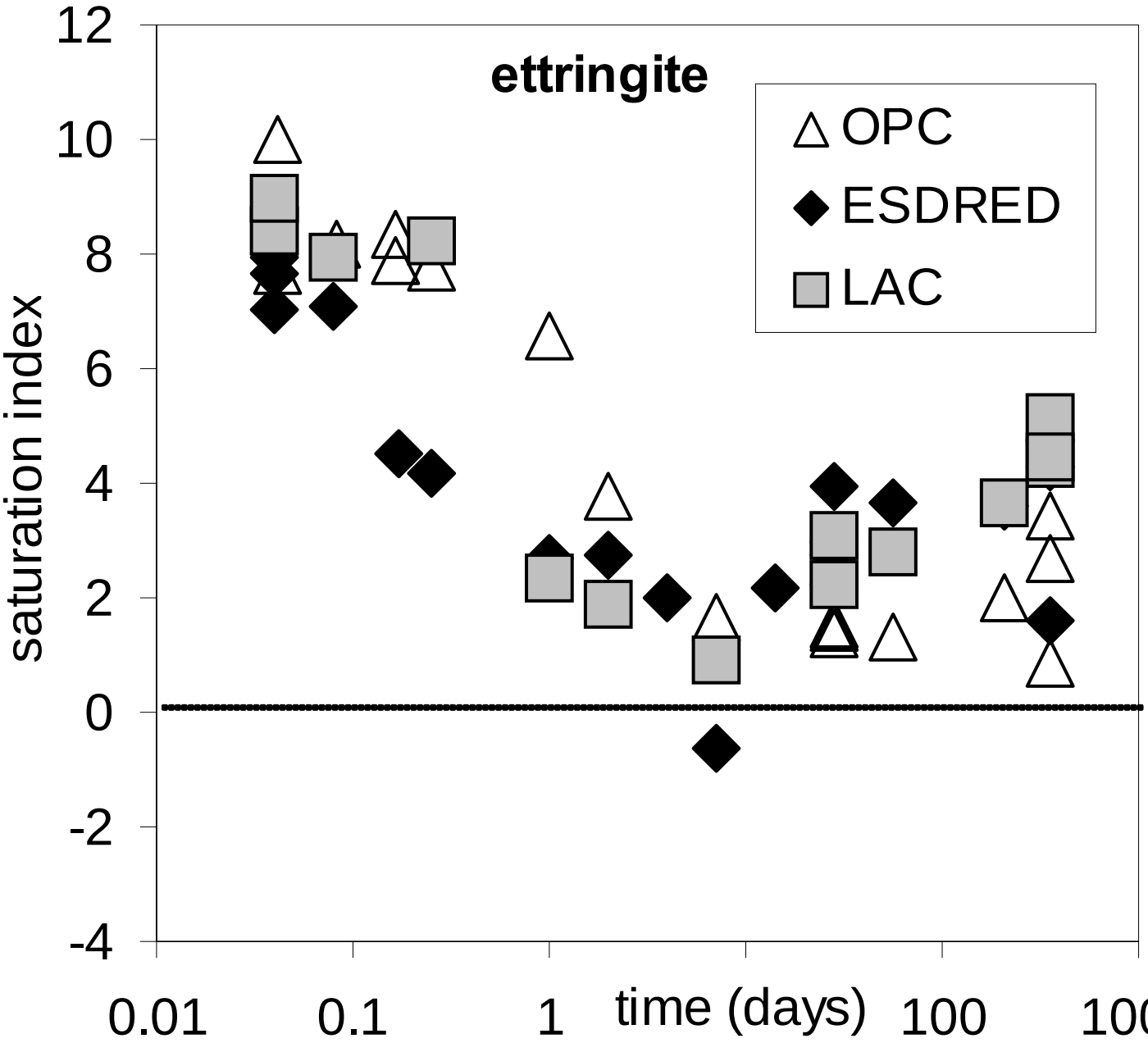
- Slag with OPC and SiO_2
- 0-1 days: similar to OPC,
- >1 days: slag + SiO_2:
  - Reducing conditions (HS-)
  - no portlandite
  - pH decreases
- Main hydration products
  - C-S-H (low C/S), ettringite -> strätlingite?
- pH decreases with time (12.3 after 1 year)
- Solution dominated by Ca, K, Na,OH and HS^-

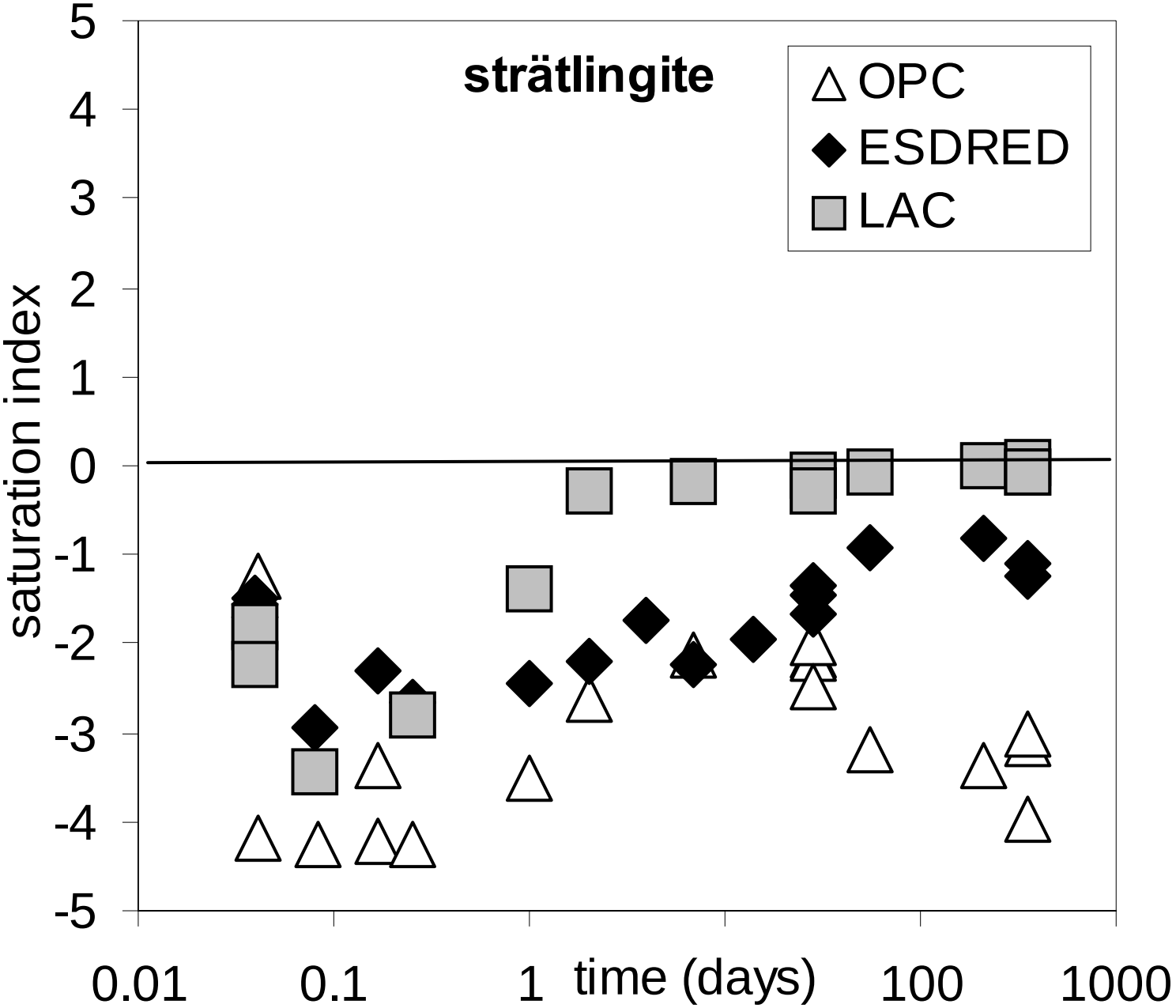
Comparison: different pore solutions

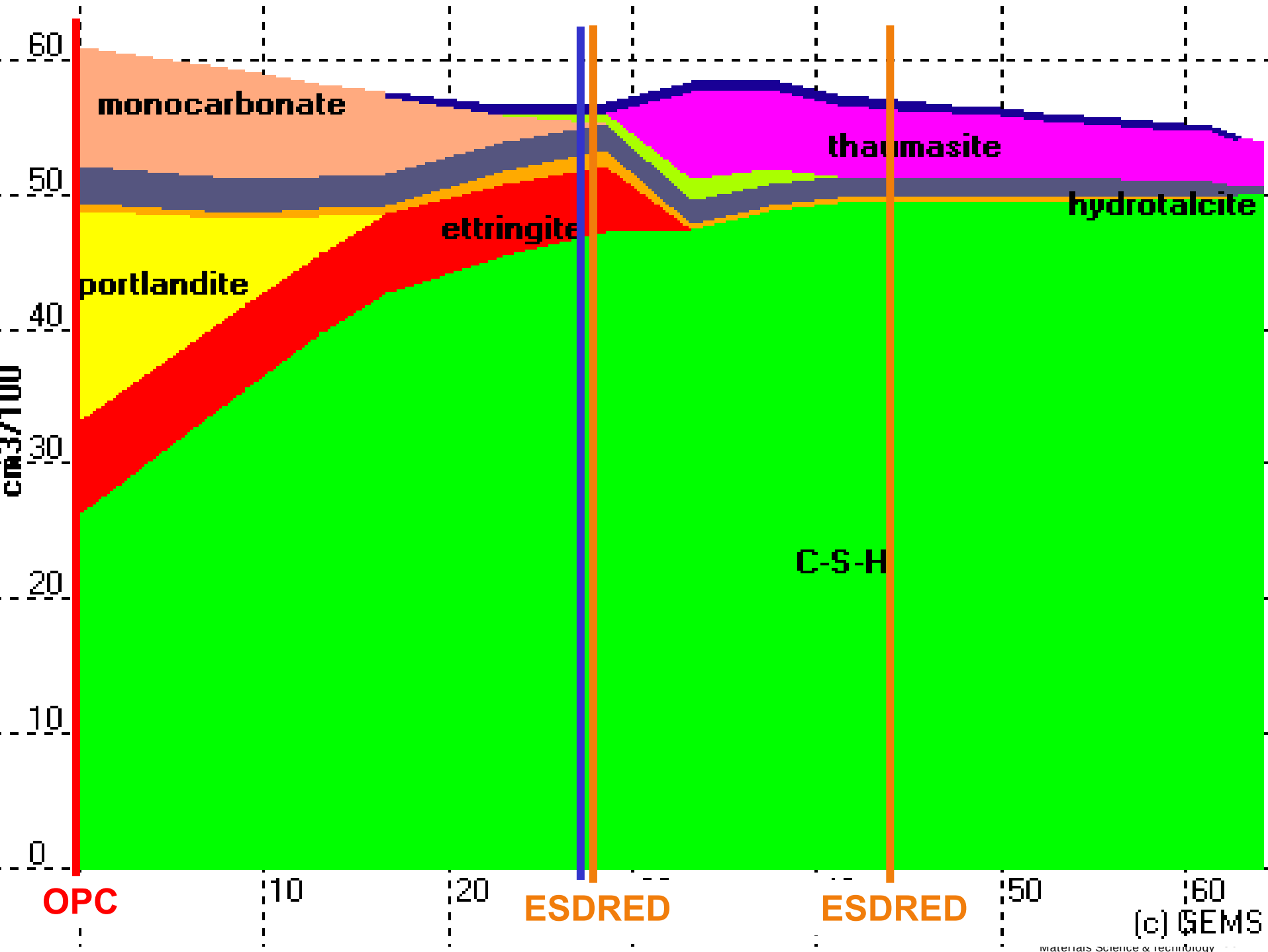


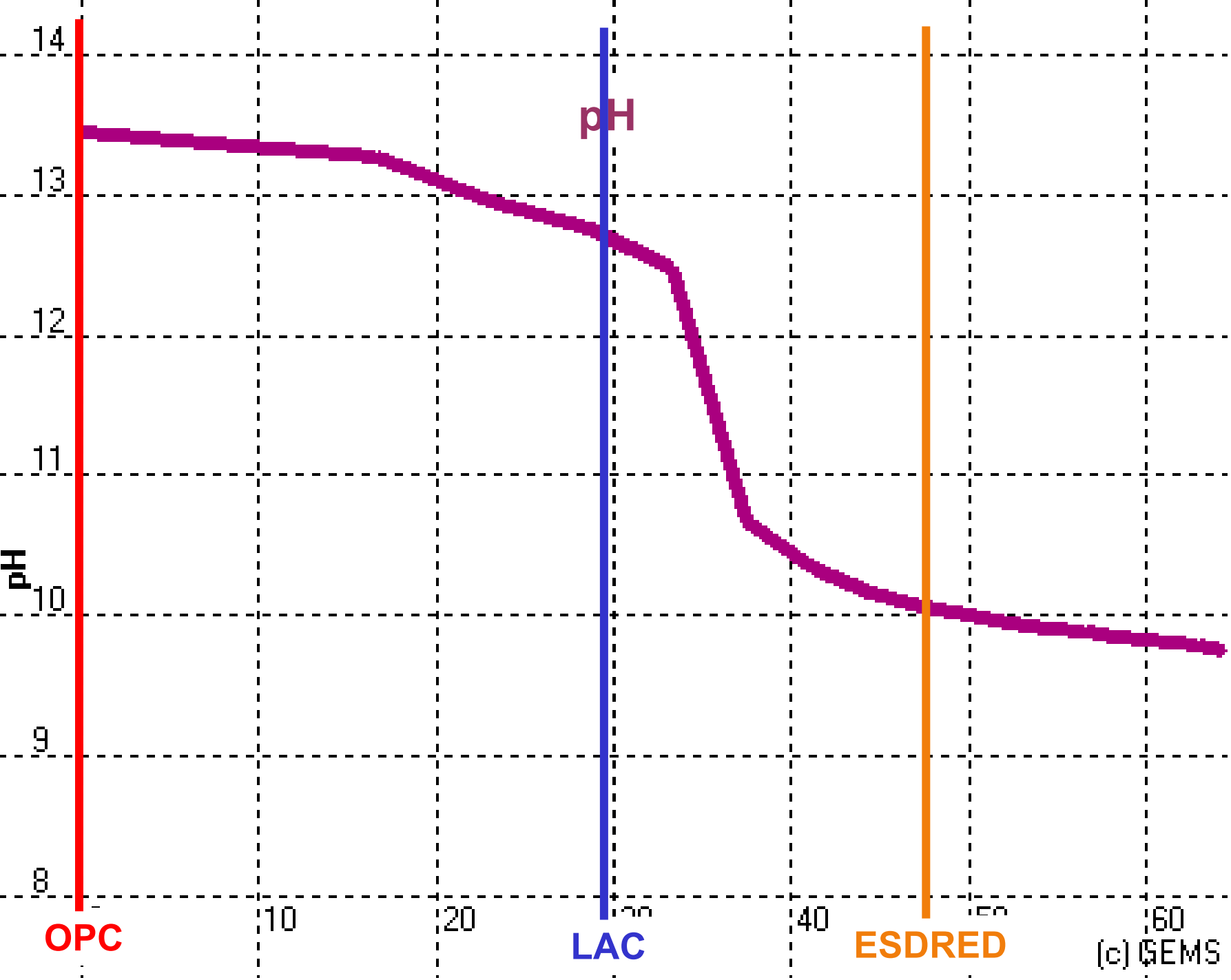
Comparison


1
0.1
0.01
0.001
Ca [mM]
10
10.5
11
11.5
12
12.5
13
13.5
14
pH
ESDRED:
60% CEM I
40% silica fume
accelerator
oversaturated with respect
to portlandite
OPC
CEM I HS
LAC
90% CEM III/B
10% nanosilica


ettringite
OPC
ESDRED
LAC
saturation index
12
10
8
6
4
2
0
-2
-4
0.01
0.1
1
time (days)
100
1000


strätlingite
OPC
ESDRED
LAC
saturation index
5
4
3
2
1
0
-1
-2
-3
-4
-5
0.01
0.1
1
time (days)
100
1000


monocarbonate
thaumasite
hydrotalcite
ettringite
portlandite
C-S-H
cm3/100
60
50
40
30
20
10
0
OPC
10
20
ESDRED
ESDRED
50
60
(c) GEMS


pH
14
13
12
11
10
9
8
pH
10
20
40
60
OPC
LAC
ESDRED
(c) GEMS

Conclusions

- OPC
  - hydration consistent with previous hydration studies
  - pH = 13.3 after 12 months

- ESDRED (CEM I + 40 % SiO_2)
  - Initially similar to OPC
  - Silica fume dissolution proceeds slowly
  - C-S-H: Initially C/S ~ 1.5, after 10 days ↓ (final C/S ~ 0.9)
  - Portlandite consumed after 10 days
  - Alkali and pH ↓ (after 12 months: pH = 11.3)

- LAC (CEM III/B + 10% SiO_2)
  - Initially similar to OPC
  - HS^- increases with time – reducing conditions
  - pH = 12.3 after 12 months