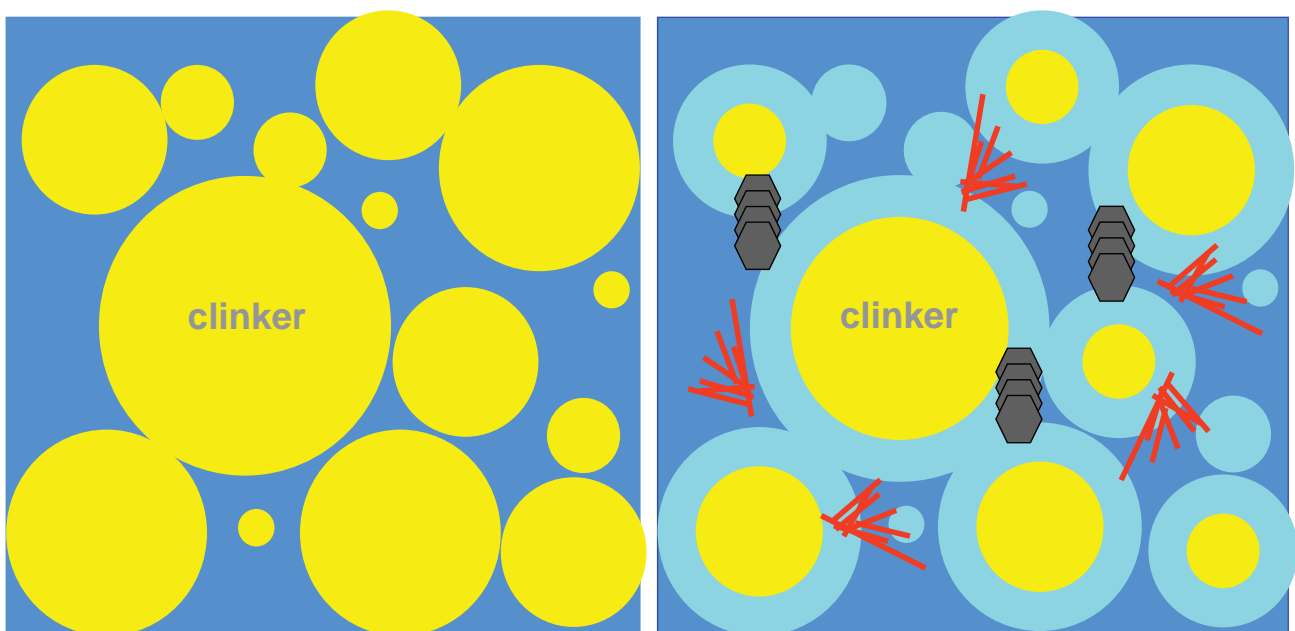


5) Hydration modelling

- a) Model of Parrot & Killoh
- b) Hydration modelling with GEMS

Hydration



● C-S-H ■ Portlandite ✶ Ettringite

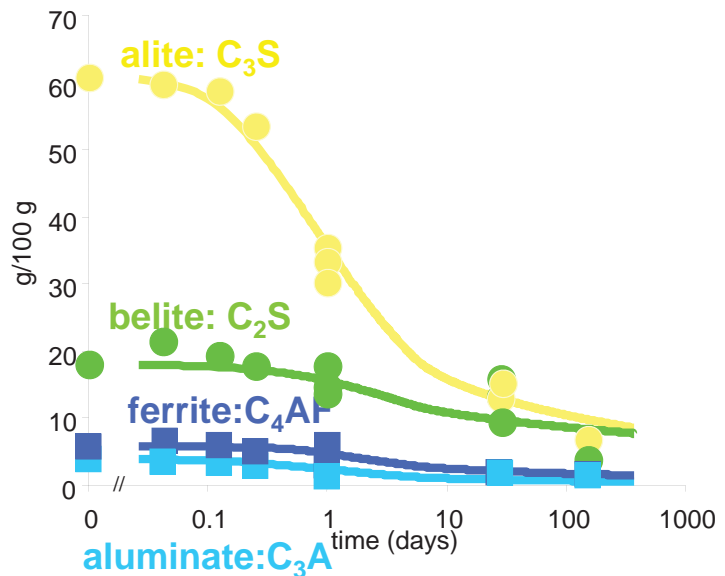
Empirical Approach: Parrot and Killoh (1984)

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

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

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

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



Cement specific input: surface area, w/c, composition

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3

Modeling: Dissolution

Empirical Approach: Parrot and Killoh (1984)

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

nucleation

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

diffusion

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

shell

degree of hydration

$$\alpha_t = \alpha_{t-1} + \Delta t \cdot R_{t-1} \cdot (1 + 3.333 \cdot (H \cdot w/c - \alpha_t))^4$$

for $\alpha_t > H \cdot w/c$.

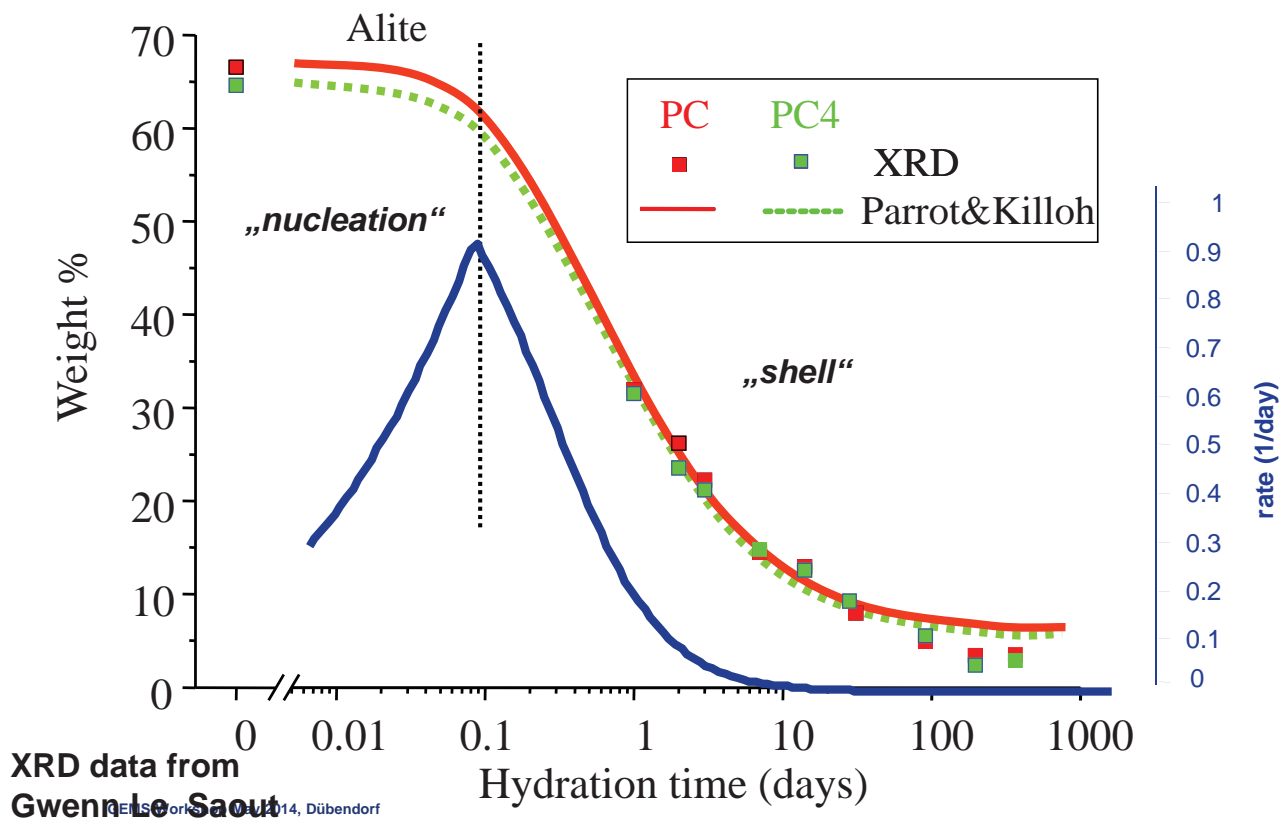
	alite	belite	alum.	ferrite
K_1	1.5	0.5	1.0	0.37
N_1	0.7	1.0	0.85	0.7
K_2	0.05	0.006	0.04	0.015
K_3	1.1	0.2	1.0	0.4
N_3	3.3	5.0	3.2	3.7
H	1.33	1.33	1.33	1.33

**Cement specific input:
surface area, w/c**

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4

Modeling: Dissolution



5

Modeling: Dissolution

Empirical Approach: Parrot and Killoh adapted
Lothenbach et al. (2008) 38, 848-860

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

nucleation

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

diffusion

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

shell

degree of hydration

$$\alpha_t = \alpha_{t-1} + \Delta t \cdot R_{t-1} \cdot (1 + 3.333 \cdot (H \cdot w/c - \alpha_t))^4$$

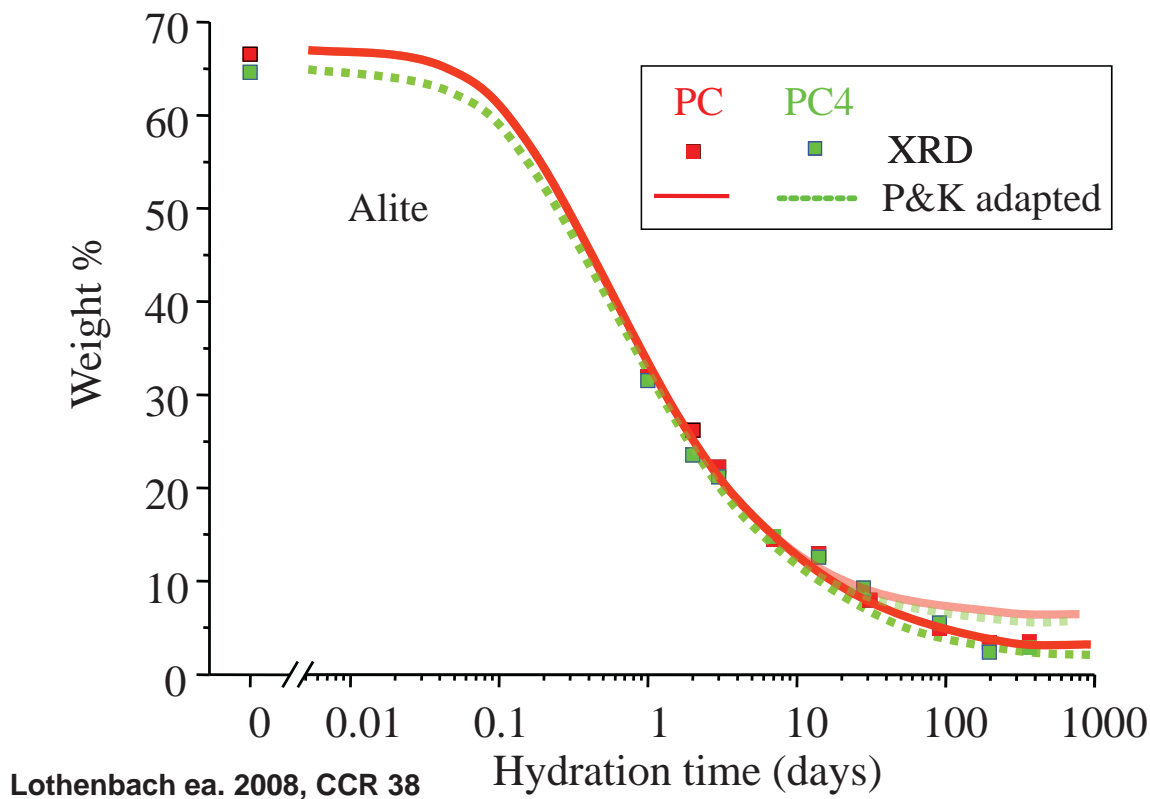
for $\alpha_t > H \cdot w/c$.

	alite	belite	alum.	ferrite
K_1	1.5	0.5	1.0	0.37
N_1	0.7	1.0	0.85	0.7
K_2	0.05	0.02	0.04	0.015
K_3	1.1	0.7	1.0	0.4
N_3	3.3	5.0	3.2	3.7
H	2.0	1.55	1.8	1.65

Cement specific input:
surface area, w/c

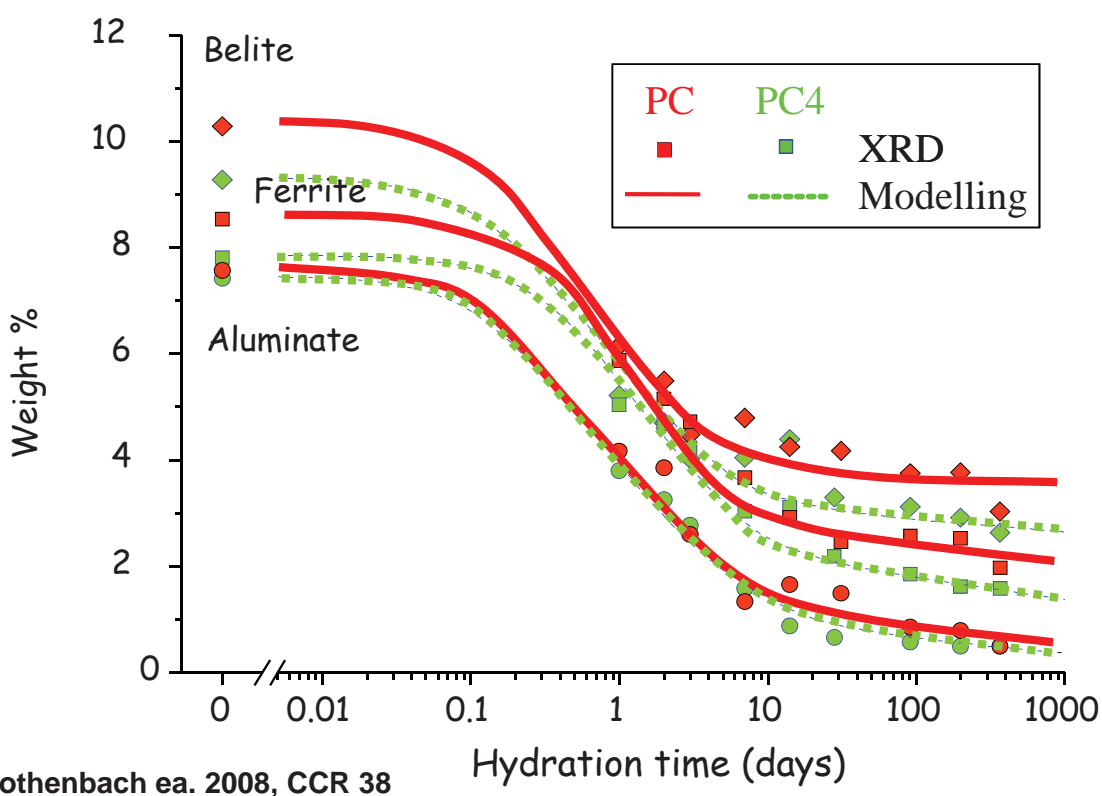
6

Modeling: Dissolution



7

Modeling: Dissolution



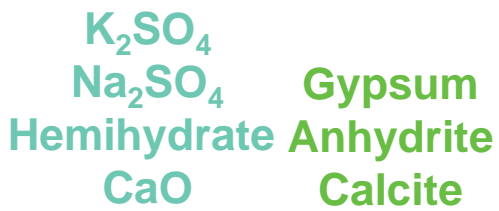
8

Multi-component input

I Slowly soluble clinkers



II Soluble solids

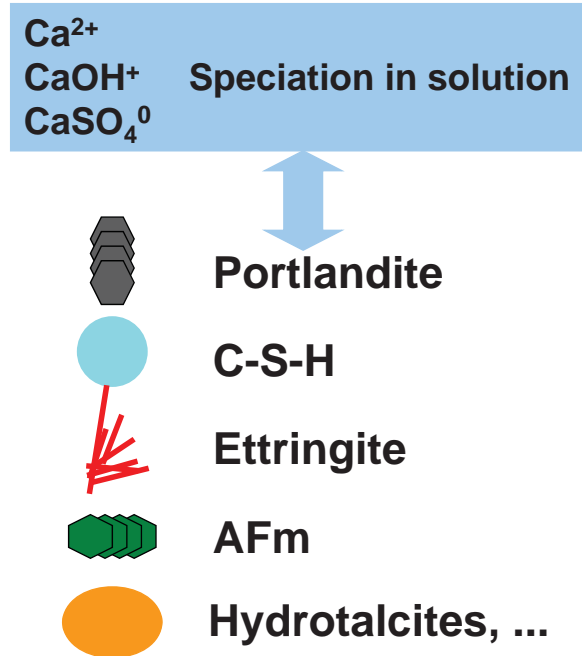


III Water



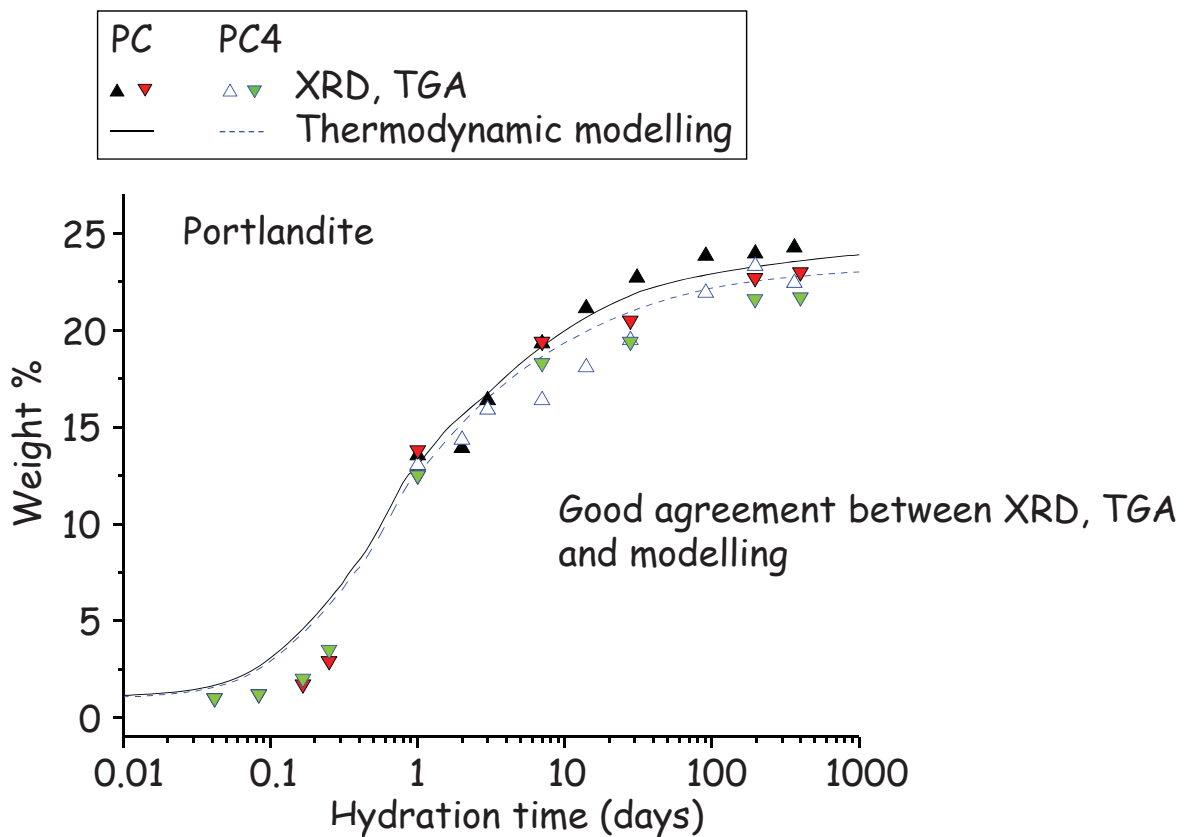
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Thermodynamic modeling GEMS-PSI



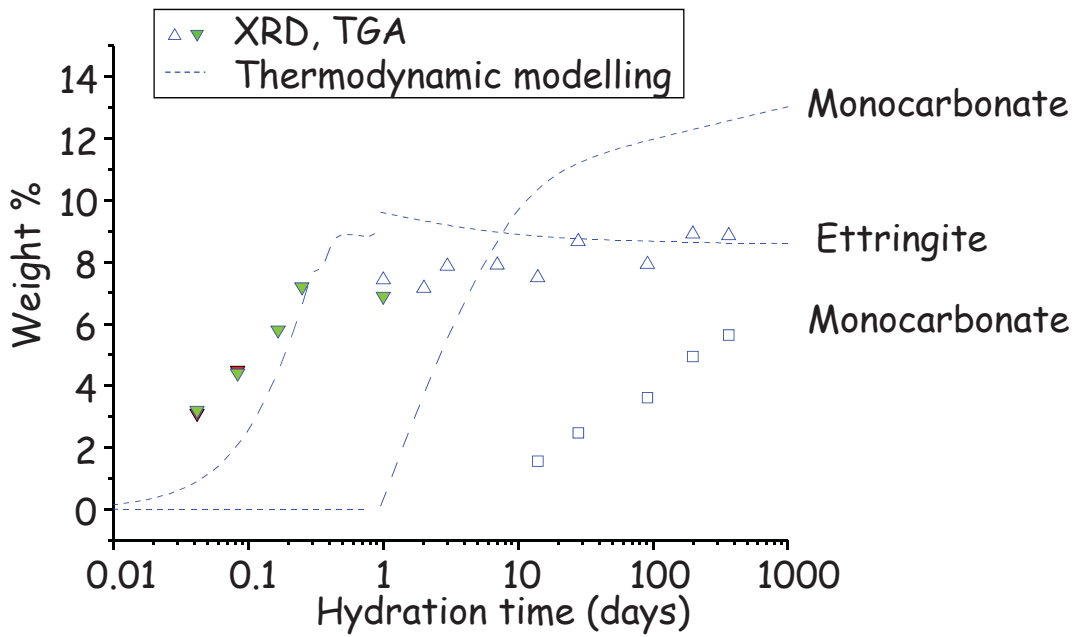
9

Output data, Portlandite



Lothenbach ea. 2008, CCR 38

10



- Overestimation of monocarbonate (\leq hemicarbonate, Al in C-S-H)
- Correct amount of ettringite in the PC sample

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Lothenbach et al. 2008, CCR 38

11

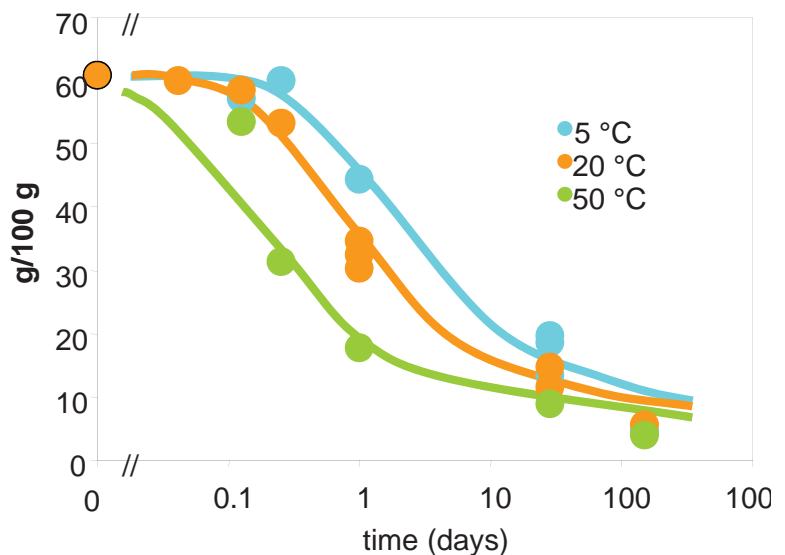
Modeling: Temperature

Arrhenius equation

$$R_T = A e^{-\frac{E_a}{RT}}$$

E_a : literature

alite dissolution

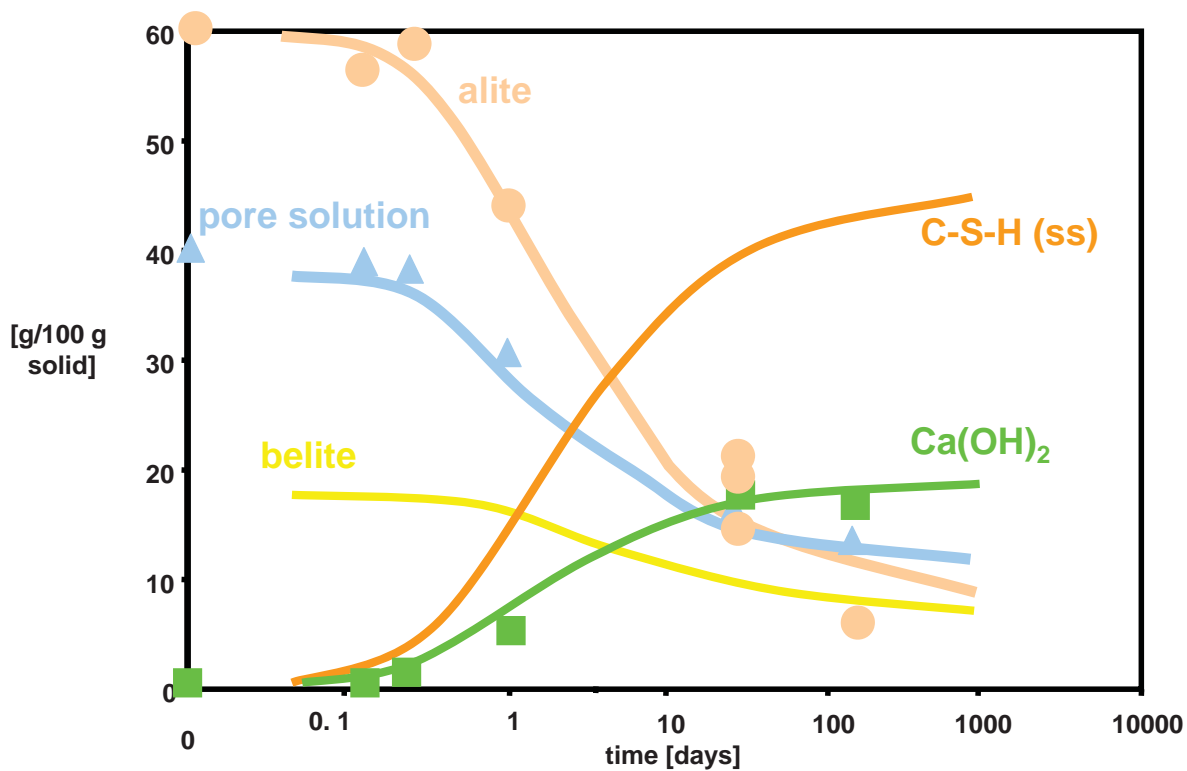


Lothenbach et al. (2008) CCR 38, 1-18

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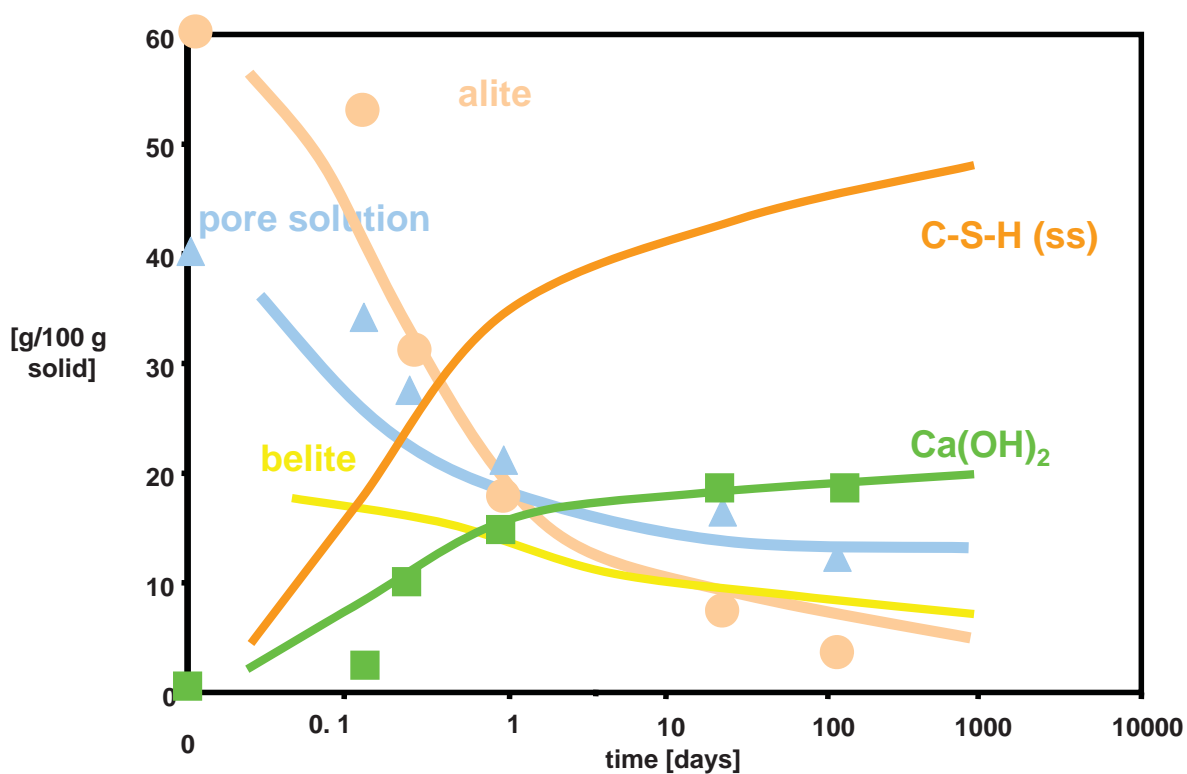
12

Ca- and Si-hydrates: 5 °C



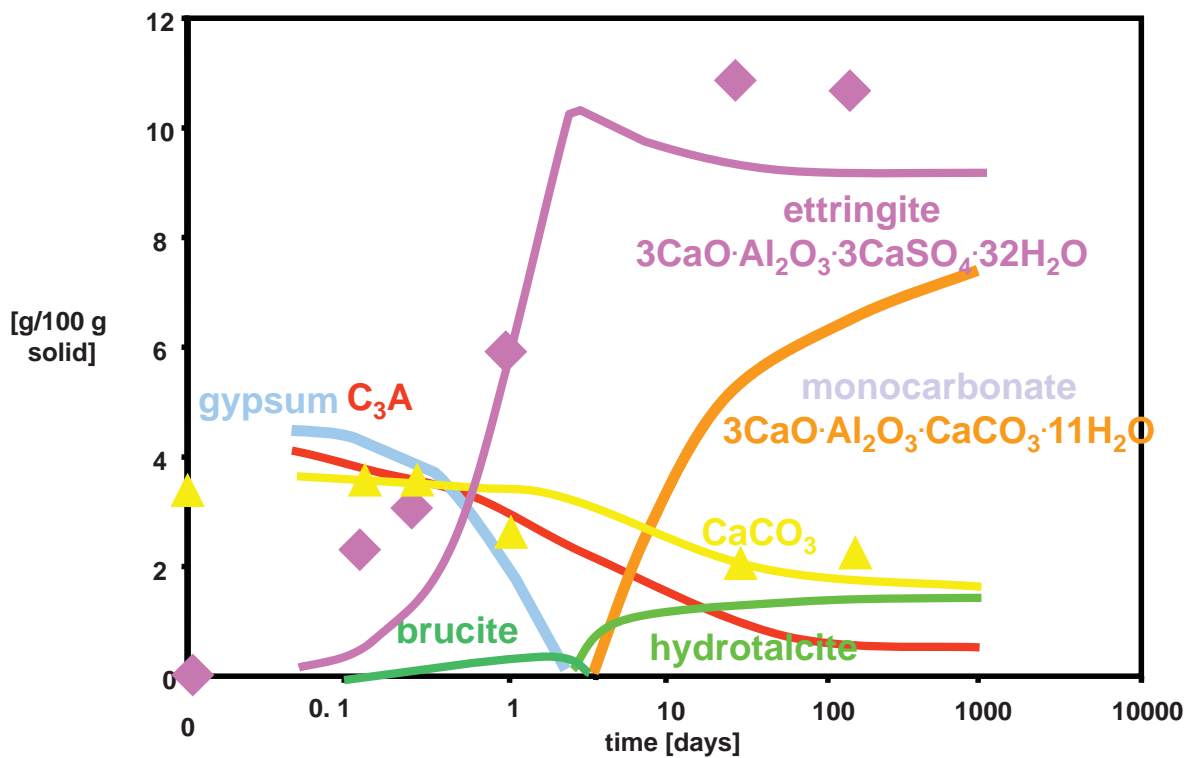
13

Ca- and Si-hydrates: 50 °C



14

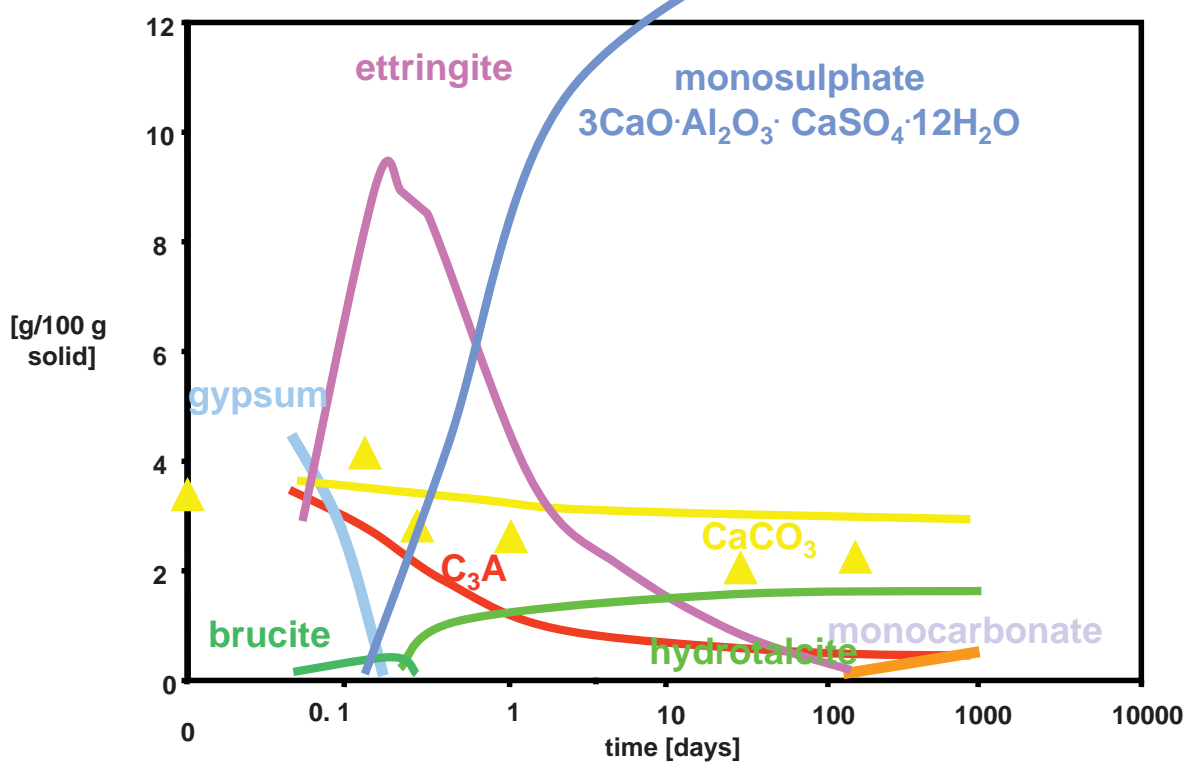
Al-, SO₄⁻, CO₃: 5 °C



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Al-, SO₄⁻, CO₃: 50 °C



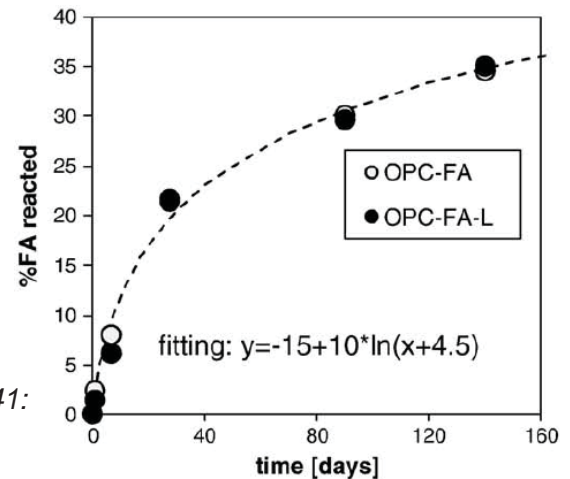
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Conclusion

- Empirical approach of P&K (adapted)
 - Describes observed dissolution (> 1 day) in OPC well
 - Simple to use
 - Influencing parameters: **surface area, w/c, temperature**
 - Purely empirical, other models can be used
 - Other influences: pH, composition of pore solution, ... not included

- Other models can be used
 - Any (empirical) equation which describes the reaction of solid as a function of time



De Weerd et al. (2011) CCR 41:
Reaction degree of fly ash

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Modeling: Dissolution

$$R_{t,T} = \frac{K_1}{N_1} (1 - \alpha_t) (-\ln(1 - \alpha_t))^{(1-N_1)} \left(\frac{rh - 0.55}{0.45} \right)^4 \frac{\text{surface area}}{385} e^{-\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right)}$$

$$R_{t,T} = \frac{K_2 \times (1 - \alpha_t)^{2/3}}{1 - (1 - \alpha_t)^{1/3}} \left(\frac{rh - 0.55}{0.45} \right)^4 e^{-\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right)}$$

$$R_{t,T} = K_3 \times (1 - \alpha_t)^{N_1} \left(\frac{rh - 0.55}{0.45} \right)^4 e^{-\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right)}$$

Relative surface area factor used for „nucleation and growth“ only (relative to Dalziel & Gutteridge, 1986)

Influence of temperature Arrhenius equation Ea values: Lothenbach et al., 2008

Influence of the relative humidity as proposed in Parrot and Killoh, 1984

Hydration in closed systems: rh =1

Modeling: Dissolution

$$R_{t,T} = \frac{K_1}{N_1} (1 - \alpha_t) (-\ln(1 - \alpha_t))^{(1-N_1)} \left(\frac{rh - 0.55}{0.45} \right)^4 \frac{\text{surface area}}{385} e^{-\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right)}$$

$$R_{t,T} = \frac{K_2 \times (1 - \alpha_t)^{2/3}}{1 - (1 - \alpha_t)^{1/3}} \left(\frac{rh - 0.55}{0.45} \right)^4 e^{-\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right)}$$

$$R_{t,T} = K_3 \times (1 - \alpha_t)^{N_3} \left(\frac{rh - 0.55}{0.45} \right)^4 e^{-\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right)}$$

degree of hydration of each clinker phase

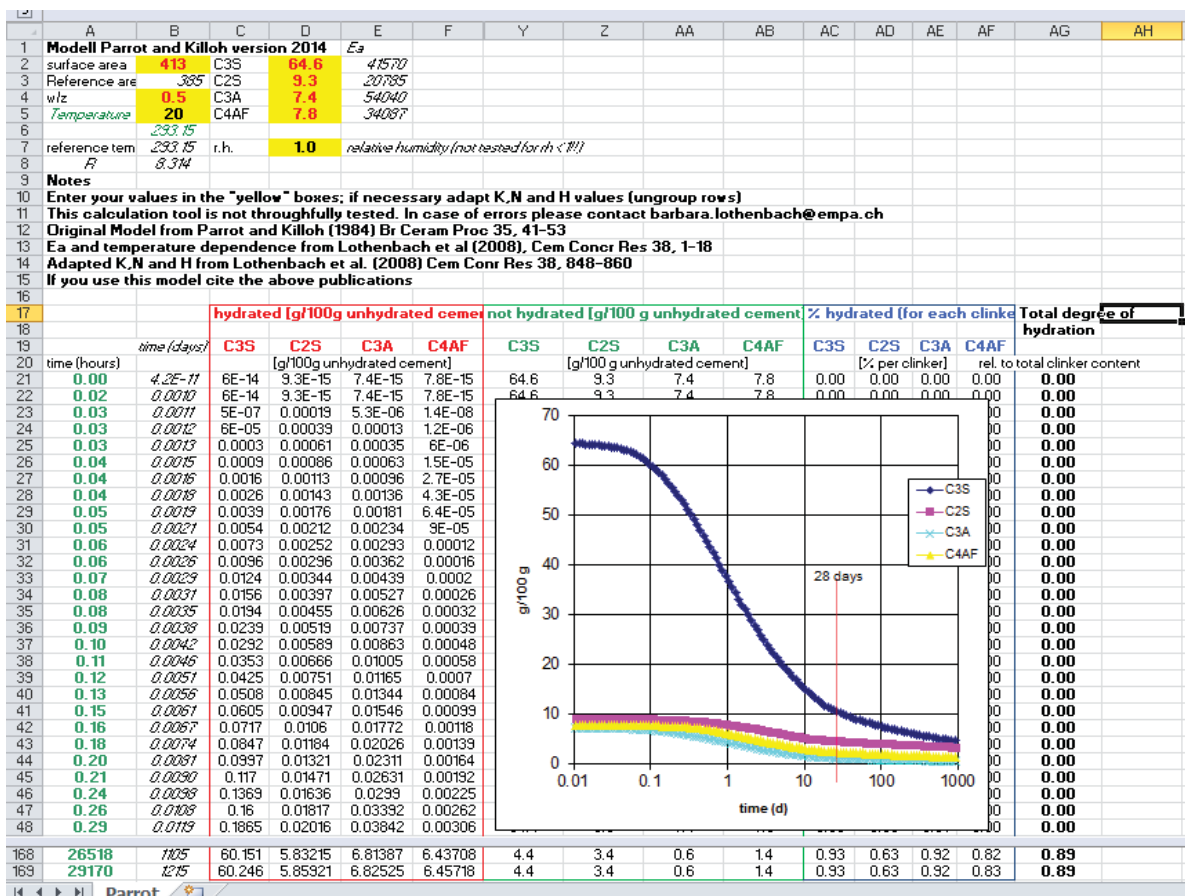
- *initial* $\alpha_t = \alpha_{t-1} + \Delta t \cdot R_{t-1}$
- *later, for $\alpha_{t-1}(\text{total}) > H \cdot w/c$;*
 $H \cdot w/c = \text{critical degree of hydration}$
 $\alpha_t = \alpha_{t-1} + \Delta t \cdot R_{t-1} \cdot (1 + 3.333 \cdot (H \cdot w/c - \alpha_t))^4$

Hydration is
reduced with time
at low w/c

Cement specific input: surface area [m²/kg], w/c, composition

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Parrot and Killoh model as Excel file



20

E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V	W	X	Y	Z	AA
Parrot and Killoh, 1984 "Nucleat" "Diffusio" "Shell form" thenbach et al., 2008 "Nucleat" "Diffusio" "Shell formation"																						
41570						C3S	K	1.5	0.05	1.1		C3S	K	1.5	0.05	1.1						
20785						N	H	1.33		3.3		N	H	2		3.3						
54040						C2S	K	0.5	0.006	0.2		C2S	K	0.5	0.02	0.7		2	1.8			
34087						H		1		5		H		1		5		0.5	1			
relative humidity (not tested for rh < 100%)						C3A	K	1.33		1		C3A	K	1.55		1		1.55	1.4			
						H		0.85		3.2		H		0.85		3.2		0.85	1			
necessary adapt K,N and H values (ungroup rows)						C4AF	K	1.33		0.4		C4AF	K	1.8		0.4		1.8	0.37			
tested. In case of errors please contact barbara.lothen						N	H	0.7		3.7		N	H	1.45		3.7		1.65	1.5			
4) Br Ceram Proc 35, 41-53						C3S		1.5	1.1	0.05		C2S		0.5	0.2	0.01		C3A		1	0.04	
thenbach et al (2008), Cem Concr Res 38, 1-18						C4AF		0.37	0.015	0.4		C2S		1	0.5	0.01		C3A		0.85	3.2	
I. (2008) Cem Conr Res 38, 848-860						C4AF		0.7	0.015	0.4		C2S		0.85	3.2	0.04		C3A		0.37	0.4	0.02
cations						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
hydrated cement)						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
time function						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
Nucleatio "Shell f" "Diffusio" "rate"						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
degree "Nucle:" "Shell for" "Diffusio" degree						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
1E-15 1E-15 1E-15 1E-15						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0 0 0 0						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0.0000 0.0000 0.0000						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0.0000 0.0000 0.0000						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0.0000 0.0000 0.0000						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0.0000 0.0000 0.0000						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0.0000 0.0000 0.0000						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0.0000 0.0000 0.0000						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0.0000 0.0000 0.0000						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0.0000 0.0000 0.0000						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0.0000 0.0000 0.0000						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0.0000 0.0000 0.0000						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0.0000 0.0000 0.0000						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0.0000 0.0000 0.0000						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0.0000 0.0000 0.0000						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0.0000 0.0000 0.0000						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0.0000 0.0000 0.0000						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0.0000 0.0000 0.0000						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0.0000 0.0000 0.0000						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0.0000 0.0000 0.0000						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0.0000 0.0000 0.0000						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0.0000 0.0000 0.0000						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0.0000 0.0000 0.0000						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0.0000 0.0000 0.0000						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0.0000 0.0000 0.0000						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0.0000 0.0000 0.0000						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0.0000 0.0000 0.0000						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0.0000 0.0000 0.0000						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0.0000 0.0000 0.0000						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0.0000 0.0000 0.0000						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0.0000 0.0000 0.0000						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0.0000 0.0000 0.0000						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0.0000 0.0000 0.0000						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0.0000 0.0000 0.0000						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0.0000 0.0000 0.0000						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0.0000 0.0000 0.0000						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0.0000 0.0000 0.0000						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0.0000 0.0000 0.0000						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0.0000 0.0000 0.0000						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0.0000 0.0000 0.0000						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0.0000 0.0000 0.0000						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0.0000 0.0000 0.0000						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0.0000 0.0000 0.0000						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0.0000 0.0000 0.0000						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0.0000 0.0000 0.0000						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0.0000 0.0000 0.0000						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0.0000 0.0000 0.0000						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0.0000 0.0000 0.0000						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0.0000 0.0000 0.0000						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0.0000 0.0000 0.0000						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0.0000 0.0000 0.0000						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0.0000 0.0000 0.0000						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0.0000 0.0000 0.0000						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0.0000 0.0000 0.0000						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0.0000 0.0000 0.0000						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0.0000 0.0000 0.0000						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0.0000 0.0000 0.0000						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0.0000 0.0000 0.0000						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0.0000 0.0000 0.0000						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0.0000 0.0000 0.0000						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0.0000 0.0000 0.0000						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0.0000 0.0000 0.0000						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0.0000 0.0000 0.0000						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0.0000 0.0000 0.0000						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0.0000 0.0000 0.0000						C4AF		0.7	0.4	0.02		C2S		0.7	0.4	0.02		C3A		0.7	0.4	0.02
0.0000 0																						

Parrot:G:PC:0:0:1:20:0:mass:S:

Controls Sampling Results Config 11/04/2014, 13:01

OPC with limestone
Parrot and Killoh adapted according Lothenbach et al. 2008

	iTm	iV	iP	iTC	iNv	iTau	ipXi	iNu
0	1000	0	1	20	0	0	0	
1	1501	0	1	20	0	0	0	500
2	1	0	0	0	0	0	0	1
cTm	1148	0	1	20	0	0	0	148

Reaction from Excel

	Time (days)	Reacted C3S
0	0	0
1	0	0
2	0	0

Cement specific input

```

$ Parrot and Killoh adapted (H set to 2, 1.55, 1.8 and 1.65), influence ...
$Clinker phases from Bogue calculations (in case of Rietveld data correc...

$ cement specific input; enter data as [g/100g]
$ surface area (m2/kg)
modC[0][5] =: 413;
$ w/z
modC[1][5] =: 0.40;
$ C3S (in g/100g)
modC[2][5] =: 64.64;
$ C2S (in g/100g)
modC[3][5] =: 9.28;
$ C3A (in g/100g)
modC[4][5] =: 7.42;
$ C4AF (in g/100g)
modC[5][5] =: 7.81;
$ calcite
xd_{{Cal}} =: 4.57;
$ free lime
xd_{{Lim}} =: 0.89;
$ gypsum
xd_{{Gp}} =: 3;
$ anhydrite
xd_{{Anh}} =: 0;
$ hemihydrate
xd_{{hemihydrate}} =: 0;
$ Aragonite

```

	modC[0]	modC[1]	modC[2]
0	4.16667e-011	6.46e-014	
1	0.001	6.46e-014	
2	0.0011	4.69473e-007	
3	0.0012	5.95605e-005	
4	0.0013	0.000337479	0
5	0.0015	0.000851873	
6	0.0016	0.001598878	0
7	0.0018	0.002591409	0
8	0.0019	0.003853374	0
9	0.0021	0.00541697	0
10	0.0024	0.007321916	0
11	0.0026	0.009615555	0
12	0.0029	0.012353404	0
13	0.0031	0.015600015	0
14	0.0035	0.019430078	0
15	0.0038	0.023929757	0
16	0.0042	0.029198264	0
17	0.0046	0.03534969	0
18	0.0051	0.042515114	0
19	0.0056	0.050845036	0

Architecture of GEMS file

- Input always in g/100g
- The amount of clinker reacted copied from EXCEL file
- Inputs needed in GEMS:
 - surface area [m²/kg]
 - w/c
 - C₃S, C₂S, C₃A, C₄AF (pure phases)
 - Calcite, free lime, gypsum, anhydrite, hemihydrate, periclase, Na₂SO₄ and K₂SO₄ (-> soluble alkalis)
 - Na₂O, K₂O, MgO and SO₃ in clinker (as g/g clinker) optional

Architecture of GEMS file

- Process: controls below input
 - E_a (activation energy)
 - Conversion of different input parameter
 - Correction factors for minor elements in clinker
 - Amount of input water
 - Calculations of the dissolution of minor elements
 - Alkali uptake by C-S-H
 - Only valid at high C/S ratio

Do not change!

Alkali uptake

$$R_d = \frac{c_{solid} \cdot liquid}{c_{liquid} \cdot C - S - H} \frac{[ml]}{[g]};$$

$$c_{liquid} = c_{tot} - c_{solid};$$

$$c_{solid} = \frac{c_{tot}}{1 + \frac{liquid}{C - S - H \cdot R_d}}$$

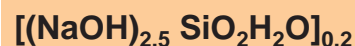
! Rough estimate for OPC!!

$$R_d \sim 0.42 \text{ ml/g}$$

cf. Hong, Glasser, CCR 29, 1893-1903
 Lothenbach, Winnefeld CCR 36, 209-226

Other options:

Use of alkali-silicate endmembers in the C-S-H solid solutions:



Kulik et al. (2007) Geochim. Cosmochim. Acta 71 (12, 1) A530.

Lothenbach et al. (2012) Cement and Concrete Research, 42 (2), 410-423.

! does not work well at pH 11 or below

- **Development of new CSH model with alkali and aluminium and anions ... for GEMS in progress** (output of sinergia project CASH)
- **CSH models with sorption** (Nonat et al.)

Architecture of GEMS file

- Process: sampling: definition of output
 - X-axis: log (time)
 - Mass in g/100 g of hydrated cement
 - All data corrected from g/100 g unhydrated cement to g/100 g hydrated cement (corresponds to conditions of XRD, TGA measurements); can easily be changed, but you will have to convert XRD/TGA data
 - Amount of clinkers (with impurities)
 - Amount of hydrates (! Check single system file for the presence of additional solids and include them in the list)
 - Amount of pore solution (including dissolved species)

Check single system file for additional solids

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NeIt	9999	149	Next	0	I	0	J	148	Jp	148
------	------	-----	------	---	---	---	---	-----	----	-----

pSTkey Parrot:G:PC:0:0:1:20:0:	cTm 11
--------------------------------	--------

cTau	0	cpXi	0	cXi	1	cNu
------	---	------	---	-----	---	-----

cpH	0	cpe	0	cEh	0	cT
-----	---	-----	---	-----	---	----


```

$ Abscissa
xp[J] =: lg(modC[J][0]);

$ Ordinates (in g/100 g unhydrated cement)
$ clinkers include also minor elements
yp[J][0] =: (modC[2][5]-xd_[{C3S}]/modC[24][5]);
yp[J][1] =: (modC[3][5]-xd_[{C2S}]/modC[25][5]);
yp[J][2] =: (modC[4][5]-xd_[{C3A}]/modC[26][5]);
yp[J][3] =: (modC[5][5]-xd_[{C4AF}]/modC[27][5]);
yp[J][4] =: phM[{CSHQ}]-xa_[{K2O}]-xa_[{Na2O}];
yp[J][5] =: phM[{Portlandite}];
yp[J][6] =: phM[{Gypsum}];
yp[J][7] =: phM[{syngenite}];
yp[J][8] =: phM[{Calcite}];
yp[J][9] =: phM[{SO4_CO3_Aft}]+phM[{CO3_SO4_Aft}];
yp[J][10] =: phM[{SO4_OH_Afm}]+phM[{OH_SO4_Afm}];
yp[J][11] =: phM[{C4AcH11}];
yp[J][12] =: phM[{C4Ac0.5H12}];
yp[J][13] =: phM[{C2ASH8}];
yp[J][14] =: phM[{C3AH6}];
yp[J][15] =: phM[{OH-hydrotalcite}];
yp[J][16] =: phM[{C3FS0.84H4.32}];

$ correction to hydrated cement possible
$ /(1+modC[1][5]-phM[{aq_gen}]/100) =1+0.4-mass H2O dissolved/100
$ =mass hydrated cement (after removal of pore water)
  
```

modC[2][5] -> total C3S
xd_[{C3S}] -> C3S dissolved at time t
= C3S not reacted

modC[24][5] -> correction for impurities; = 0.99 in our example

phM[{Portlandite}] -> mass of Portlandite in g
! Spelling has to correspond exactly to single component!

$\frac{1}{1 + \text{modC}[1][5] - \text{phM}[\text{aq_gen}]/100}$
= 1 + 0.4 - mass H₂O unreacted/100
= mass hydrated cement (after removal of pore water)

For comparison with XRD/TGA

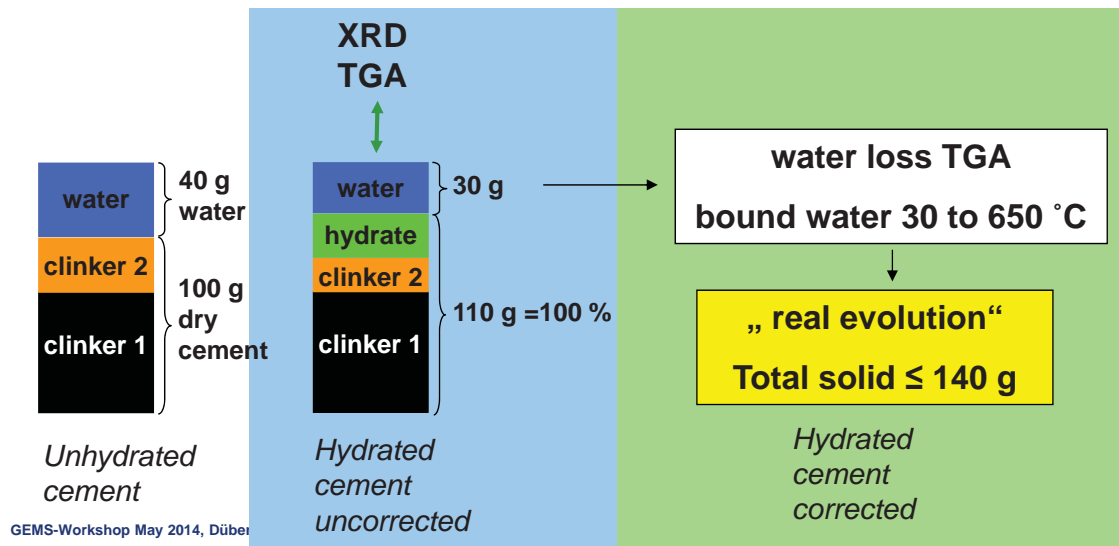
Different outputs possible

■ Y-axis Mass in g/100 g of hydrated cement

$\text{phM}[\{\text{Portlandite}\}]/(1+\text{modC}[1][5]-\text{phM}[\{\text{aq_gen}\}]/100)$
 correction of the output $/ (1+0.4-\text{mass H}_2\text{O unreacted}/100)$
 \Rightarrow / mass hydrated cement (after removal of pore water)

■ Y-axis Mass in g/100 g of original cement

$\text{phM}[\{\text{Portlandite}\}] \Rightarrow$ correct measurements to 100 dry weight



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Architecture of GEMS file

■ Process: Results: output

■ X-axis: log (time)

■ Y-axis Mass in g/100 g of hydrated cement

■ Experimental data, same format as calculated data

- Number of data points can be adapted by „Record:Remake“

■ Data used to prepare graph, can be exported to Excel or other softwares by copy/paste

Parrot:G:PC:0:0:1:20:0:mass:S:

Controls Sampling Results Config 11/04/2014, 13:01

OPC with limestone

Unit of x-axis

Unit of y-axis

y-axis labels

X-axis Time (10^x days)

y-axis (in g/100 g of unhydrated cement as defined in page sampling)

pX Nam	time	Alite	Belite	Aluminate	Ferrite
0	-10.380211	64.64	9.28	7.42	7.81
1	-3	64.64	9.28	7.42	7.81
2	-2.9586073	64.64	9.2798144	7.4199947	7.81
3	-2.9208187	64.63994	9.2796103	7.4198716	7.8099988
4	-2.8860566	64.639663	9.2793857	7.4196528	7.8099994
5	-2.8239087	64.639148	9.2791388	7.4193734	7.8099854
6	-2.79588	64.638401	9.2788672	7.4190377	7.809973
7	-2.7447275	64.637409	9.2785684	7.4186438	7.8099566
8	-2.7212464	64.636147	9.2782399	7.4181878	7.8099358
9	-2.6777807	64.634583	9.2778786	7.4176638	7.8099101
10	-2.6197888	64.632678	9.2774812	7.4170651	7.8098788
11	-2.5850266	64.630384	9.2770441	7.4163837	7.8098411
12	-2.537602	64.627647	9.2765635	7.4156103	7.8097961
13	-2.5086383	64.6244	9.2760349	7.4147346	7.8097429
14	-2.455932	64.62057	9.2754537	7.4137448	7.80968
15	-2.4202164	64.61607	9.2748145	7.4126276	7.8096062
16	-2.3767507	64.610802	9.2741117	7.4113683	7.8095198
17	-2.3372422	64.60465	9.2733388	7.40995	7.8094189
18	-2.2924298	64.597485	9.272489	7.4083542	7.8093015
19	-2.251812	64.589155	9.2715547	7.40656	7.8091649
20	-2.2146702	64.579488	9.2705275	7.4045438	7.8090064
21	-2.1739252	64.568285	9.2693982	7.4022797	7.8088227
22	-2.1307683	64.55532	9.2681567	7.3997383	7.8086102
23	-2.091515	64.540333	9.2667919	7.3968869	7.8083644
24	-2.0457575	64.523023	9.2652918	7.3936889	7.8080805

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Possibility to plot experimental data

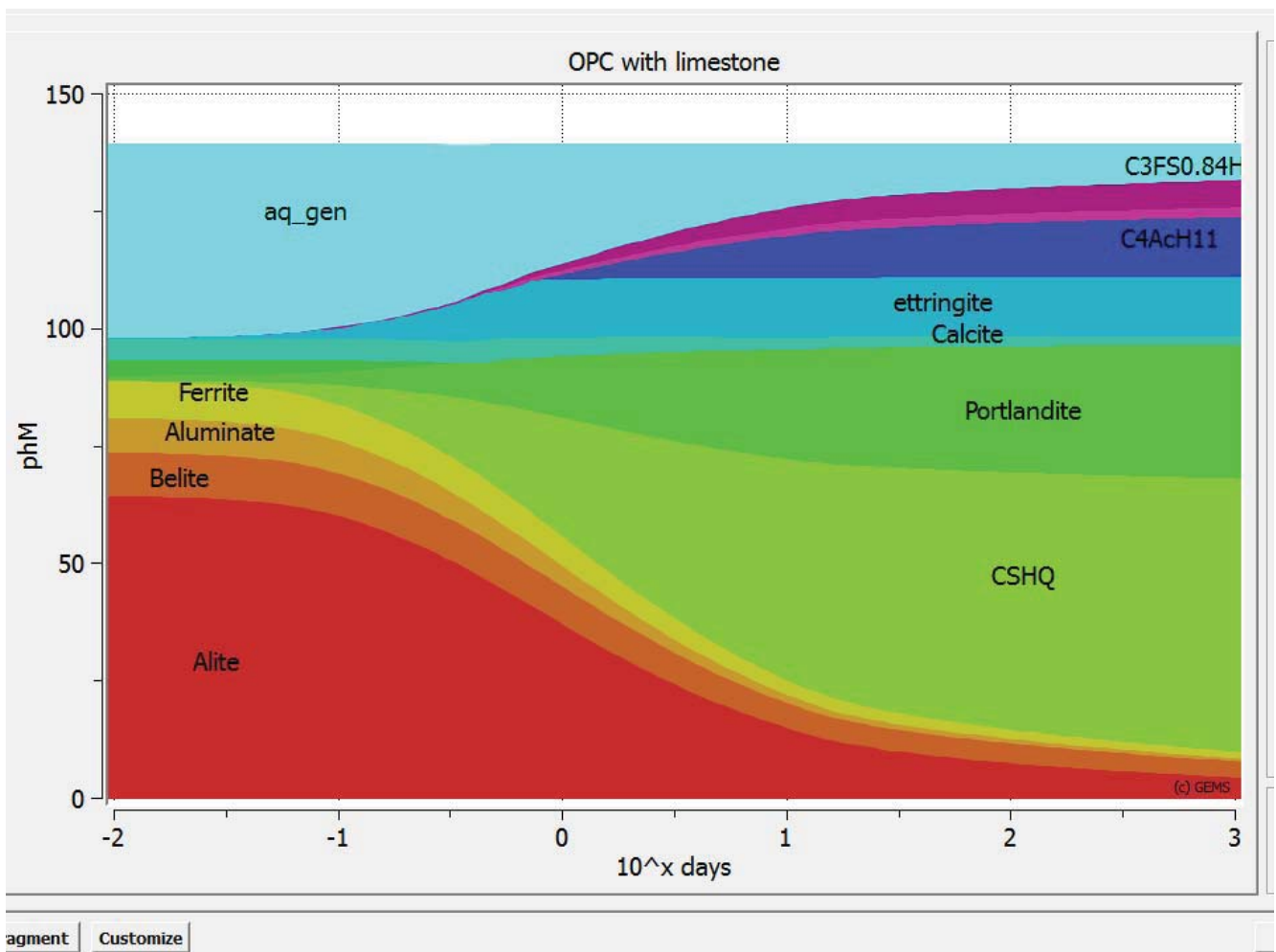
Axis labels

Experimental y-axis (in g/100 g of unhydrated cement)

pX Nam	10 ^x days	Alite	Belite	Aluminate	Ferrite	CSHQ	Portlandite
0	-10.380211	64.64	9.28	7.42	7.81	2e-008	1.00999
1	-3	64.64	9.28	7.42	7.81	2e-008	1.00999
2	-2.9586073	64.64	9.2798144	7.4199947	7.81	2.0718013e-006	1.01007
3	-2.9208187	64.63994	9.2796103	7.4198716	7.8099988	0.0002868405	1.01014
4	-2.8860566	64.639663	9.2793857	7.4196528	7.809994	0.00079178425	1.01030
5	-2.8239087	64.639148	9.2791388	7.4193734	7.8099854	0.0015295741	1.01057
6	-2.79588	64.638401	9.2788672	7.4190377	7.809973	0.0024994355	1.01098
7	-2.7447275	64.637409	9.2785684	7.4186438	7.8099566	0.0037155196	1.01148
8	-2.7212464	64.636147	9.2782399	7.4181878	7.8099358	0.0052018728	1.01207
9	-2.6777807	64.634583	9.2778786	7.4176638	7.8099101	0.006990096	1.01283
10	-2.6197888	64.632678	9.2774812	7.4170651	7.8098788	0.0091759751	1.01370
11	-2.5850266	64.630384	9.2770441	7.4163837	7.8098411	0.011707991	1.01478
12	-2.537602	64.627647	9.2765635	7.4156103	7.8097961	0.014682244	1.01607
13	-2.5086383	64.6244	9.2760349	7.4147346	7.8097429	0.018160641	1.01758
14	-2.455932	64.62057	9.2754537	7.4137448	7.80968	0.022214518	1.01938
15	-2.4202164	64.61607	9.2748145	7.4126276	7.8096062	0.026925862	1.0214
16	-2.3767507	64.610802	9.2741117	7.4113683	7.8095198	0.032388753	1.02388
17	-2.3372422	64.60465	9.2733388	7.40995	7.8094189	0.038711034	1.02671
18	-2.2924298	64.597485	9.272489	7.4083542	7.8093015	0.046016227	1.03000
19	-2.251812	64.589155	9.2715547	7.40656	7.8091649	0.054445755	1.03381
20	-2.2146702	64.579488	9.2705275	7.4045438	7.8090064	0.06416146	1.03822
21	-2.1739252	64.568285	9.2693982	7.4022797	7.8088227	0.075348516	1.04333
22	-2.1307683	64.55532	9.2681567	7.3997383	7.8086102	0.088218728	1.04922
23	-2.091515	64.540333	9.2667919	7.3968869	7.8083644	0.10301433	1.05603
24	-2.0457575	64.523023	9.2652918	7.3936889	7.8080805	0.1200123	1.06387

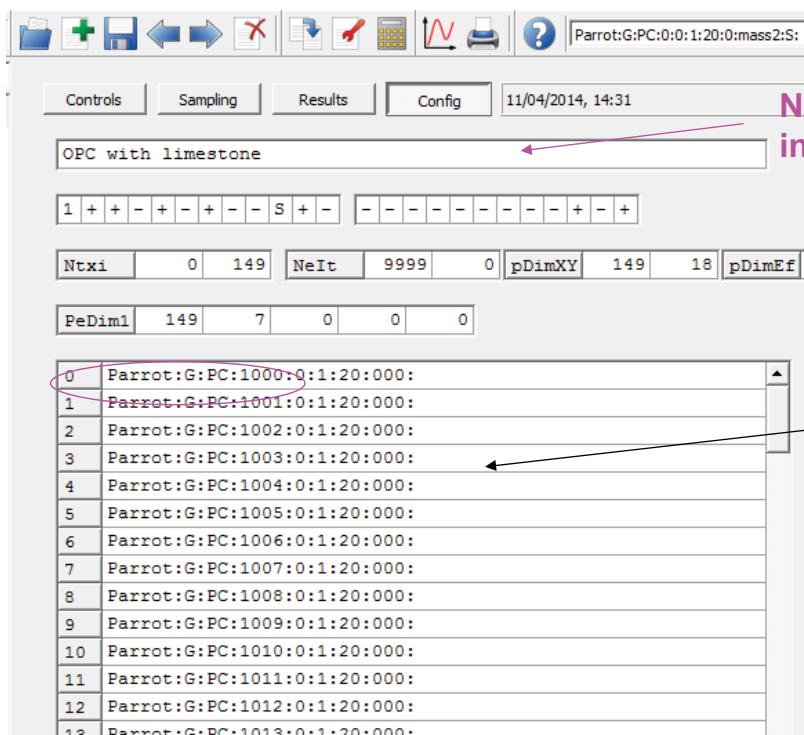
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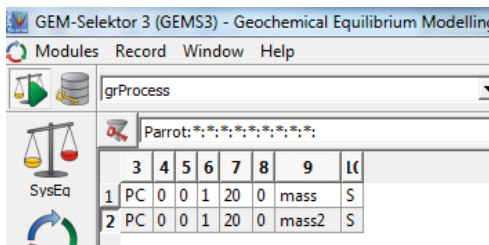
Architecture of GEMS file

■ Process: Config: single system files



Names of the „parent file“
in „Single-System Equilibria“

Names of the „kid files“
produced:
The results of each calculation
can be checked



Remake

Number of experimental points

Number of data categories

Spin boxes below define the dynamic memory configuration of the process simulator.

Dimensions of sampled and experimental data

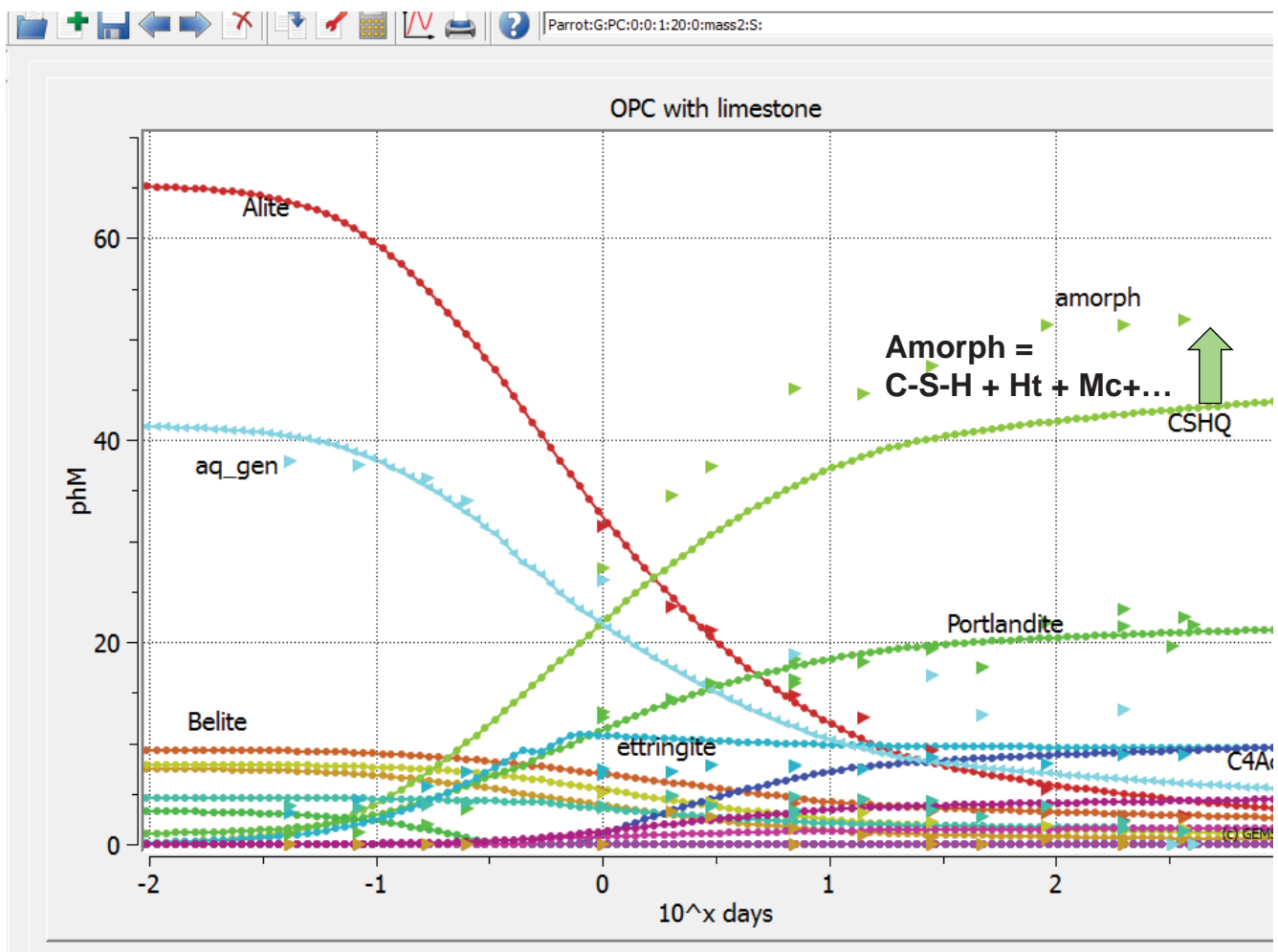
- nPS - Number of steps (1 to 9999) to be performed in this simulation (default: 21); also length of
- Number of 'modC' array columns (1 to 40, 0 - not used) to store process control values; number of
- Number of columns in the 'yp' table (0 to 200) to keep the simulated data sampled by the pgExpr s
be nPS.
- Number of columns in the 'xp' table (0 to 4) to keep the simulated data sampled by the pgExpr scr
nPS.
- Number of rows in the xEp, yEp arrays for experimental data (optional)
- Number of columns in the xEp, yEp arrays for experimental data (optional)

Optional data vectors (of length nPS) can be used for accumulating current process control values for all steps allocated using checkboxes below. The assignment operator (with J index) in the script will override any values vector from the respective process iterator.

Allocation of optional data vectors

- ☐ CSD variant # ('vTm')
- ☐ Volume V, l ('vV')
- ☐ Pressure P, bar
- ☐ Temperature T ('vT')
- ☐ Constraints # ('vNV')
- ☐ Process extent
- ☐ Process extent pXi ('vpXi')
- ☐ Kinetic parameters ('vKin')
- ☐ Time Tau ('vT')

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Sampling of aqueous concentrations

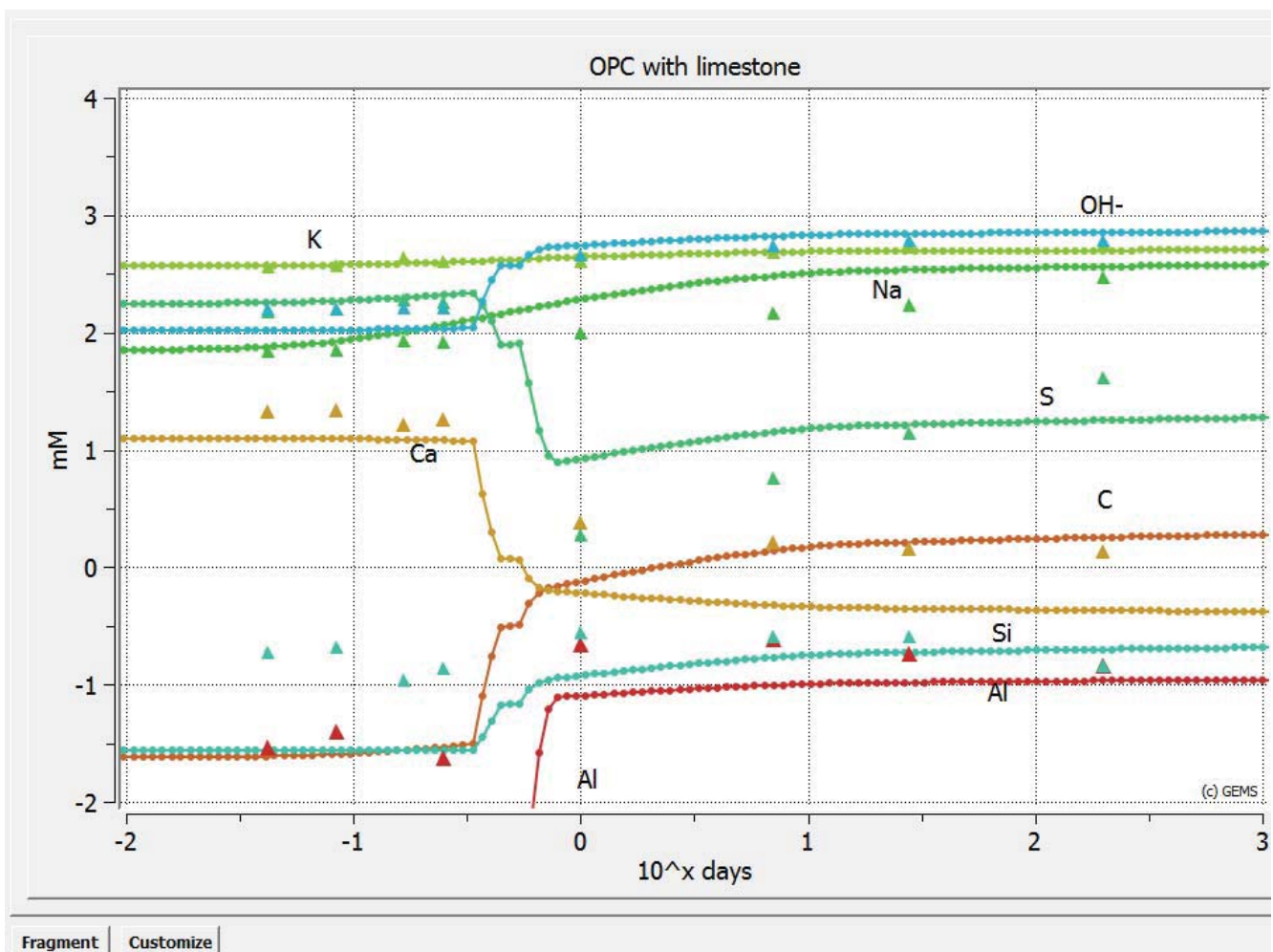
- Controls (= input) identical
- Page sampling and results adapted

Controls	Sampling	Results	Config	11/04/2014, 15:13	
NeIt	9999	149	Next	0	
I	0	J	148	Jp	148
pSTkey Parrot:G:PC:0:0:1:20:0:					
cTm	1148	cNV	0		
cTau	0	cpXi	0	cXi	1
cNu	148				
cpH	0	cpe	0	cEh	0
cT	293.15				

```

$ Abscissa
xp[J] =: lg(modC[J][0]);
$ Ordinates (in mmol/l 1 solution) transformation molal -> molar
yp[J][0] =: lg(m_t[Al]*x[{H2O}]*18.0153/phVol[{aq_gen}]*1000);
yp[J][1] =: lg(m_t[C]*x[{H2O}]*18.0153/phVol[{aq_gen}]*1000);
yp[J][2] =: lg(m_t[Ca]*x[{H2O}]*18.0153/phVol[{aq_gen}]*1000);
yp[J][3] =: lg(m_t[Fe]*x[{H2O}]*18.0153/phVol[{aq_gen}]*1000);
yp[J][4] =: lg(m_t[K]*x[{H2O}]*18.0153/phVol[{aq_gen}]*1000);
yp[J][5] =: lg(m_t[Mg]*x[{H2O}]*18.0153/phVol[{aq_gen}]*1000);
yp[J][6] =: lg(m_t[Na]*x[{H2O}]*18.0153/phVol[{aq_gen}]*1000);
yp[J][7] =: lg(m_t[S]*x[{H2O}]*18.0153/phVol[{aq_gen}]*1000);
yp[J][8] =: lg(m_t[Si]*x[{H2O}]*18.0153/phVol[{aq_gen}]*1000);
yp[J][9] =: lg(my[OH-]*x[{H2O}]*18.0153/phVol[{aq_gen}]*1000);
    
```

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Example

■ Calculate volumes of the hydrating cement

■ Hint:

- Duplicate process «mass»
- Exchange phM by phVol
- use for clinkers: $\text{/mmDC}\{\text{C3S}\} \cdot \text{vol}\{\text{C3S}\}$
 „mmDC[{}]" Mass of component
 „vol[{}]" Volume of component

Controls	Sampling	Results	Config	09/09/2012, 11:02
----------	----------	---------	--------	-------------------

NeIt	9999	149	Next	0	I	0	J	148	Jp	148
------	------	-----	------	---	---	---	---	-----	----	-----

pSTkey PAR_KIL:G:calcite:0:0:1:20:0: cTm 114

cTau	0	cpXi	0	cXi	1	cNu
------	---	------	---	-----	---	-----

cpH	0	cpe	0	cEh	0	cT
-----	---	-----	---	-----	---	----

```

$ Abscissa
xp[J] =: lg(modC[J][0]);

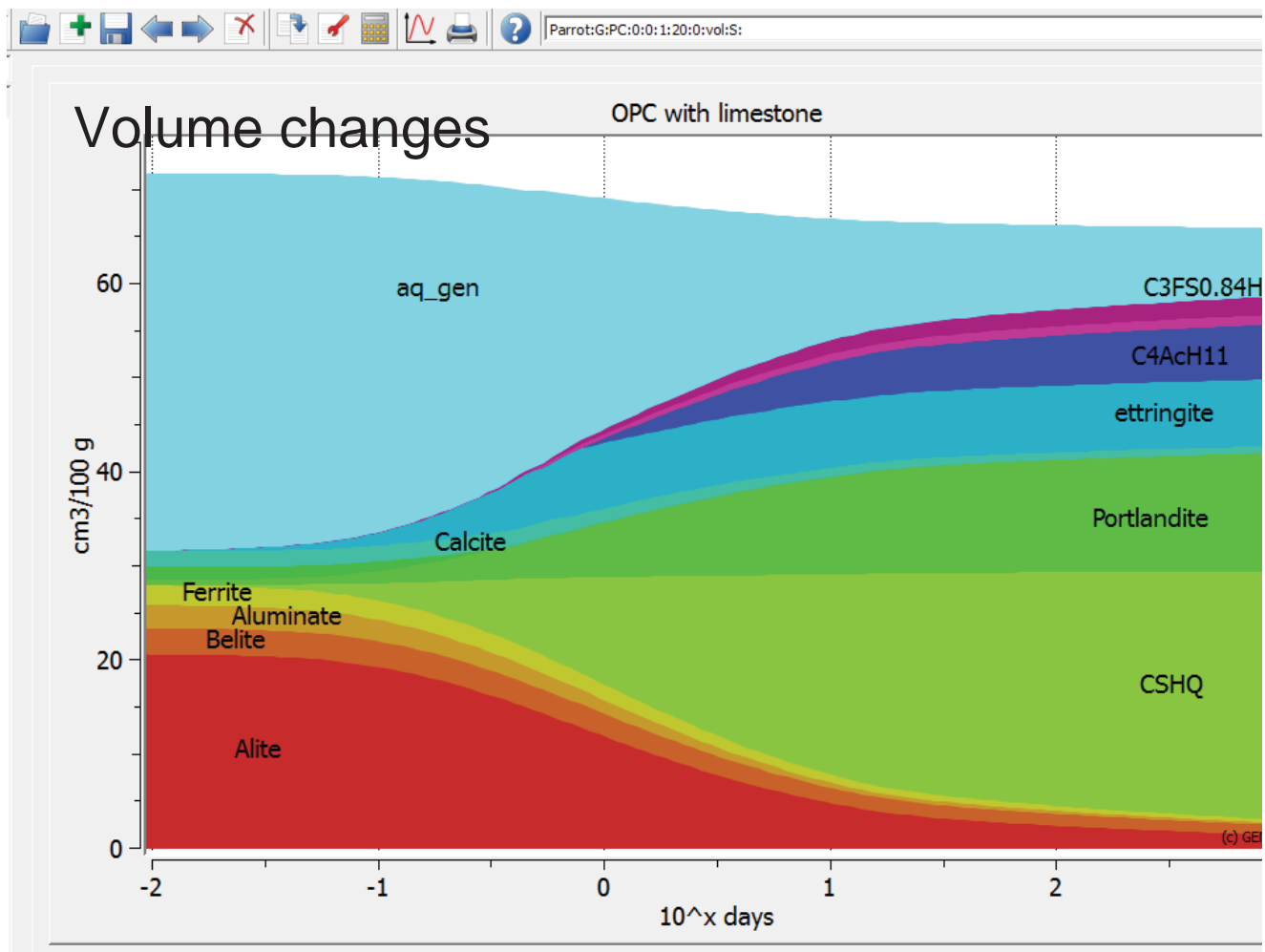
$ Ordinates (in cm3/100 g unhydrated cement)

$clinkers include also minor elements
yp[J][0] =: (modC[2][5]-xd_{C3S})/modC[24][5]/mmDC[{C3S}]*vol[{C3S}];
yp[J][1] =: (modC[3][5]-xd_{C2S-beta})/modC[25][5]/mmDC[{C2S-beta}]*vol[{C2S-beta}];
yp[J][2] =: (modC[4][5]-xd_{C3A})/modC[26][5]/mmDC[{C3A}]*vol[{C3A}];
yp[J][3] =: (modC[5][5]-xd_{C4AF})/modC[24][5]/mmDC[{C4AF}]*vol[{C4AF}];
yp[J][4] =: phVol[{Tob_jen_ss}];
yp[J][5] =: (phVol[{ettringite-Al}]+phVol[{ettringite-Fe}]);
yp[J][6] =: phVol[{Portlandite}];
yp[J][7] =: phVol[{Gypsum}];
yp[J][8] =: phVol[{Calcite}];
yp[J][9] =: (phVol[{monosulphate}]+phVol[{OH_SO4_AFm}]+phVol[{SO4_OH_AFm}]);
yp[J][10] =: phVol[{Brucite}];
yp[J][11] =: phVol[{OH-hydratcalcite}];
yp[J][12] =: phVol[{monocarbonate}];
yp[J][13] =: phVol[{aq_gen}];
$ End
    
```

Expressed as volumes

$\text{/mmDC}\{\text{C3S}\} \cdot \text{vol}\{\text{C3S}\}$
 „mmDC[{}]" Mass of component
 „vol[{}]" Volume of component

$\text{phVol}\{\text{Gypsum}\}$:
 volume (in cm^3) of gypsum



Hydration modelling

■ Further possibilities

- Volume
- Porosity, chemical shrinkage
- Enthalpie \rightarrow calorimetry
(use $h_{TP}(\text{enthalpy}) \cdot x(\text{moles}) = \text{total heat}$)
- ...

■ How can we define input?

- XRF + extended Bogue calculations
- XRD + XRF data for all minor elements

Example: coupling XRD and enthalpy calculations

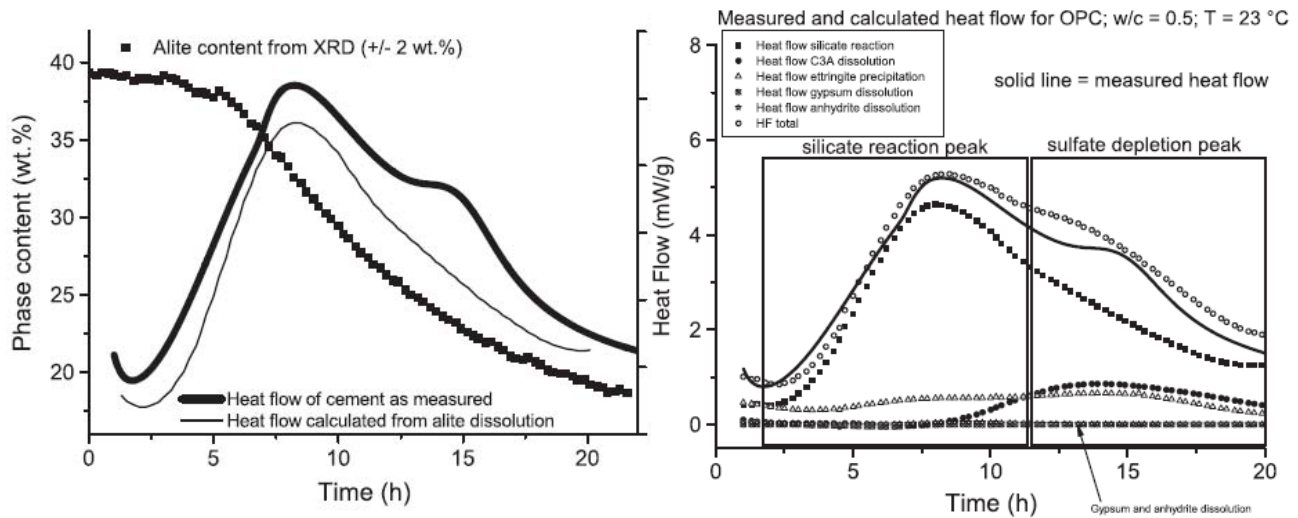


fig. 2. Alite content during cement hydration determined by means of X-ray diffraction, heat flow calculated from X-ray results and heat flow of the cement measured with a heat flow calorimeter (XRD results from ref. [31]).

fig. 4. Comparison between calculated heat flow and measured heat flow.

Janssen et al. 2012, CCR 42

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