GEMS workshop 2014

5) Hydration modelling

a) Model of Parrot & Killoh

b) Hydration modelling with GEMS

Hydration

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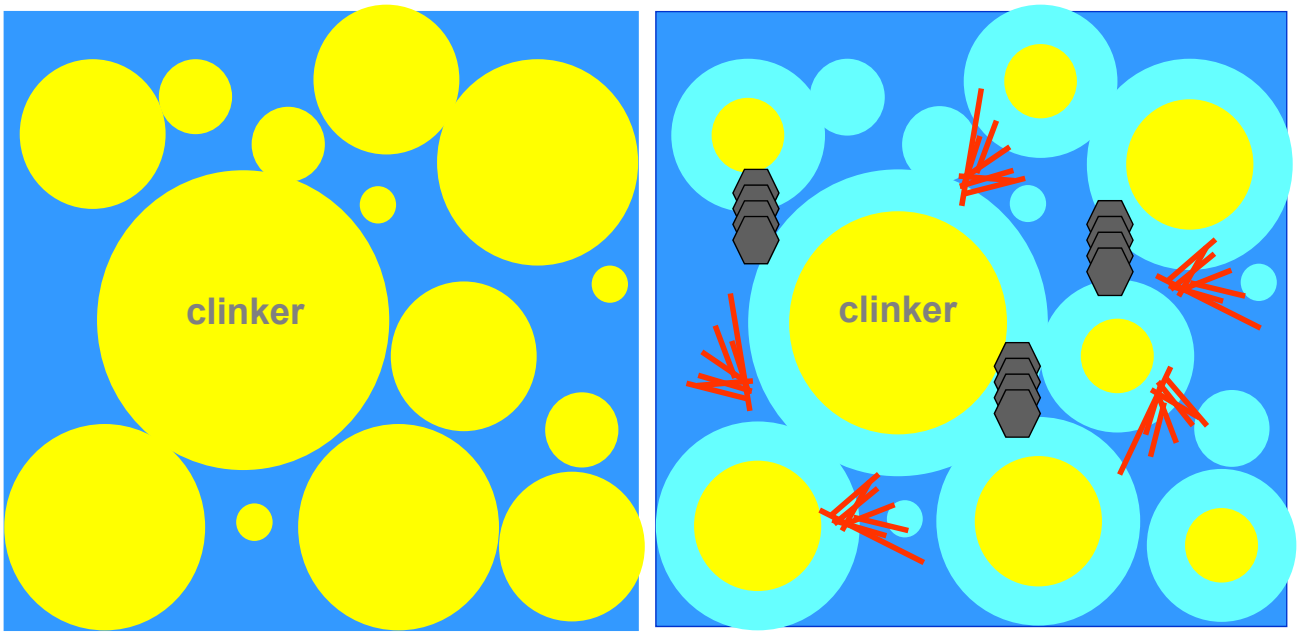

Modeling: Dissolution

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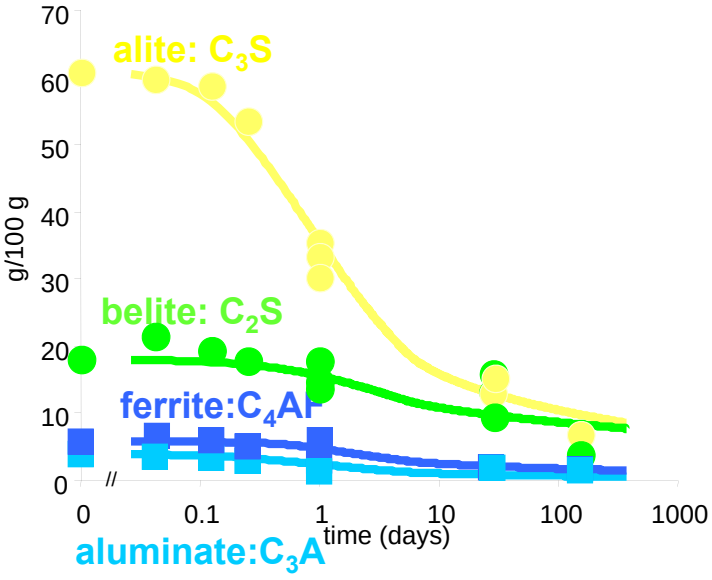
Empirical Approach: Parrot and Killoh (1984)

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

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

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

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



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

Modeling: Dissolution

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Empirical Approach: Parrot and Killoh (1984)

nucleation

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

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

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

degree of hydration

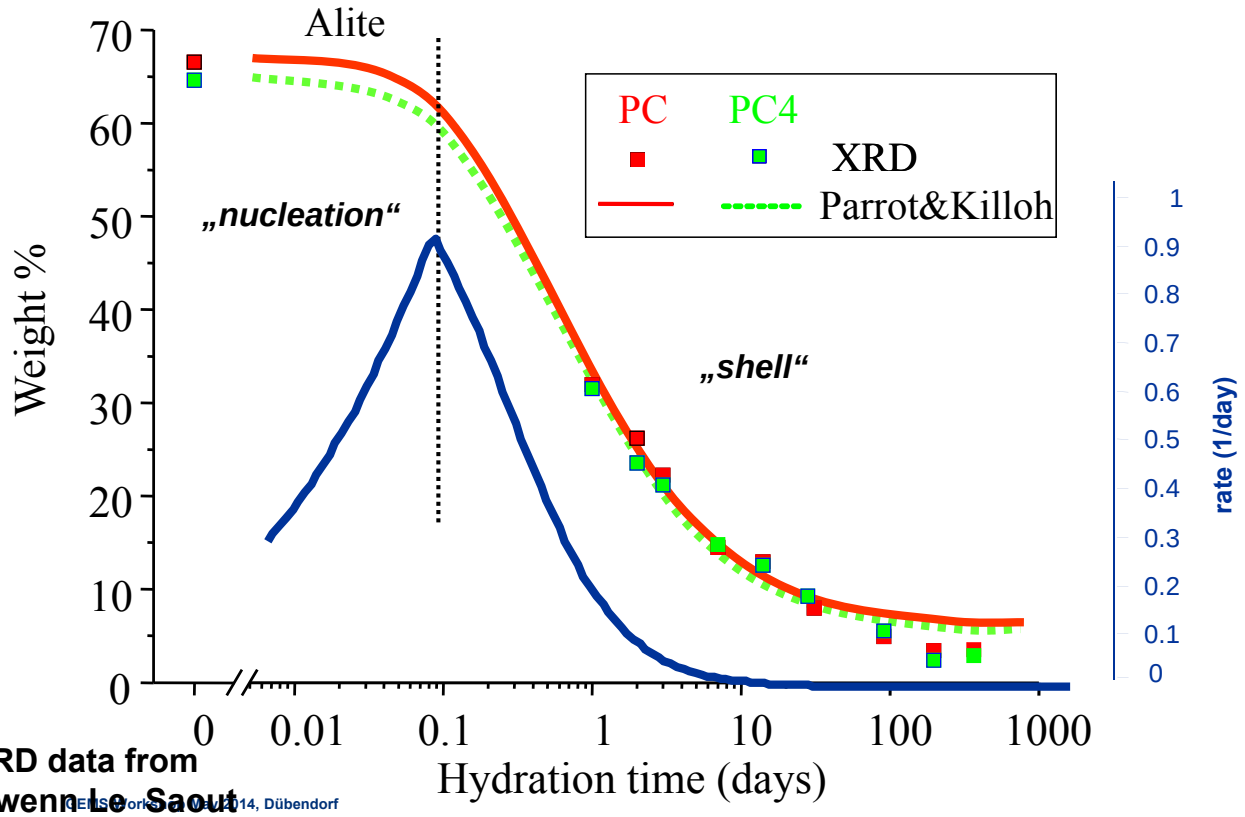
$$\alpha_t = \alpha_{t-1} + \Delta t \cdot R_{t-1} \cdot (1+3.333 \cdot (H \cdot {}^{w}/_{c} - \alpha_t))^4$$

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

Modeling: Dissolution



XRD data from Gwenn Le Saout

Modeling: Dissolution

Empirical Approach: Parrot and Killoh adapted

Lothenbach et al. (2008) 38, 848-860

nucleation

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

diffusion

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

shell

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

degree of hydration

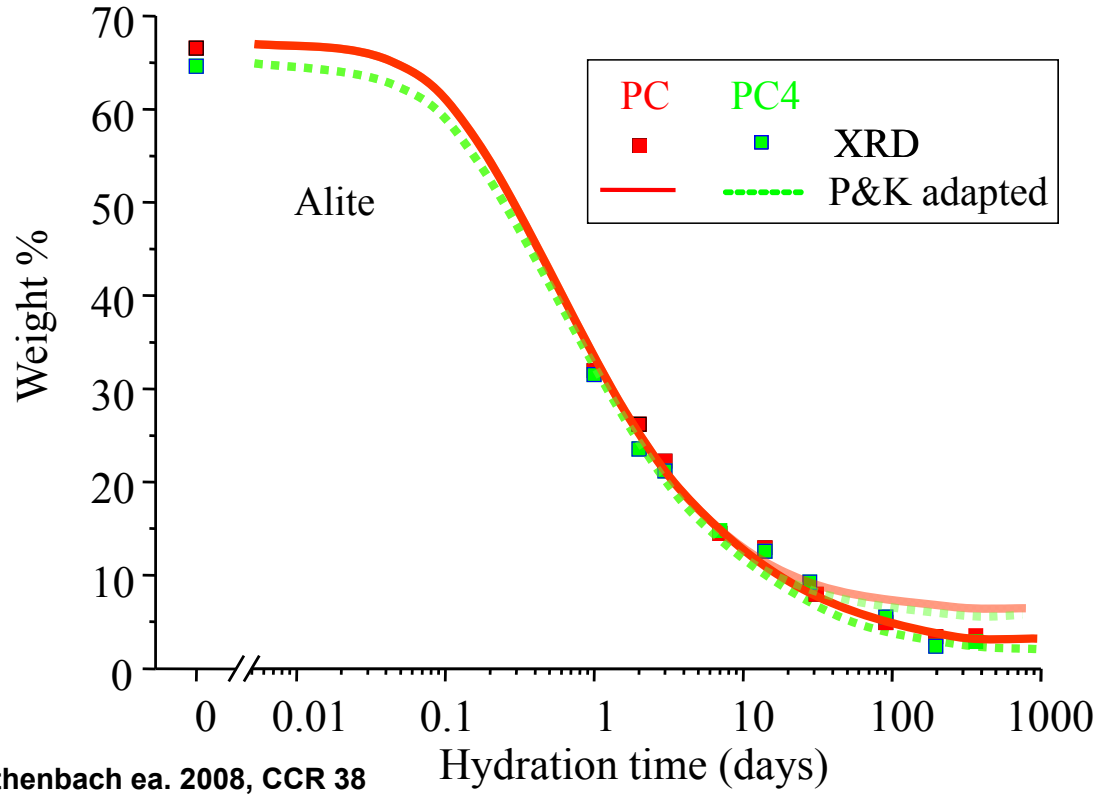
$$\alpha_t = \alpha_{t-1} + \Delta t \cdot R_{t-1} \cdot (1+3.333 \cdot (H \cdot {}^{w}/_{c} - \alpha_t))^4$$

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**

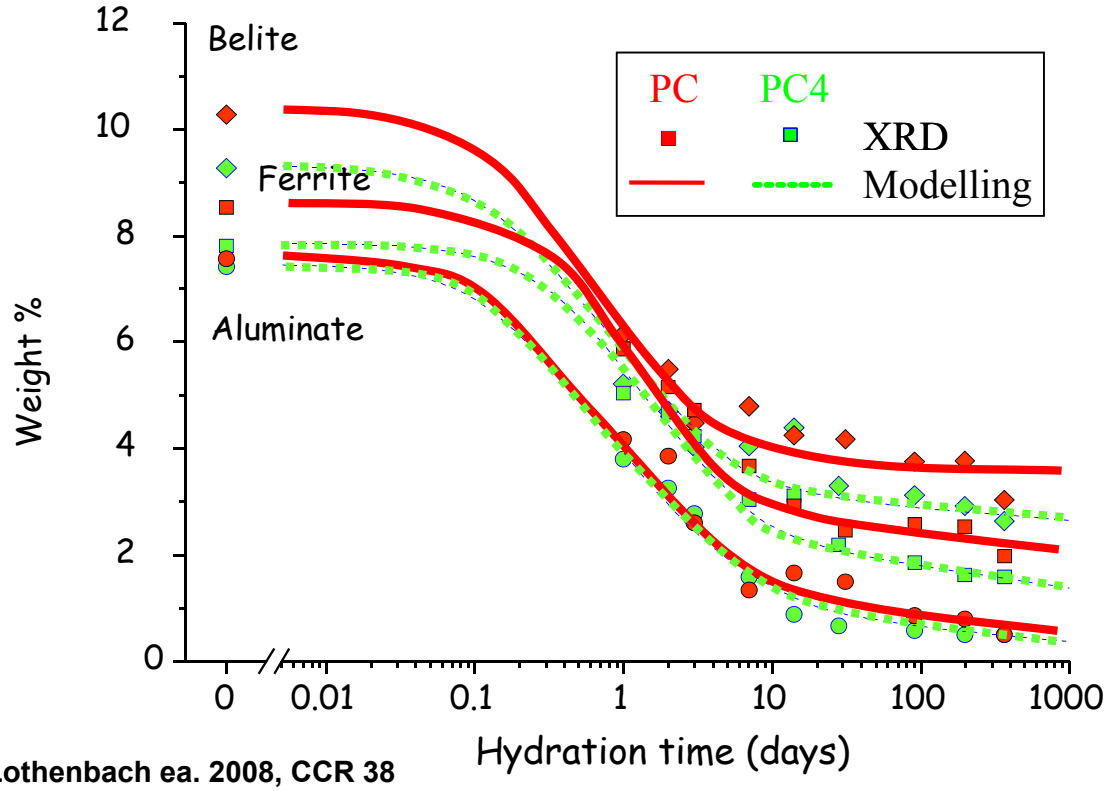
Cement specific input: surface area, w/c

Modeling: Dissolution



Lothenbach ea. 2008, CCR 38

Modeling: Dissolution



Lothenbach ea. 2008, CCR 38

Thermodyn. calculations

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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

Portlandite

C-S-H

Ettringite

AFm

Hydrotalcites, ...

Output data, Portlandite

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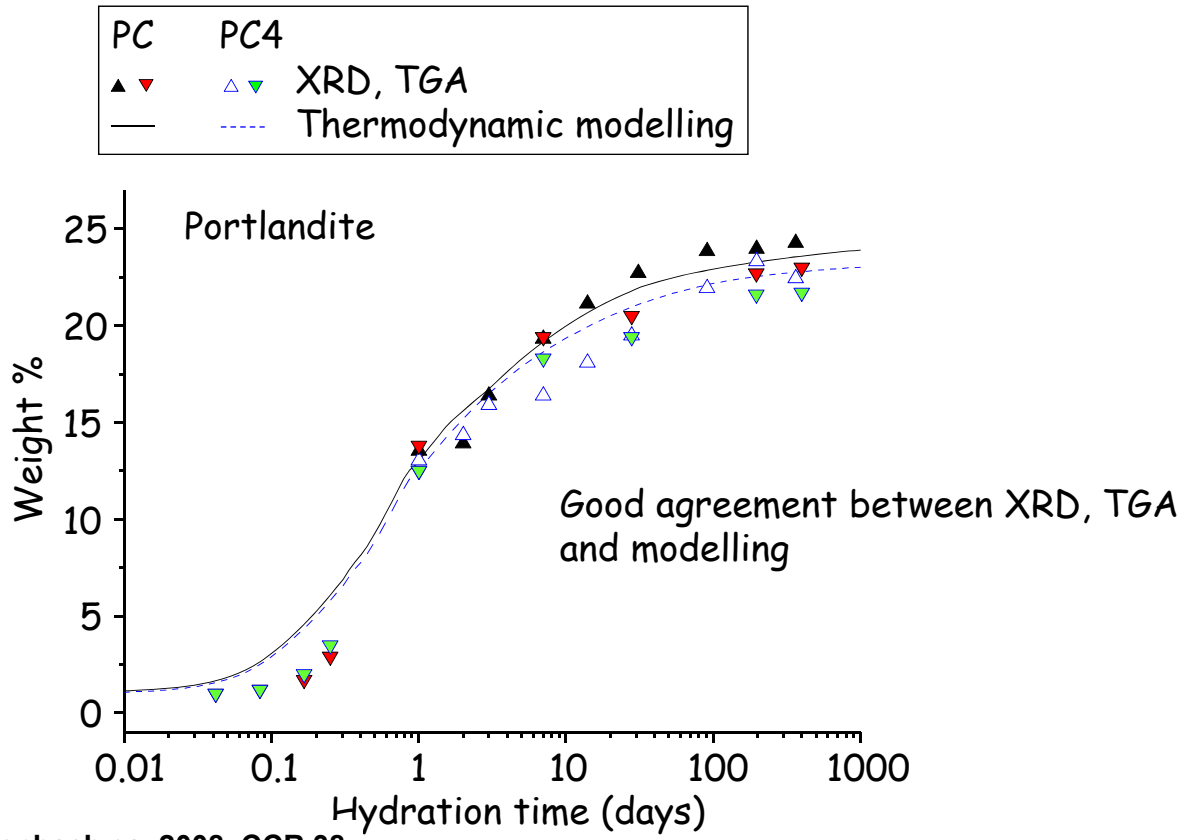
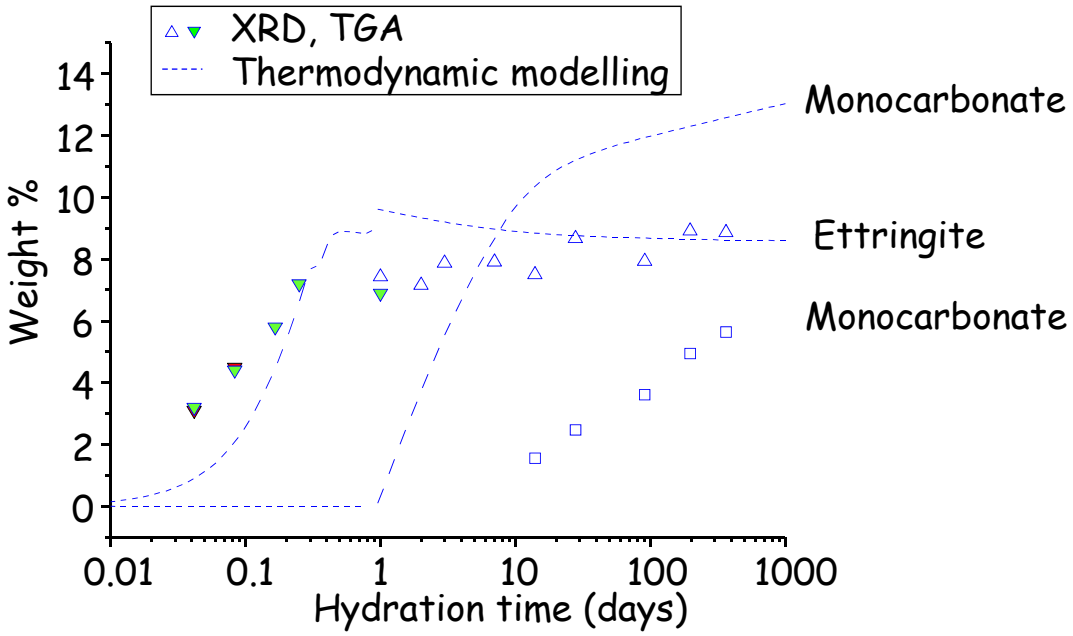


Lothenbach ea. 2008, CCR 38

Output data, AFt, AFm phases



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

Lothenbach ea. 2008, CCR 38

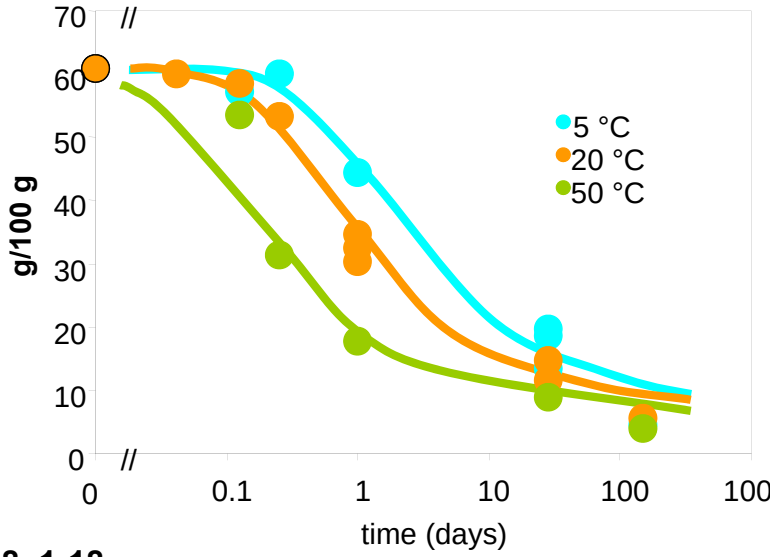
Modeling: Temperature

Arrhenius equation

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

E_a: literature

alite dissolution



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

Ca- and Si-hydrates: 5 °C

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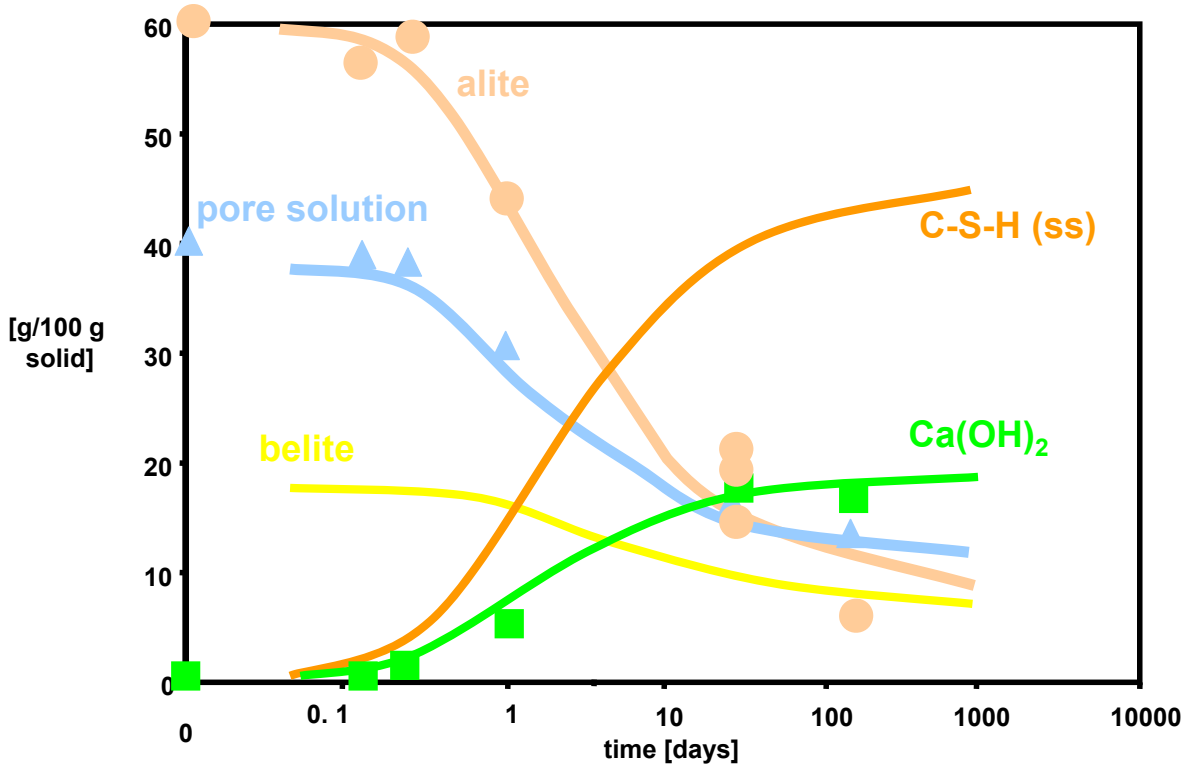

Ca- and Si-hydrates: 50 °C

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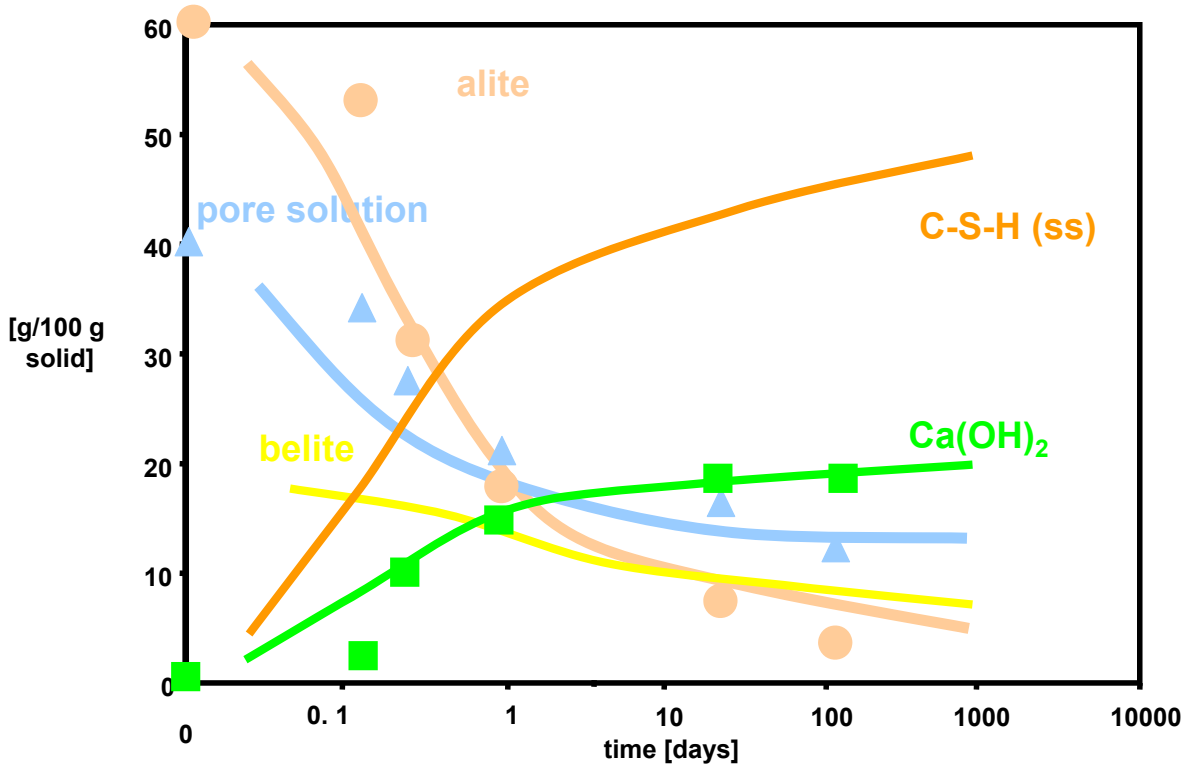

Al-, SO_4-, CO_3: 5 °C

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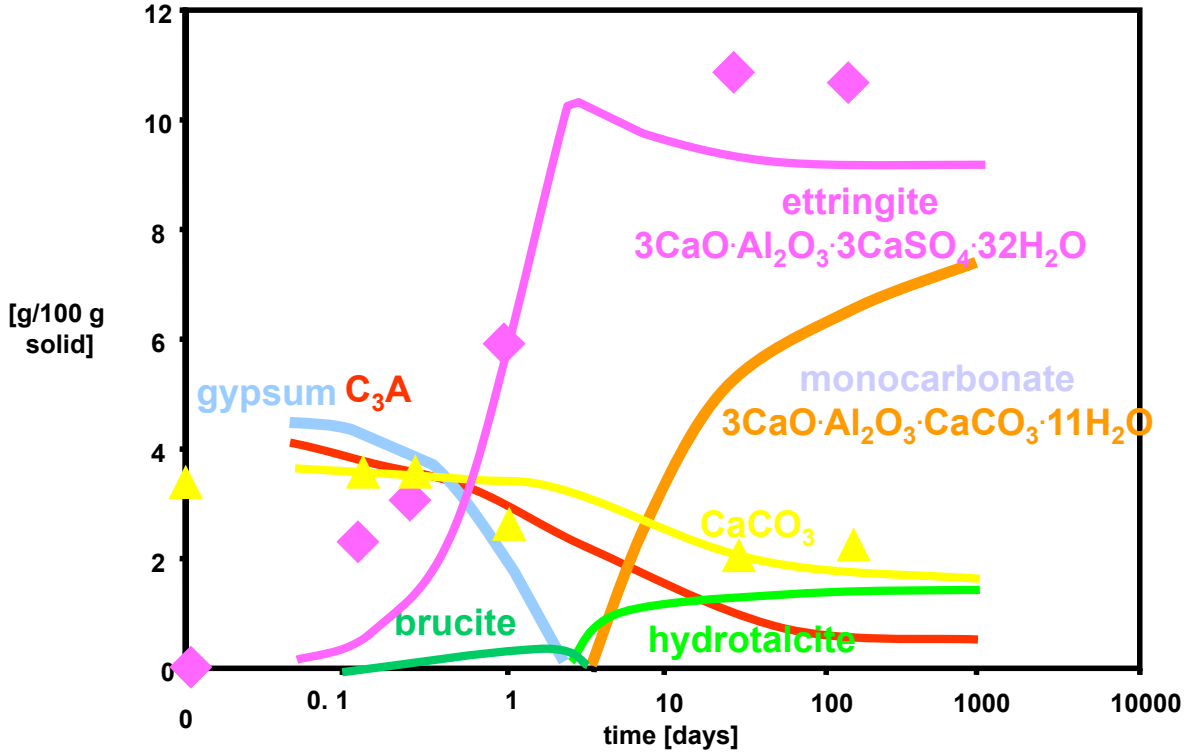

Al-, SO_4-, CO_3: 50 °C

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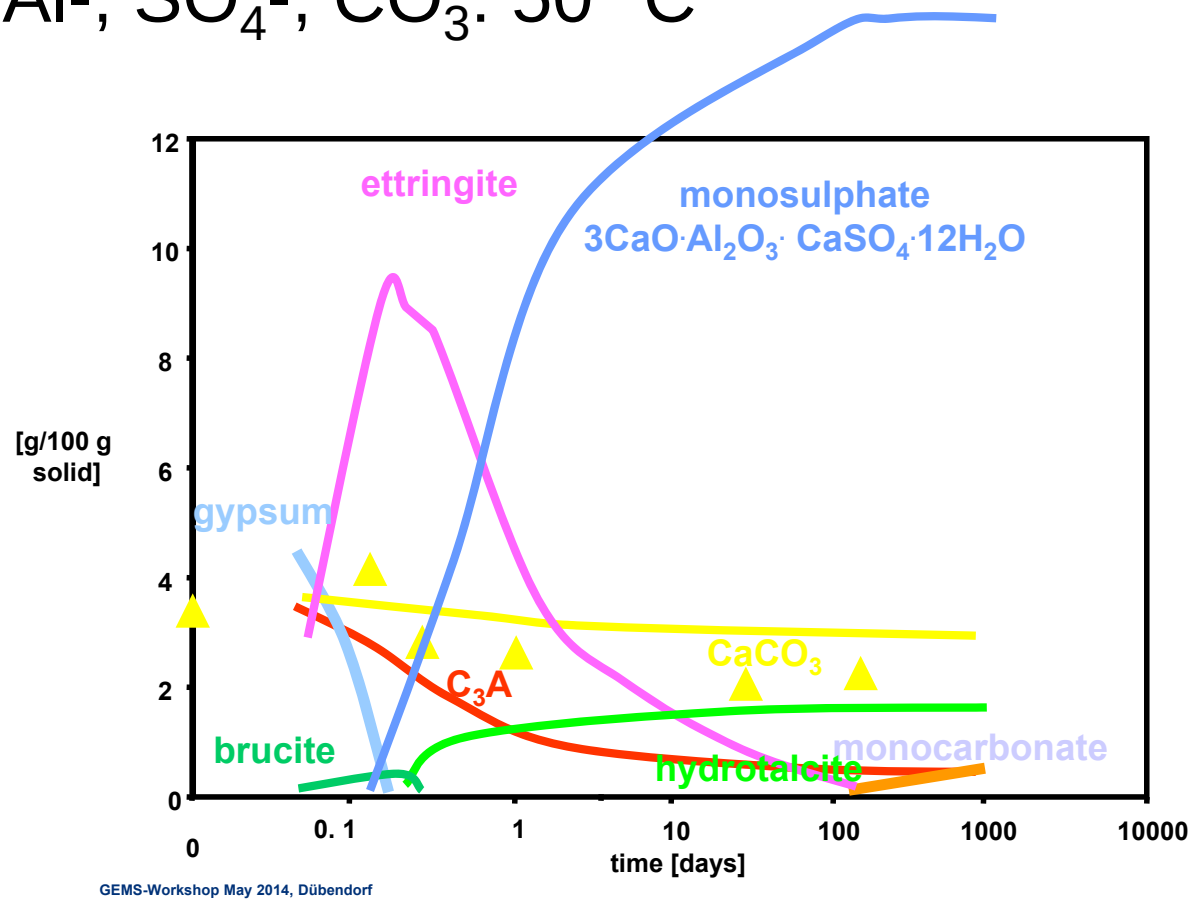
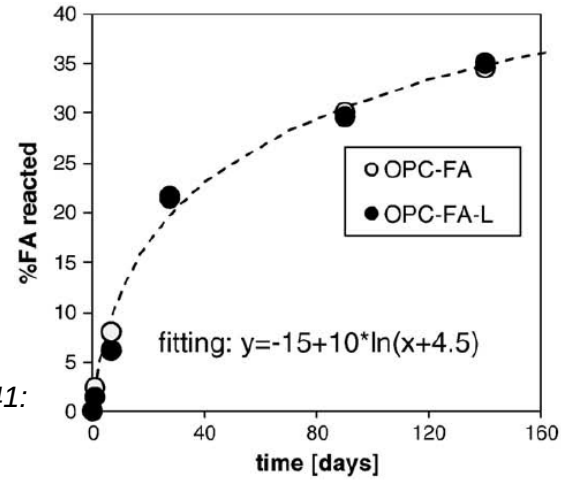


Conclusion

- 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 Weerdt ea (2011) CCR 41: Reaction degree of fly ash

Modeling: Dissolution

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

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

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

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

Cement specific input: surface area [m^2/kg], w/c, composition

Modeling: Dissolution

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

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

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

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** = *critical degree of hydration*

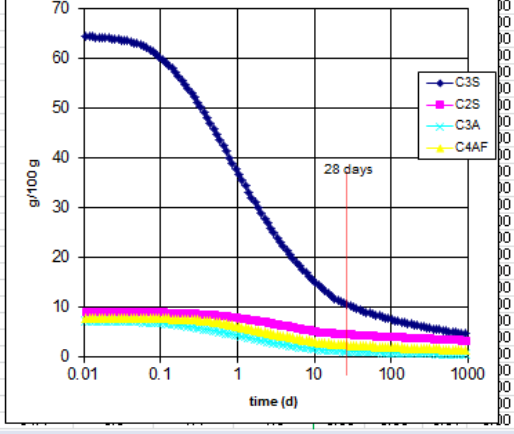
$$\alpha_t = \alpha_{t-1} + \Delta t \cdot R_{t-1} \cdot (1+3.333 \cdot (H \cdot w/c - \alpha_t))^4$$

Hydration is reduced with time at low w/c

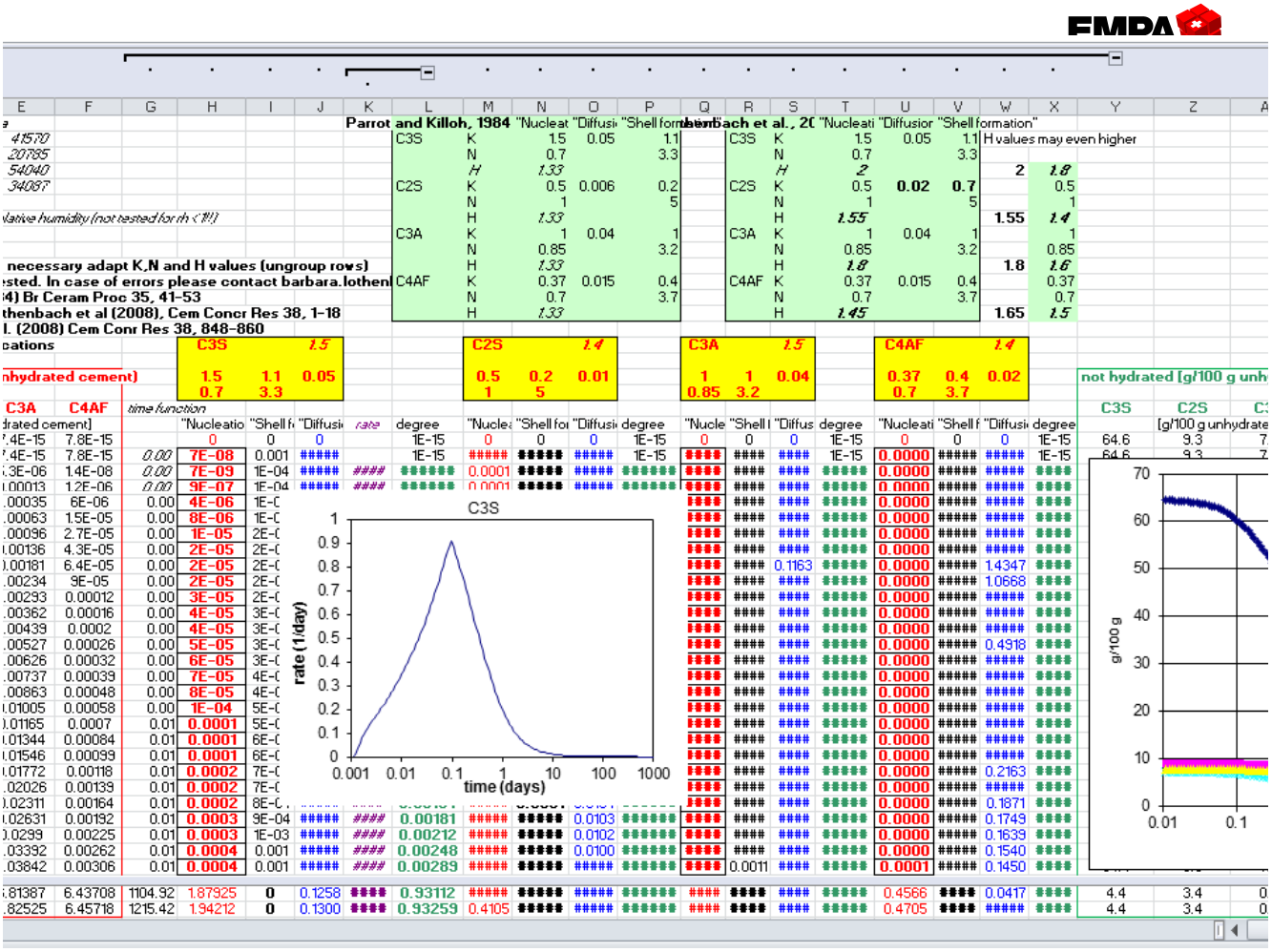
Cement specific input: surface area [m²/kg], w/c, composition

Parrot and Killoh model as Excel file

	A	B	C	D	E	F	Y	Z	AA	AB	AC	AD	AE	AF	AG	AH
1	**Modell Parrot and Killoh version 2014**				*Ea*											
2	surface area	**413**	C3S	**64.6**	*41570*											
3	Reference are	*385*	C2S	**9.3**	*20785*											
4	w/z	**0.5**	C3A	**7.4**	*54040*											
5	*Temperature*	**20**	C4AF	**7.8**	*34087*											
6		*293.15*														
7	reference tem	*293.15*	r.h.	**1.0**	*relative humidity (not tested for rh < 1!!)*											
8	*R*	*8.314*														
9	**Notes**															
10	**Enter your values in the "yellow" boxes; if necessary adapt K,N and H values (ungroup rows)**															
11	**This calculation tool is not throughfully tested. In case of errors please contact barbara.lothenbach@empa.ch**															
12	**Original Model from Parrot and Killoh (1984) Br Ceram Proc 35, 41-53**															
13	**Ea and temperature dependence from Lothenbach et al (2008), Cem Concr Res 38, 1-18**															
14	**Adapted K,N and H from Lothenbach et al. (2008) Cem Conr Res 38, 848-860**															
15	**If you use this model cite the above publications**															
16																
17			**hydrated [g/100g unhydrated cemer**				**not hydrated [g/100 g unhydrated cement**				**% hydrated (for each clinke**				**Total degree of hydration**	
18																
19		*time (days)*	**C3S**	**C2S**	**C3A**	**C4AF**	**C3S**	**C2S**	**C3A**	**C4AF**	**C3S**	**C2S**	**C3A**	**C4AF**		
20	time (hours)		[g/100g unhydrated cement]				[g/100 g unhydrated cement]				[% per clinker]				rel. to total clinker content	
21	**0.00**	*4.2E-11*	6E-14	9.3E-15	7.4E-15	7.8E-15	64.6	9.3	7.4	7.8	0.00	0.00	0.00	0.00	**0.00**	
22	**0.02**	*0.0010*	6E-14	9.3E-15	7.4E-15	7.8E-15	64.6	9.3	7.4	7.8	0.00	0.00	0.00	0.00	**0.00**	
23	**0.03**	*0.0011*	5E-07	0.00019	5.3E-06	1.4E-08									**0.00**	
24	**0.03**	*0.0012*	6E-05	0.00039	0.00013	1.2E-06									**0.00**	
25	**0.03**	*0.0013*	0.0003	0.00061	0.00035	6E-06									**0.00**	
26	**0.04**	*0.0015*	0.0009	0.00086	0.00063	1.5E-05									**0.00**	
27	**0.04**	*0.0016*	0.0016	0.00113	0.00096	2.7E-05									**0.00**	
28	**0.04**	*0.0018*	0.0026	0.00143	0.00136	4.3E-05									**0.00**	
29	**0.05**	*0.0019*	0.0039	0.00176	0.00181	6.4E-05									**0.00**	
30	**0.05**	*0.0021*	0.0054	0.00212	0.00234	9E-05									**0.00**	
31	**0.06**	*0.0024*	0.0073	0.00252	0.00293	0.00012									**0.00**	
32	**0.06**	*0.0026*	0.0096	0.00296	0.00362	0.00016									**0.00**	
33	**0.07**	*0.0029*	0.0124	0.00344	0.00439	0.0002									**0.00**	
34	**0.08**	*0.0031*	0.0156	0.00397	0.00527	0.00026									**0.00**	
35	**0.08**	*0.0035*	0.0194	0.00455	0.00626	0.00032									**0.00**	
36	**0.09**	*0.0038*	0.0239	0.00519	0.00737	0.00039									**0.00**	
37	**0.10**	*0.0042*	0.0292	0.00589	0.00863	0.00048									**0.00**	
38	**0.11**	*0.0046*	0.0353	0.00666	0.01005	0.00058									**0.00**	
39	**0.12**	*0.0051*	0.0425	0.00751	0.01165	0.0007									**0.00**	
40	**0.13**	*0.0056*	0.0508	0.00845	0.01344	0.00084									**0.00**	
41	**0.15**	*0.0061*	0.0605	0.00947	0.01546	0.00099									**0.00**	
42	**0.16**	*0.0067*	0.0717	0.0106	0.01772	0.00118									**0.00**	
43	**0.18**	*0.0074*	0.0847	0.01184	0.02026	0.00139									**0.00**	
44	**0.20**	*0.0081*	0.0997	0.01321	0.02311	0.00164									**0.00**	
45	**0.21**	*0.0090*	0.117	0.01471	0.02631	0.00192									**0.00**	
46	**0.24**	*0.0098*	0.1369	0.01636	0.0299	0.00225									**0.00**	
47	**0.26**	*0.0108*	0.16	0.01817	0.03392	0.00262									**0.00**	
48	**0.29**	*0.0119*	0.1865	0.02016	0.03842	0.00306									**0.00**	
168	**26518**	*1105*	60.151	5.83215	6.81387	6.43708	4.4	3.4	0.6	1.4	0.93	0.63	0.92	0.82	**0.89**	
169	**29170**	*1215*	60.246	5.85321	6.82525	6.45718	4.4	3.4	0.6	1.4	0.93	0.63	0.92	0.83	**0.89**	



Parrot



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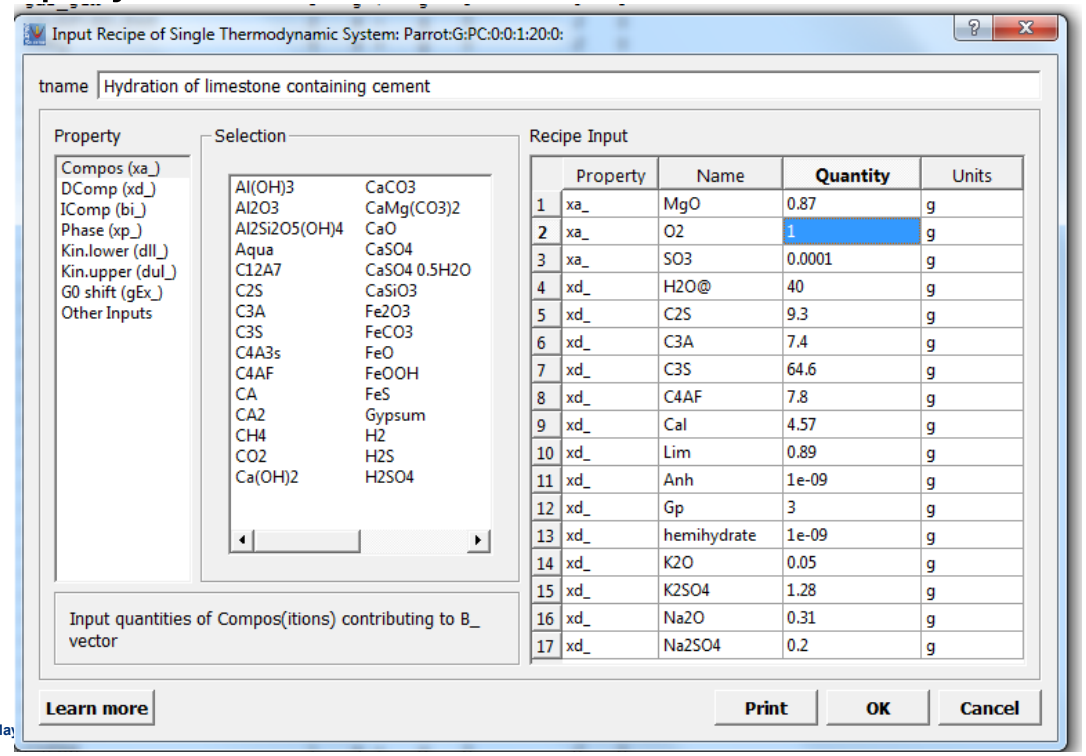
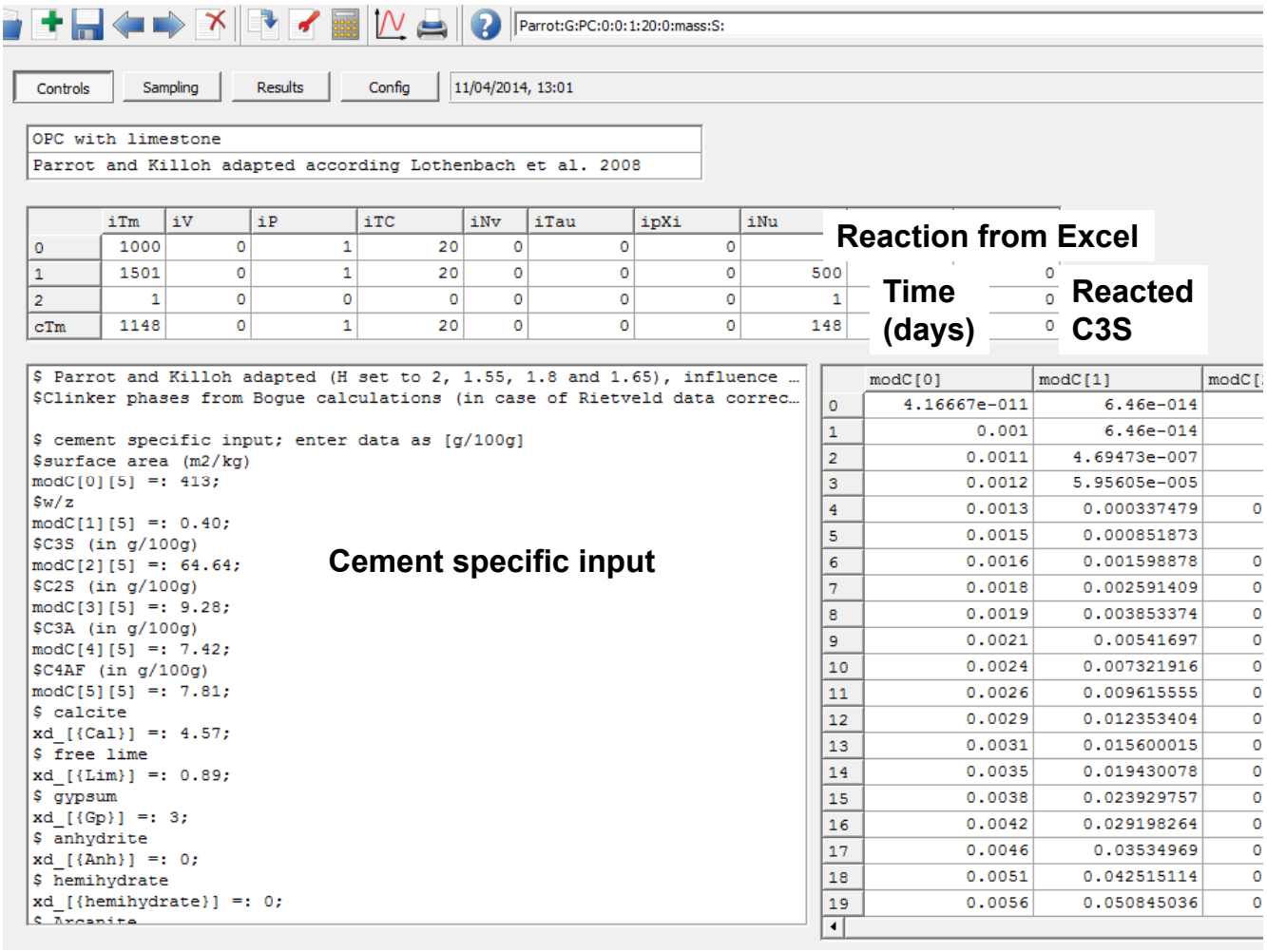
Hydration modelling EXCEL + GEMS

1. Open project Parrot





	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

	modC[0]	modC[1]	modC[
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

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Architecture of GEMS file

- Input always in g/100g
- The amount of clinker reacted copied from EXCEL file
- Inputs needed in GEMS:
  - surface area [m^2/kg]
  - w/c
  - C_3S, C_2S, C_3A, C_4AF (pure phases)
  - Calcite, free lime, gypsum, anhydrite, hemihydrate, periclase, Na_2SO_4 and K_2SO_4 (-> soluble alkalis)
  - Na_2O, K_2O, MgO and SO_3 in clinker (as g/g clinker) optional

Architecture of GEMS file

- Process: controls below input
  - Ea (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 ~ 0.42 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:

$[(NaOH)_{2.5}\ SiO_2H_2O]_{0.2}$
$[(KOH)_{2.5}\ SiO_2H_2O]_{0.2}$

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

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 inlcude 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[{CSH0}]-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)
```

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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!

/(1+modC[1][5]-phM[{aq_gen}]/100)
=1+0.4-mass H_2O unreacted/100
= mass hydrated cement
(after removal of pore water)

For comparison with XRD/TGA

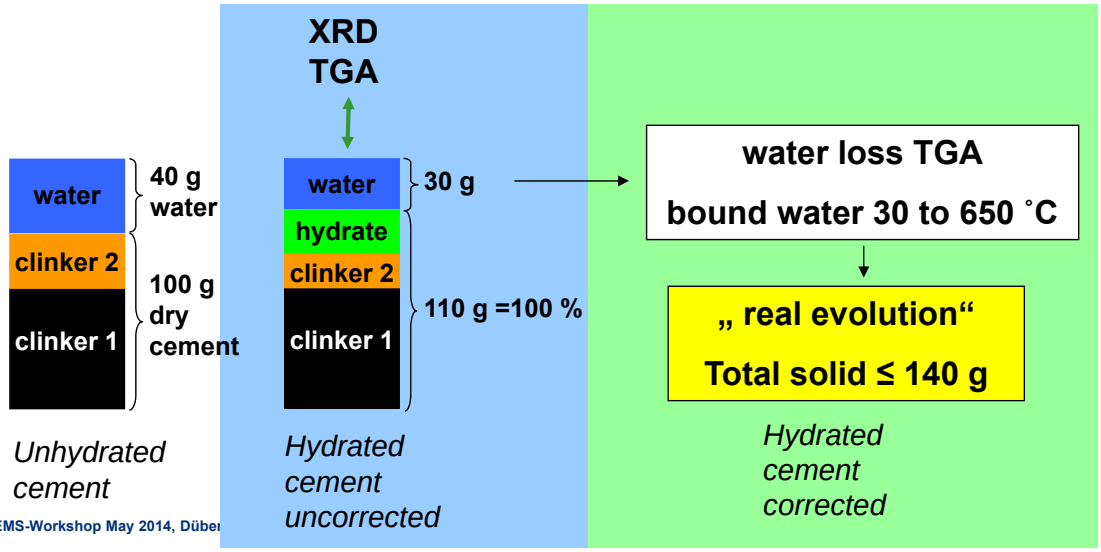
Different outputs possible

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

  phM[{Portlandite}]/(1+modC[1][5]-phM[{aq_gen}]/100)
  correction of the output /(1+0.4-mass H_2O unreacted/100)
  => / mass hydrated cement (after removal of pore water)

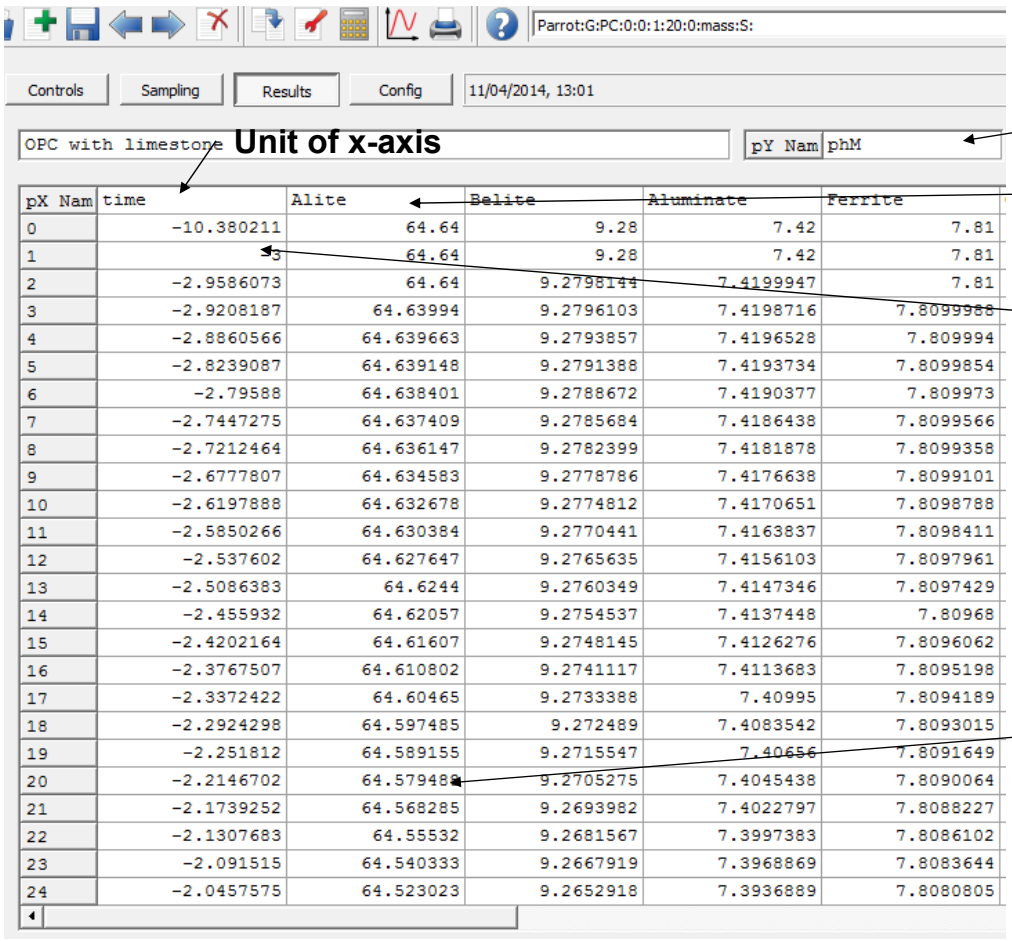
- Y-axis Mass in g/100 g of original cement

  phM[{Portlandite}] => correct measurements to 100 dry weight



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

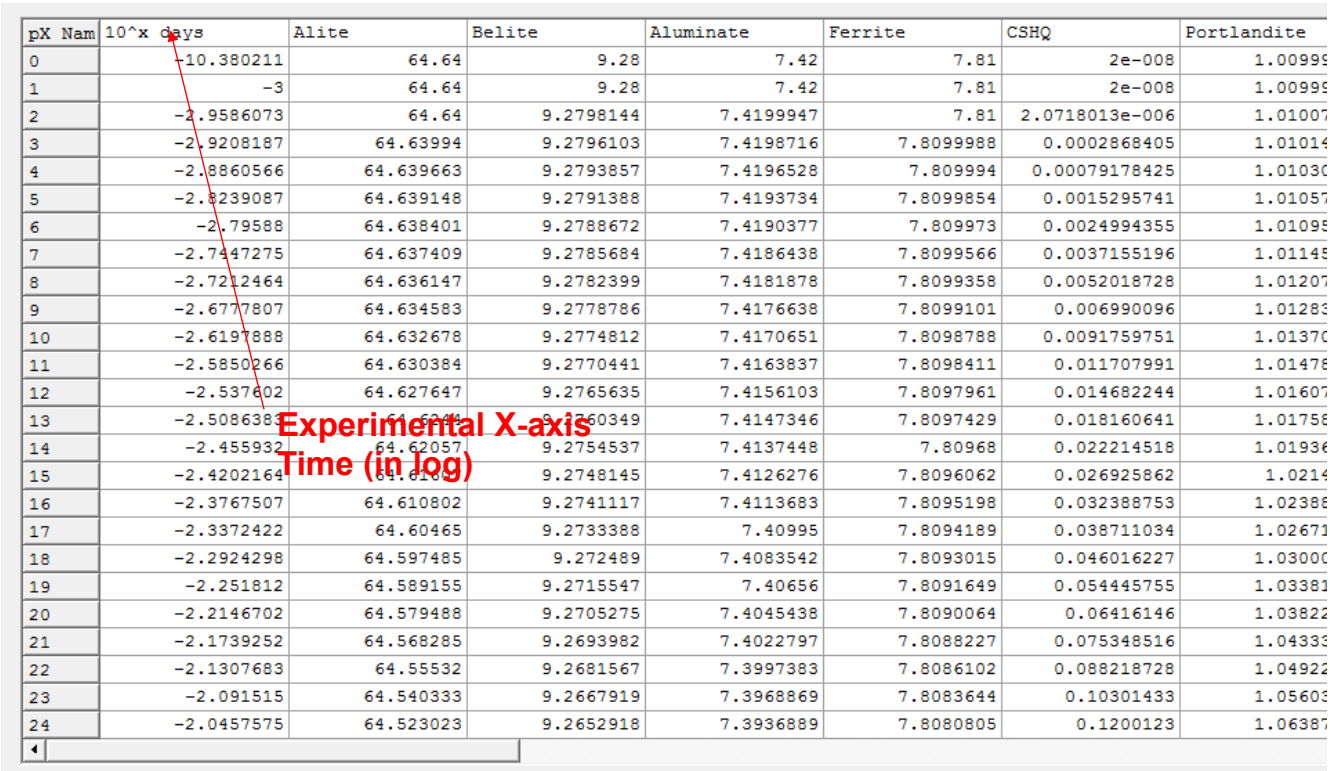


pX Nam	time	Alite	Belite	Aluminate	Ferrite
0	-10.380211	64.64	9.28	7.42	7.81
1	-3	64.64	9.28	7.42	7.81
2	-2.9586073	64.64	9.2798144	7.4199947	7.81
3	-2.9208187	64.63994	9.2796103	7.4198716	7.8099988
4	-2.8860566	64.639663	9.2793857	7.4196528	7.809994
5	-2.8239087	64.639148	9.2791388	7.4193734	7.8099854
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

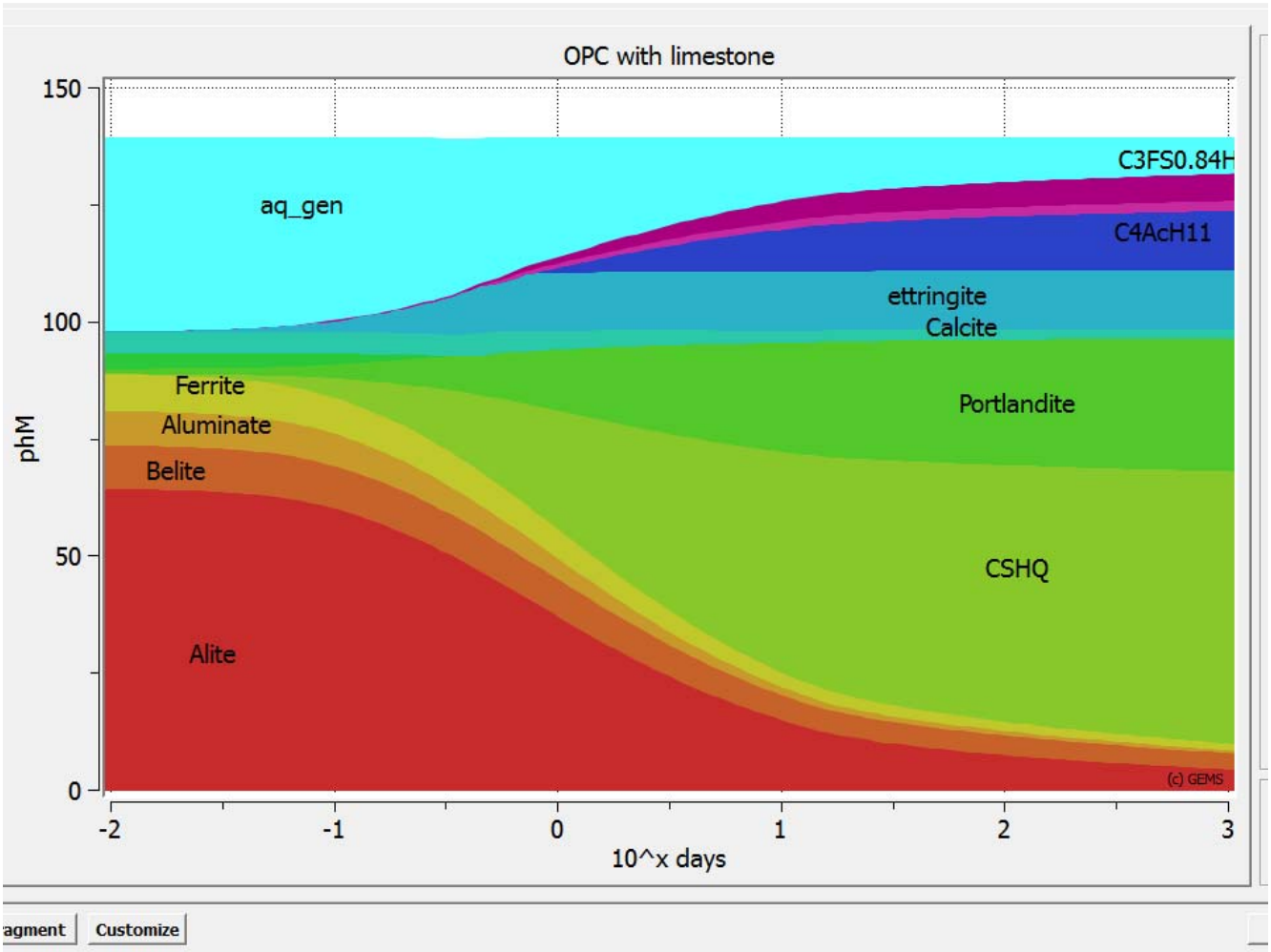
Possibility to plot experimental data

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	1.01095
7	-2.7447275	64.637409	9.2785684	7.4186438	7.8099566	0.0037155196	1.01145
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	1.01936
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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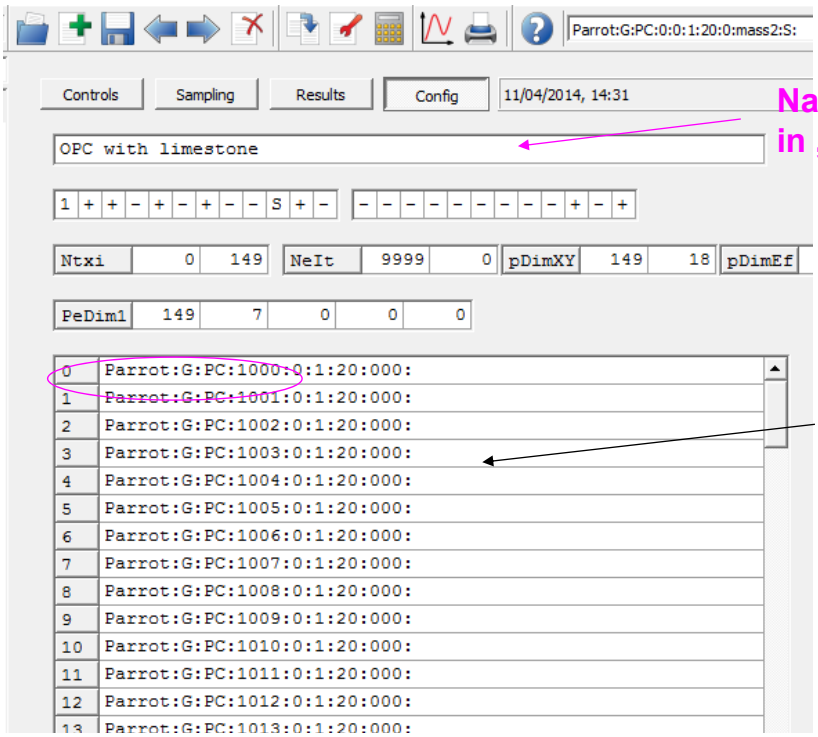
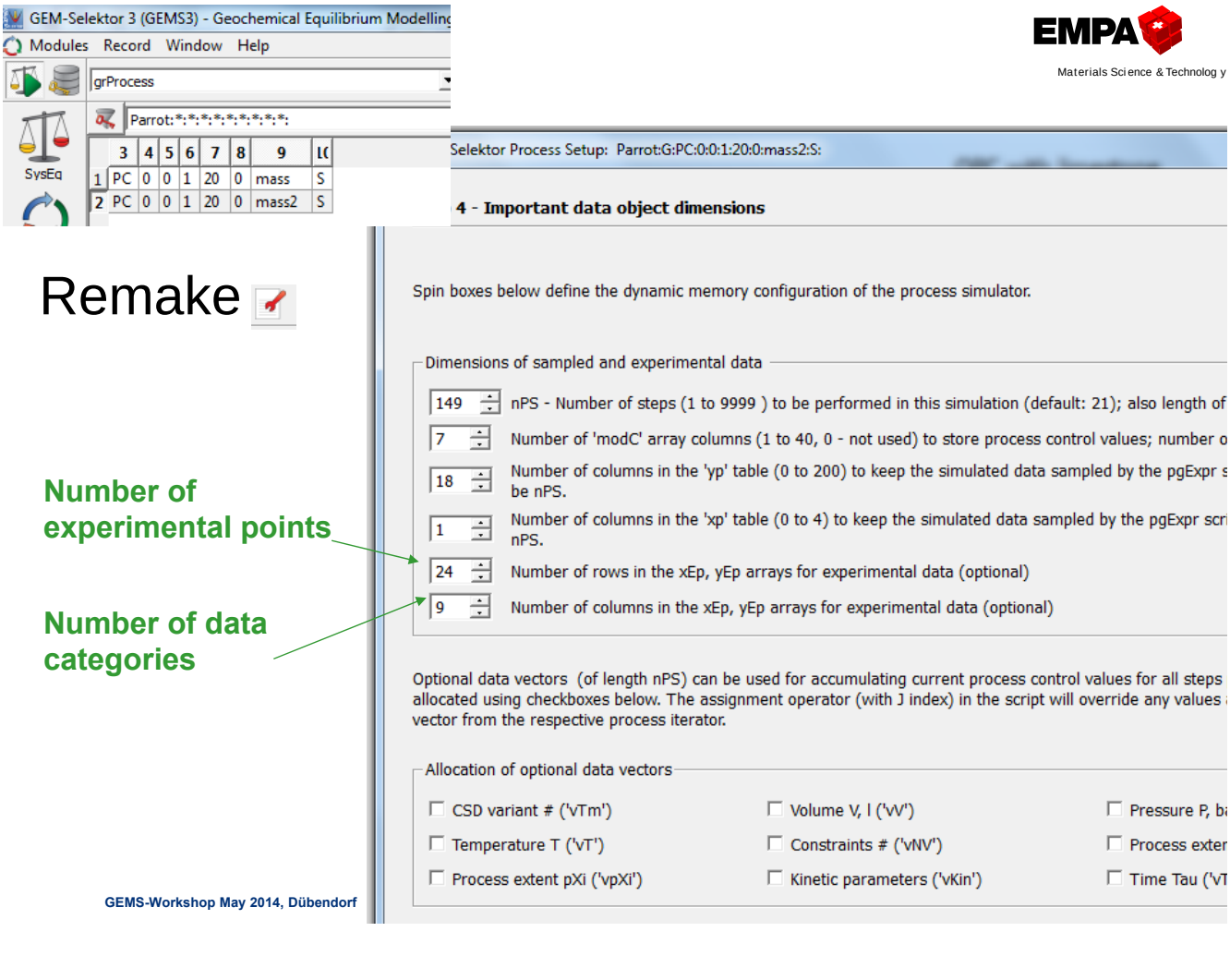
Architecture of GEMS file

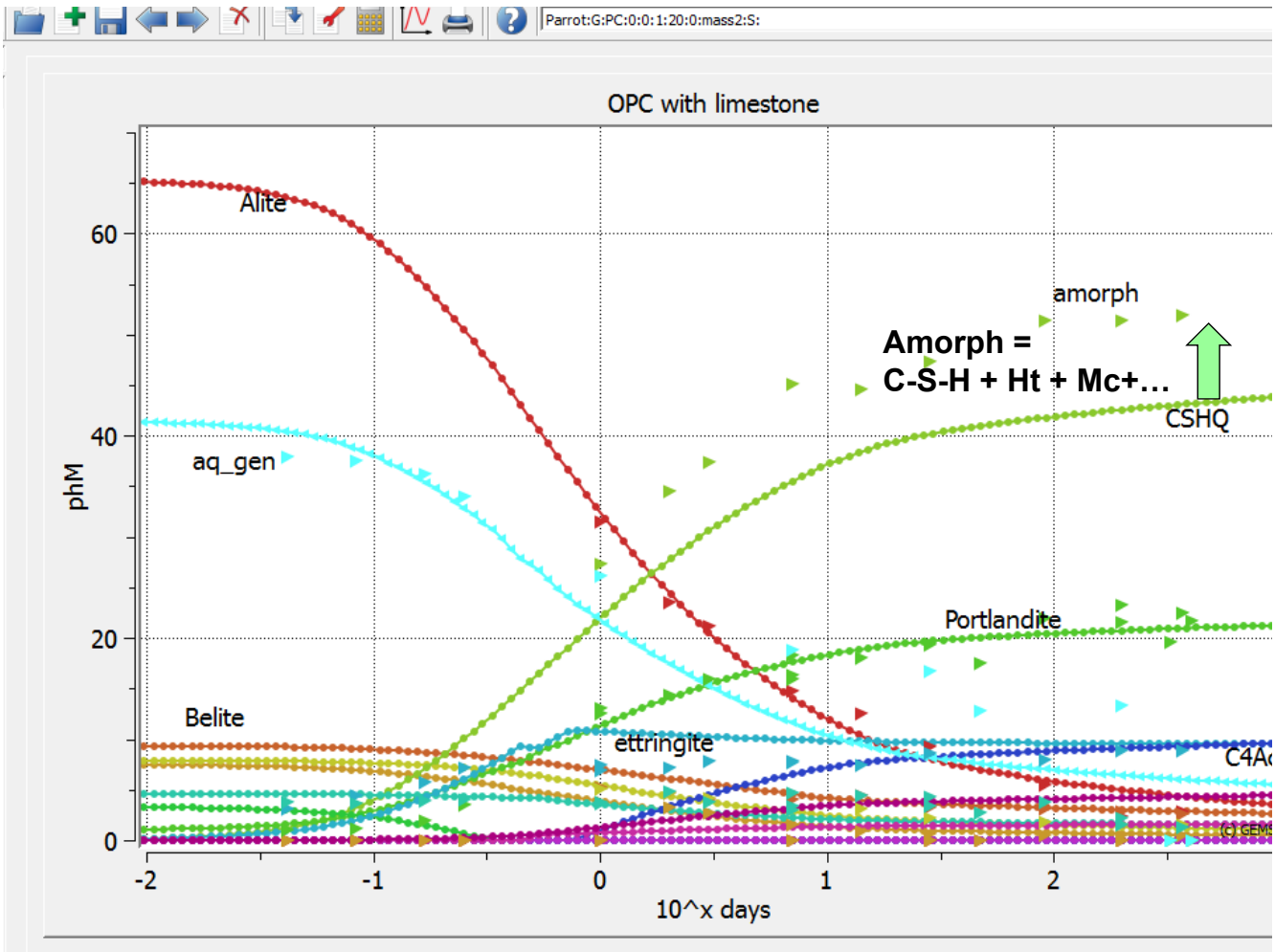
- Process: Config: single system files



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

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


GEM-Selektor 3 (GEMS3) - Geochemical Equilibrium Modelling
Modules Record Window Help
grProcess
Parrot:*:*:*:*:*:*:*:*:*:
SysEq
Selektor Process Setup: Parrot:G:PC:0:0:1:20:0:mass2:S:
4 - Important data object dimensions
Remake
Spin boxes below define the dynamic memory configuration of the process simulator.
Dimensions of sampled and experimental data
149 nPS - Number of steps (1 to 9999) to be performed in this simulation (default: 21); also length of
7 Number of 'modC' array columns (1 to 40, 0 - not used) to store process control values; number o
18 Number of columns in the 'yp' table (0 to 200) to keep the simulated data sampled by the pgExpr s
be nPS.
1 Number of columns in the 'xp' table (0 to 4) to keep the simulated data sampled by the pgExpr scri
nPS.
24 Number of rows in the xEp, yEp arrays for experimental data (optional)
9 Number of columns in the xEp, yEp arrays for experimental data (optional)
Number of experimental points
Number of data categories
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')
Temperature T ('vT')
Constraints # ('vNV')
Process extent pXi ('vpXi')
Kinetic parameters ('vKin')
GEMS-Workshop May 2014, Dübendorf


Parrot:G:PC:0:0:1:20:0:mass2:S:
OPC with limestone
Alite
amorph
Amorph =
C-S-H + Ht + Mc+…
CSHQ
aq_gen
Portlandite
Belite
ettringite
C4A
phM
60
40
20
0
-2
-1
0
1
2
10^x days

Sampling of aqueous concentrations

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

Controls | Sampling | Results | Config | 11/04/2014, 15:13

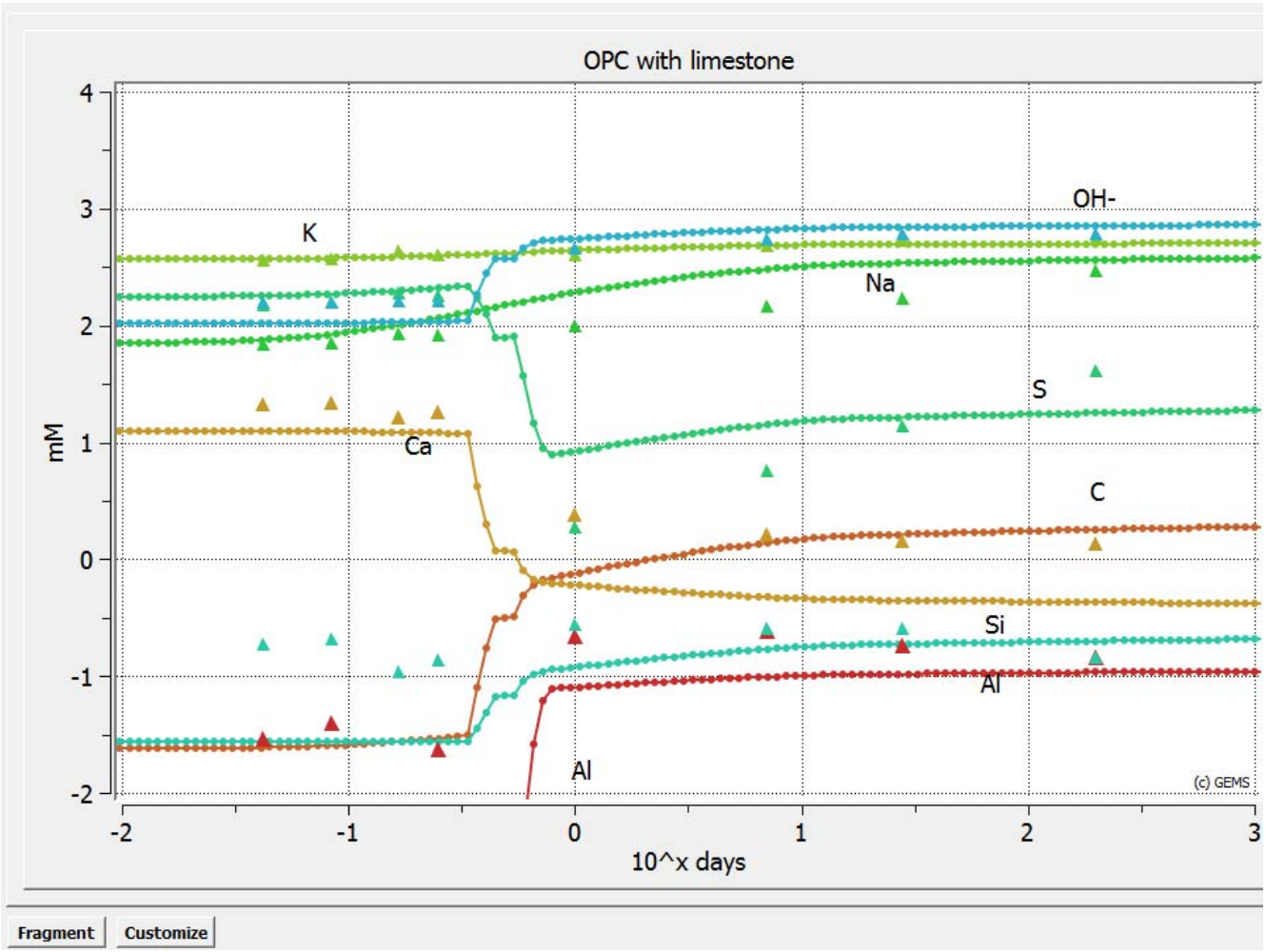
NeIt	9999	149	Next	0	I	0	J	148	Jp	148

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

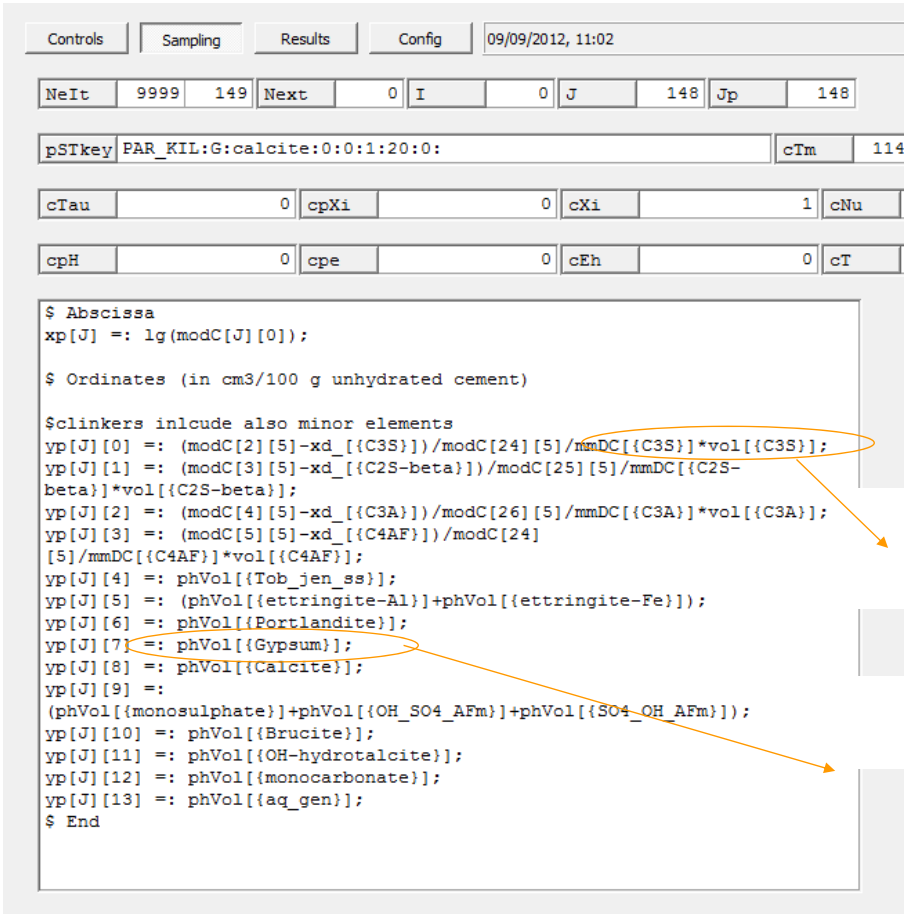
```
$ Abscissa
xp[J] =: lg(modC[J][0]);
$ Ordinates (in mmol/1 l solution) transformation molal -> molar
yp[J][0] =: lg(m_t{Al}*x[{H2O@}]*18.0153/phVol[{aq_gen}]*1000);
yp[J][1] =: lg(m_t[{C}]*x[{H2O@}]*18.0153/phVol[{aq_gen}]*1000);
yp[J][2] =: lg(m_t[{Ca}]*x[{H2O@}]*18.0153/phVol[{aq_gen}]*1000);
yp[J][3] =: 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);
```

Example

- Calculate volumes of the hydrating cement

- Hint:
  - Duplicate process «mass»
  - Exchange phM by phVol
  - use for clinkers: /mmDC[{C3S}]*vol[{C3S}]
    „mmDC[{}]“ Mass of component
    „vol[{}]“ Volume of component



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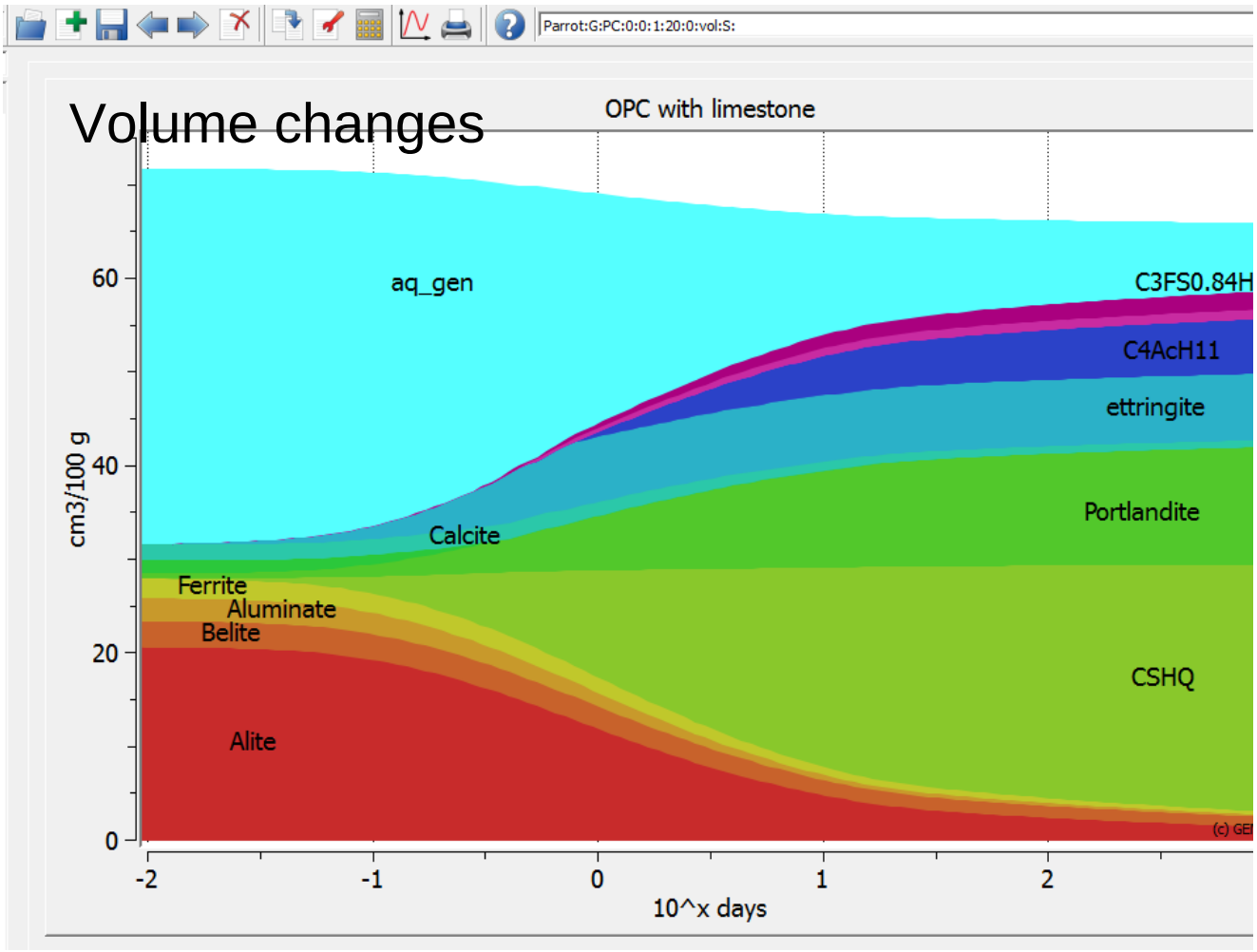
Expressed as volumes

/mmDC[{C3S}]*vol[{C3S}]
„mmDC[{}]“ Mass of component
„vol[{}]“ Volume of component

phVol[{Gypsum}]:
volume (in cm^3) of gypsum



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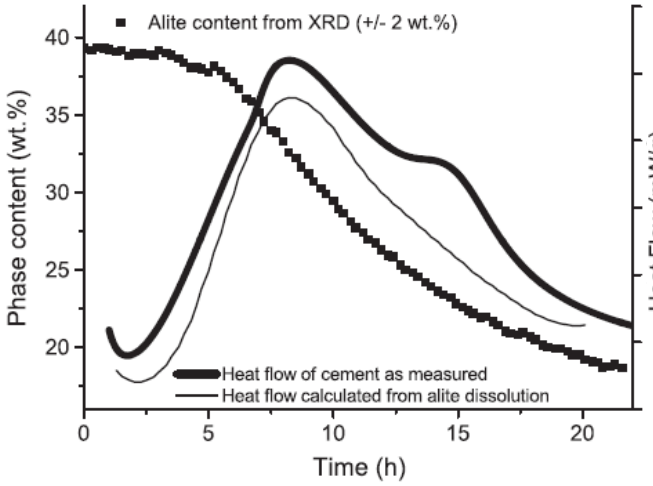
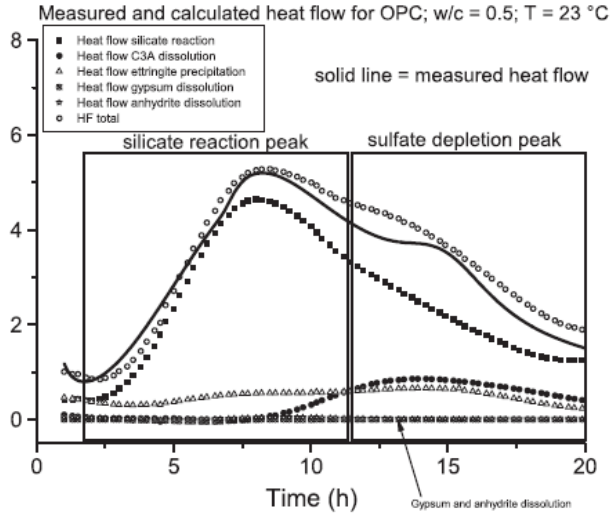
Hydration modelling

- Further possibilities
  - Volume
  - Porosity, chemical shrinkage
  - Enthalpie -> calorimetry
    (use hTP (enthalpy) * x (moles) = total heat)
  - …
- How can we define input?
  - XRF + extended Bogue calculations
  - XRD + XRF data for all minor elements

Example: coupling XRD and enthalpy calcualtions



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



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

Janssen ea 2012, CCR 42