
GEMS workshop 2020



Lecture 3

Process calculations – Hydrated Portland cement

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Tutorial – process: hydration of Portland cement

Hydration of Portland cement

- 1) Hydration of PC - single system
- 2) Influence of limestone on hydration of PC – process file
 - a) Mass based output
 - b) Volume based output
 - c) Composition of aqueous phase
- 3) Influence of fly ash on hydration of PC – process file

Single file - hydration of Portland cement

Hydration of a Portland cement

- The example will show the principle possibility to apply GEMS to simulate cement hydration.
- A cement composition from literature is used.
- 100% hydration with $w/c = 0.50$ at 20°C is assumed (other assumptions are possible).

Single file - hydration of Portland cement

The screenshot displays the GEM-Selektor 3 (GEMS3) software interface. The main window title is "GEM-Selektor 3 (GEMS3) - Geochemical Equilibrium Modelling by Gibbs Energy Minimization". The "Modelling Projects" dialog box is open, showing a list of existing projects. The "New Project" button at the bottom of the dialog is highlighted with a red box. A red arrow points from the "Modelling Projects" icon in the software's toolbar to the dialog box.

Modelling Projects

GEM-Selektor modelling projects: Select one to open, or click 'New Project...' to create

AluSiOMSA	MUSICAluminaSilica
AragCalc	Aragonite-Calcite
BermanMSS	TestsMultiSiteSolidSolutions
Ca-Sr-CO3	Solid_solutions
Ca1DolCol2GEM2MT	-test
CalcDolo	GEMS3K-test-example
CarbSea	CarbonatesAndSeawater
Flowline	test project gem2mt
GEOTHERM	Soultz_1
Kaolinite	Test-JNC
Kinetics	Mineral-Aq-Reactions
Kyanite	My1stProject
PitzTest	NaCl_CO2
SIT_port1	BU181104
Solvus	test project solvus
TestPNTDB	Test-PSI-Nagra-TDB-07-12
TestPR	test project PRSV fluid
TestSUP98	Test-SUPCRT98-linked

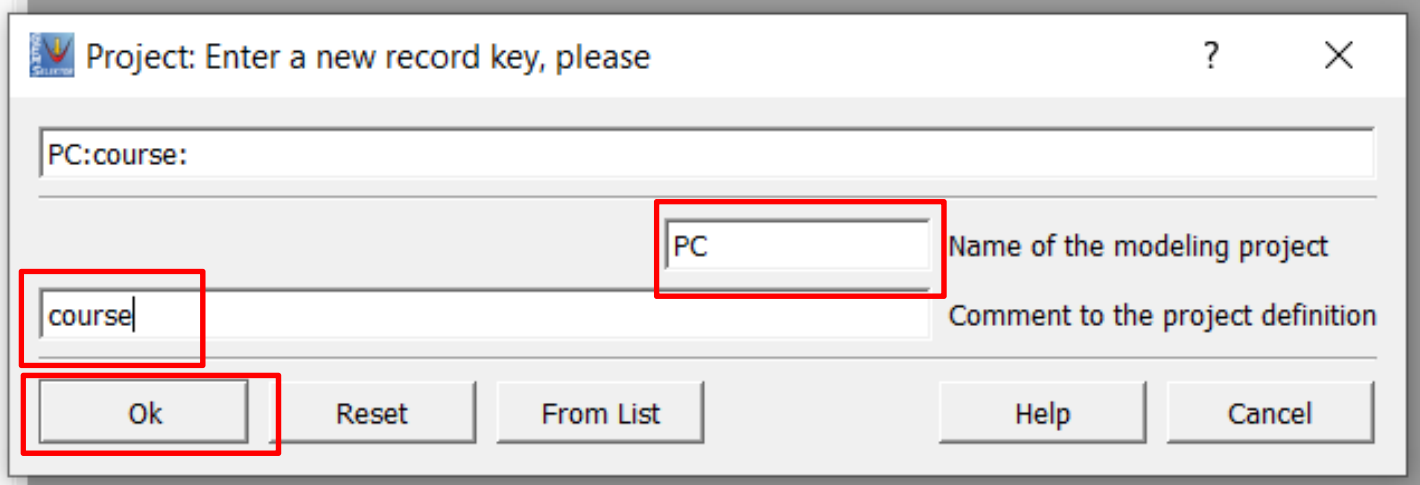
Retain setup of aqueous (and gas/fluid) phases
 Change file configuration of the selected project
 Create a new project using the selected one as a template

Activate Project Remake wizard
Re-calculate and save all equilibria (SysEq) using:
 AIA mode (simplex) Smart IA mode (SIA)

Make a new project:
 by copying records from default database by linking files from the default database

Open Project **New Project** **Learn more** **Cancel**

Single file - hydration of Portland cement



Project: Enter a new record key, please

PC:course:

PC

course

Ok Reset From List Help Cancel

Name of the modeling project

Comment to the project definition

Single file - hydration of Portland cement

Select CEMDATA18 (3rd party data base)

Basis configuration of a new Modelling Project PC

Step 1 - Selection of databases, data subsets, phase type filters

Phase/DC Filters

- Aqueous electrolyte
- Gas mixture
- Non-ideal fluids
- Plasma
- Crystalline solids
- Dispersed solids
- Liquids, glasses
- Silicate melts
- Sorption, Ion exchange
- Polyelectrolytes
- Liquid hydrocarbons
- Skip solid solutions

Built-in Database	Version
<input checked="" type="checkbox"/> 3rdparty	
<input checked="" type="checkbox"/> cemdata	18.01
<input checked="" type="checkbox"/> .	
<input type="checkbox"/> aam	18.01
<input checked="" type="checkbox"/> pc	18.01
<input checked="" type="checkbox"/> .	
<input checked="" type="checkbox"/> csh	
<input type="checkbox"/> csh2o	18.01
<input type="checkbox"/> csh3t	18.01
<input type="checkbox"/> cshkn	18.01
<input checked="" type="checkbox"/> cshq	18.01
<input checked="" type="checkbox"/> ht	18.01
<input checked="" type="checkbox"/> ss-fe3	18.01
<input checked="" type="checkbox"/> ss	18.01
<input type="checkbox"/> claysor	18-12.v0.1
<input checked="" type="checkbox"/> psi-nagra	
<input type="checkbox"/> supcrt	
<input type="checkbox"/> support	

Cement database
Deactivate; special data for alkali activated cements PC
1 CSH model selected: «CSHQ»
Data for hydrotalcite
Data for solid solutions (in cemdata)

General psi-nagra database

Recommended selection for PC and blended cements

Learn more < Back **Next >** Cancel

Single file - hydration of Portland cement

Select main elements present in PC

Basis configuration of a new Modelling Project PC

Step 2: Select Independent Components (not available if shown in light gray color)

	I	II	III	IV	V	VI	VII	VIII	
1	H							He	
2	Li	Be	B	C	N	O	F	Ne	
3	Na	Mg	Al	Si	P	S	Cl	Ar	
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co Ni
4a	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh Pd
5a	Ag	Cd	In	Sn	Sb	Te	I	Xe	
6	Cs	Ba	REE	Hf	Ta	W	Re	Os	Ir Pt
6a	Au	Hg	Tl	Pb	Bi	Po	At	Rn	
7	Fr	Ra	ACT						e(Zz)
	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb Dy Ho Er Tm
	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk Cf Yb Lu

Isotopes

Additional

Nit

...

...

...

...

...

...

...

...

...

Vol

Learn more Set Filters < Back Next > Cancel

Single file - hydration of Portland cement

Select model for calculation of the aqueous phase

Setup of aqueous and gas phases in project: C3A

Select Aqueous Electrolyte Model | Select Gas/Fluid Mixture Model

Ion-association (IA) with Davies equation, D. (default)
 IA with extended Debye-Hueckel equation (Helgeson), common b_{gamma} and a_0 , H
 IA with extended Debye-Hueckel equation (Shvarov), common b_{gamma} and a_0 , Y
 IA with extended Debye-Hueckel equation (Karpov), common b_{gamma} , individual a_0 , 3
 IA with Debye-Hueckel equation, no b_{gamma} , individual a_0 , 2
 IA with Debye-Hueckel limiting law (very low ionic strength), 1
 Do not generate; select a user-defined Phase record from database (Q, S, Z), U
 Do not include aqueous electrolyte phase into the system definition, N

Phase record key: a AQELIA aq_gen aq EDH_H

Parameters for the aqueous phase model

$b_{\text{gamma}}(1,298)$ value: 0.123

$b_{\text{gamma}}(P,T)$ mode: KOH

Common a_0 value: 3.67

Gamma (neutral species): Calculate as $b_{\text{gamma}} \cdot IS$

Gamma (water solvent): From osmotic coefficient

Molality conversion: Applied to all species

OK Cancel 1. Check 2. Learn more More details

1) constant, -> select at 298 K

2) f(pressure, temp) -> electrolyte $a_0=3.67$ for KOH

Calculates activity of water

Activity coefficients

Solubility product e. g. of gypsum

$$K_{S0} = \{Ca^{2+}\} \cdot \{SO_4^{2-}\} \cdot \{H_2O\}^2 / \{CaSO_4 \cdot 2H_2O\}$$

$$K_{S0} = \{Ca^{2+}\} \cdot \{SO_4^{2-}\} = 10^{-4.58}$$

{ } : activity; [] : concentration

$$\{Ca^{2+}\} = [Ca^{2+}] \cdot \gamma_{Ca^{2+}} \longleftarrow \text{Activity coefficient}$$

Correction of concentrations by activity coefficients, as the ions „feel“ their neighbours (other ions, solvent).

Activity coefficients depend mainly on:

- ionic strength
- other ionic species
- temperature

Activity vs. ionic strength

– selecting the right aqueous electrolyte model

Debye-Hückel $\log \gamma_{Ca^{2+}} = \frac{-AZ^2\sqrt{I}}{1+Ba\sqrt{I}}$ ionic strength $I < 0.1 \text{ M}$

Extended Debye-Hückel $\log \gamma_{Ca^{2+}} = \frac{-AZ^2\sqrt{I}}{1+Ba\sqrt{I}} + bI$

common a, common b (Helgeson)

$I < 1-2 \text{ M}$

individual a, common b (Truesdell-Jones)

$I < 1 \text{ M}$

individual a, no b

$I < 0.3 \text{ M}$

Davies $\log \gamma_{Ca^{2+}} = -AZ^2 \left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.3I \right)$

$0.1 < I < 0.5 \text{ M}$

SIT $\log \gamma_{Ca^{2+}} = \frac{-AZ^2\sqrt{I}}{1+1.5\sqrt{I}} + \sum \varepsilon m_k$


$I < 3 \text{ M}$

The calculation of activity coefficients is available as built-in function in the GEMS code.

For a detailed overview of different activity coefficients see:

C:\GEMS36\Gems3-app\Resources\doc\pdf\Activity-Coeffs.pdf and references therein

Single file - hydration of Portland cement

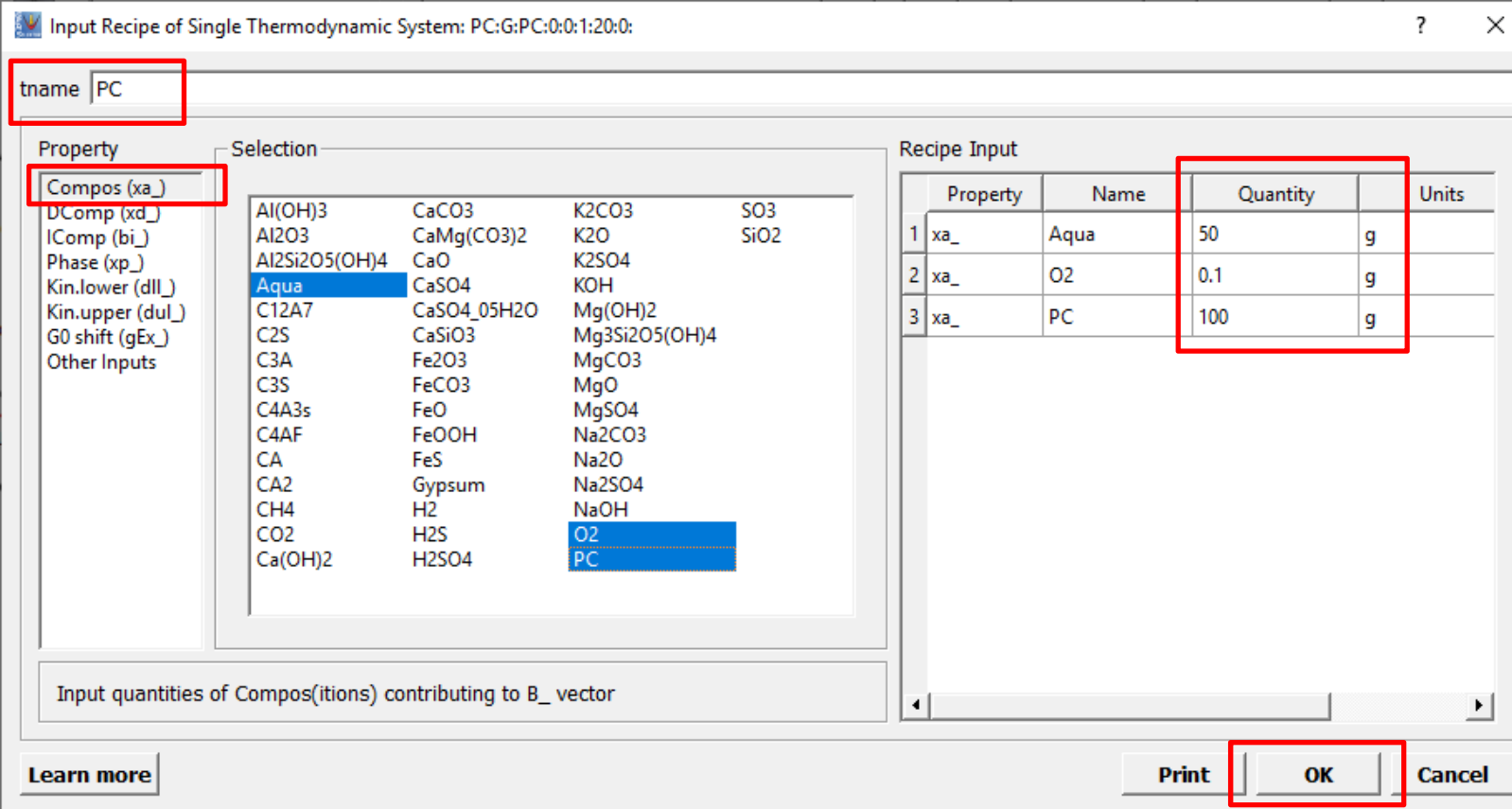
 SysEq: Please, enter a new record key: ? X

PC:G:PC:0:0:1:20:0:

<input type="text" value="PC"/>	Name of the modeling project
<input type="text" value="G"/>	Thermodynamic potential to minimize {G GV}
<input type="text" value="PC"/>	Name of the chemical system definition (CSD)
<input type="text" value="0"/>	CSD (recipe) variant number <integer >
<input type="text" value="0"/>	Volume of the system, dm3 (0 if no volume constraint)
<input type="text" value="1"/>	Pressure, bar, or 0 for Psat(H2O)g
<input type="text" value="20"/>	Temperature, C (>= 0)
<input type="text" value="0"/>	Variant number for additional constraints

Single file - hydration of Portland cement

Use recipe wizard to enter PC composition



Input Recipe of Single Thermodynamic System: PC:G:PC:0:0:1:20:0

tname PC

Property Selection

Compos (xa_)

Property	Name	Quantity	Units
1 xa_	Aqua	50	g
2 xa_	O2	0.1	g
3 xa_	PC	100	g

Input quantities of Compos(itions) contributing to B_ vector

Learn more Print OK Cancel

PC = predefined composition

Single file - hydration of Portland cement

Composition of a PC without limestone addition

Normative phase composition [g/100 g]

Alite ^c	66.5
Belite ^c	10.3
Aluminate ^c	7.5
Ferrite ^c	8.5
MgO(periclase) ^c	0.9
CaO (free) ^d	0.93
CaCO ₃ ^d	0.6
CaSO ₄ · 2H ₂ O ^d	3.1
K ₂ SO ₄ ^b	1.3
Na ₂ SO ₄ ^b	0.21

Present as solid solution in the clinker phases

K ₂ O ^d	0.054
Na ₂ O ^d	0.33
MgO ^d	0.94
SO ₃ ^d	0.11

Compos :: Predefined composition objects (PCO)

Page 1 | Settings | 13/05/2019, 10:48

+ - + - - M | 10 | 0 | 9 | 1 | 10 | 0

Lothenbach_ea_b:2008:pap: | OPC composition

	formU	AUc	CA
0	CaO	g	63.9
1	SiO2	g	20.2
2	Al2O3	g	4.9
3	Fe2O3	g	3.2
4	MgO	g	1.8
5	K2O	g	0.78
6	Na2O	g	0.42
7	CO2	g	0.26
8	SO3	g	2.29

Available in CEMDATA18 as predefined composition «PC»

Single file - hydration of Portland cement

GEM-Selektor 3 (GEMS3) - Geochemical Equilibrium Modelling by Gibbs Energy Minimization - [EqStat: Single Thermodynamic System in Project PC]

Modules Record Data Calculate View Print Window Help

SingleSystem

PC:*,*,*,*,*,*,*,*

Input: System Definition Results: Equilibrium State

Phase/species	L	T	On/	UC	Add to BC	UG	GO corr.	UK	Lower_KC	Upper_KC	KC type
aq_gen	69	a	+	g	0	J	0				
gas_gen	6	g	+	g	0	J	0				
C3 (AF) S0.84H	2	s	+	g	0	J	0				
CSHQ	6	s	+	g	0	J	0				
ettringite-AlFe	2	s	+	g	0	J	0				
ettringite-FeAl	2	s	+	g	0	J	0				
monosulph-AlFe	2	s	+	g	0	J	0				
monosulph-FeAl	2	s	+	g	0	J	0				
straetlingite	2	s	+	g	0	J	0				
ettringite	2	s	+	g	0	J	0				
SO4_OH_AfM	2	s	+	g	0	J	0				
OH_SO4_AfM	2	s	+	g	0	J	0				
SO4_CO3_AfT	2	s	+	g	0	J	0				
CO3_SO4_AfT	2	s	+	g	0	J	0				
hydrotalc-pyro	2	s	+	g	0	J	0				
MSH	2	s	+	g	0	J	0				
Al(OH)3am	1	s	+	g	0	J	0				
Al(OH)3mic	1	s	+	g	0	J	0				
Gibbsite	1	s	+	g	0	J	0				
Kaolinite	1	s	+	g	0	J	0				
Graphite	1	s	+	g	0	J	0				
Mayenite	1	s	+	g	0	J	0				
Belite	1	s	+	g	0	J	0				
Aluminate	1	s	+	g	0	J	0				
Alite	1	s	+	g	0	J	0				
Ferrite	1	s	+	g	0	J	0				
CA	1	s	+	g	0	J	0				
CA2	1	s	+	g	0	J	0				
C2AH75	1	s	+	g	0	J	0				
C3AH6	1	s	+	g	0	J	0				
C4AH11	1	s	+	g	0	J	0				
C4AH13	1	s	+	g	0	J	0				
C4AH19	1	s	+	g	0	J	0				
CAH10	1	s	+	g	0	J	0				
C4AsH105	1	s	+	g	0	J	0				
C4AsH12	1	s	+	g	0	J	0				
C4AsH14	1	s	+	g	0	J	0				
C4AsH16	1	s	+	g	0	J	0				
C4AsH9	1	s	+	g	0	J	0				
...											

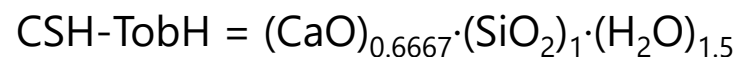
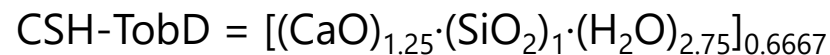
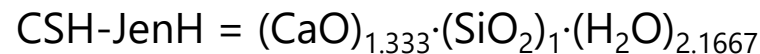
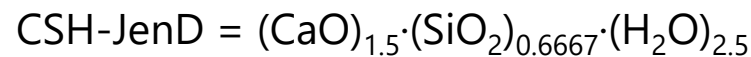
System: T = 298.15 K; P = 1.00 bar; V = 0 L;

all main cement hydrates included in this project

Single file - hydration of Portland cement

C-S-H is modeled as a solid solution of 6 different species:

Phase/species	L	T	On/	UC	Add to BC	UG	GO corr.	UK	Lower_KC	Upper_KC	KC type
aq_gen	69	a	+	g	0	J	0				
gas_gen	6	g	+	g	0	J	0				
C3 (AF) S0.84H	2	s	+	g	0	J	0				
CSHQ	6	s	+	g	0	J	0				
CSHQ-JenD		I	+	M	0	J	0	M	0	1000000	B
CSHQ-JenH		I	+	M	0	J	0	M	0	1000000	B
CSHQ-TobD		I	+	M	0	J	0	M	0	1000000	B
CSHQ-TobH		I	+	M	0	J	0	M	0	1000000	B
KSiOH		I	+	M	0	J	0	M	0	1000000	B
NaSiOH		I	+	M	0	J	0	M	0	1000000	B



Kulik D.A., Cem. Concr. Res. 41 (2011), 477.

The 4 C-S-H species are in ss with (hypothetical) Na- and K-silicates to model alkali binding by C-S-H.

Lothenbach, B., Kulik, D., Matschei, T., Balonis, M., Baquerizo, L., Dilnesa, B.Z., Miron, D.G., Myers, R. (2018) Cemdata18: A chemical thermodynamic database for hydrated Portland cements and alkali-activated materials *Cement and Concrete Research*, 115, 472-506.

Single file - hydration of Portland cement

Before calculation, deactivate the following phases:

- Goethite, hematite, quartz, ...
(form at high temperature after long times)
- C_3AH_6 , gibbsite, AH_3 (depending on reaction time), ...
- Thaumassite (formation fast at low temp. Very slow at ambient temp and above)
- others:
Ettringite Al/Fe ss
Monosulfate Al/Fe ss
 C_4AH_{13} , C_4AH_{19}

In general it is recommended:

- Use either the pure phase or the ss (deactivate the other); in this case C_4AH_{13} & C_4AH_{19}
- **Look at the results, compare with experimental data !**

Input: System Definition		Results: Equilibrium State			
Phase/species	L	T	On/	UC	Add to BC
aq_gen	75	a	+	g	0
gas_gen	6	g	+	g	0
C3(AF)S0.84H	2	s	+	g	0
CSHQ	6	s	+	g	0
ettringite-AlFe	2	s	-	g	0
ettringite-FeAl	2	s	-	g	0
monosulph-AlFe	2	s	-	g	0
monosulph-FeAl	2	s	-	g	0
stratlingite	2	s	+	g	0
ettringite	2	s	+	g	0
SO4_OH_AfM	2	s	+	g	0
OH_SO4_AfM	2	s	+	g	0
SO4_CO3_AfT	2	s	+	g	0
CO3_SO4_AfT	2	s	+	g	0
hydrotalc-pyro	2	s	+	g	0
MSH	2	s	+	g	0
Al(OH)3am	1	s	+	g	0
Al(OH)3mic	1	s	+	g	0
Gibbsite	1	s	-	g	0
Kaolinite	1	s	+	g	0
Graphite	1	s	+	g	0
Mayenite	1	s	+	g	0
Belite	1	s	+	g	0
Aluminate	1	s	+	g	0
Alite	1	s	+	g	0
Ferrite	1	s	+	g	0
CA	1	s	+	g	0
CA2	1	s	+	g	0
C2AH75	1	s	+	g	0
C3AH6	1	s	+	g	0
C4AH11	1	s	-	g	0
C4AH13	1	s	-	g	0
C4AH19	1	s	-	g	0
CAH10	1	s	+	g	0

Single file - hydration of Portland cement

Experimental conditions: React 100 g PC with 50 g water (add 0.1 g air CO₂-free)

1. 2.

gas
liquid
solid

System:
PC:G:PC:0:0:1:20:0:

Iter	1: 3: 265
Gaseous	0.100827
Aqueous	13.4363
Liquid	0
Solid	136.563
pH	13.5844
pe	7.56096
IS	0.351746

13.4 g pore solution

136.6 g solid cement paste

pH = 13.58

"+" = oxidising

Ionic strength = 0.35 M

Accept Dismiss

Convergence problem - workaround

Pa_SPP	Tolerances and controls: GEMSGUI v.3.7.0 and GEMS3K v.3.7.0									
Pa_DK	1e-005	Pa_IIM	7000	Pa_LLG	30000	Pa_AG	1	Pa_DGC	0.01	
Pa_DHB	1e-013	Pa_DFY	1e-005	1e-005	1e-005	1e-005	1e-005	1e-005	1e-005	1e-006
Pa_DB	1e-017	Pa_DS	1e-020	Pa_XMI	1e-013	1e-013	1e-033	1e-020	1e-005	
Pa_EPS	1e-010	0.001	Pa_GAN	1	1000	0.001	Pa_DG	1000		
Pa_DPV	130	1	0	Pa_DF	0.01	0.01	Pa_DNS	12.05		
Pa_PE	1	Pa_PC	2	Pa_PRD	2	-5	1	Pa_DKI	1e-010	

Covergence tolerance parameter:
use higher value, e.g. 1e-004,
maximum seems to be 5e-003

Minimum amount of stable phases:
use lower value, e.g. 1e-023

Smoothing parameter:
use low positive value, e.g. 0.01

In case of problems
Do not touch the other values !!!

Single file - hydration of Portland cement

Predicted stable phase assemblage

Si-Hydrogarnet

C-S-H

ettringite

hemicarbonat

monocarbonat

portlandite

hydrotalcite

Phase/species	L	T	Amount (mol)	logSI/Activity
⊕ a aq_gen	69	a	0.74137655	1.182e-08
⊕ g gas_gen	6	g	0.0031839843	-1.857e-08
⊕ s C3 (AF) S0.84H	2	s	0.04076995	5.09e-09
⊕ s CSHQ	6	s	0.44660884	8.212e-09
⊕ s ettringite-AlFe	2	s	0	-1
⊕ s ettringite-FeAl	2	s	0	-1
⊕ s monosulph-AlFe	2	s	0	-1
⊕ s monosulph-FeAl	2	s	0	-1
⊕ s straetlingite	2	s	0	-1.43
⊕ s ettringite	2	s	0.0097500233	-3.139e-08
⊕ s SO4_OH_AFm	2	s	0	-1
⊕ s OH_SO4_AFm	2	s	0	-1
⊕ s SO4_CO3_AFt	2	s	0	-0.02336
⊕ s CO3_SO4_AFt	2	s	0	-0.02336
⊕ s C4Ac0.5H12	1	s	0.0033530233	6.289e-08
⊕ s C4Ac0.5H9	1	s	0	-4.902
⊕ s C4AcH11	1	s	0.0043671699	-2.068e-08
⊕ s C6AsH13	1	s	0	-29.53
⊕ s C6AsH9	1	s	0	-37.75
⊕ s Aragonite	1	s	0	-1.619
⊕ s Calcite	1	s	0	-1.475
⊕ s lime	1	s	0	-9.961
⊕ s Portlandite	1	s	0.46432156	-1.099e-08
⊕ s Anhydrite	1	s	0	-3.615
⊕ s OH-hydrotalcite	1	s	0.01142203	1.975e-13
⊕ s Magnesite	1	s	0	-9.084
⊕ s Brucite	1	s	0	-1.358

**limestone (0.6 M.-% in the system)
fully reacted**

Single file - hydration of Portland cement

Composition of C-S-H

Input: System Definition		Results: Equilibrium State				
Phase/species	L	T	Amount (mol)	logSI/Activity	Concentration	Acti
a aq_gen	69	a	0.74137655	1.182e-08		
g gas_gen	6	g	0.0031839843	-1.857e-08		
s C3(AF)S0.84H	2	s	0.04076995	5.09e-09		
s CSHQ	6	s	0.44660884	8.212e-09		
CSHQ-JenD		I	0.16459588	0.368546	0.36854595	1
CSHQ-JenH		I	0.10337445	0.231465	0.2314653	1
CSHQ-TobD		I	0.12210382	0.273402	0.27340215	1
CSHQ-TobH		I	0.0048265065	0.010807	0.010807011	1
KSiOH		I	0.027356399	0.0612536	0.061253599	1
NaSiOH		I	0.024351789	0.054526	0.05452599	1
s ettringite AlFe	2	s	0	1		

36.9 mol-% CSH-JenD = $(\text{CaO})_{1.5} \cdot (\text{SiO}_2)_{0.6667} \cdot (\text{H}_2\text{O})_{2.5}$

23.1 mol-% CSH-JenH = $(\text{CaO})_{1.333} \cdot (\text{SiO}_2)_1 \cdot (\text{H}_2\text{O})_{2.1667}$

27.3 mol-% CSH-TobD = $[(\text{CaO})_{1.25} \cdot (\text{SiO}_2)_1 \cdot (\text{H}_2\text{O})_{2.75}]_{0.6667}$

1.1 mol-% CSH-TobH = $(\text{CaO})_{0.6667} \cdot (\text{SiO}_2)_1 \cdot (\text{H}_2\text{O})_{1.5}$

6.1 mol-% KSiOH = $[(\text{KOH})_{2.5} \text{SiO}_2 \text{H}_2\text{O}]_{0.2}$

5.5 mol-% NaSiOH = $[(\text{NaOH})_{2.5} \text{SiO}_2 \text{H}_2\text{O}]_{0.2}$

Al-intake in C-S-H: In preparation

**For alkali activated slag use
CNASH_{ss} model:**

See: Myers et al., Cem. Concr. Res. 66 (2014),
27-47.

(provided separately in CEMDATA18 as "aam")

C-S-H solid solution: 0.022 K₂O · 0.020 Na₂O · 1.582 CaO · 1 SiO₂ · 2.874 H₂O

=> Ca/Si = 1.58

Single file - hydration of Portland cement

Composition of C-S-H

Data Calculate View Print Window Help

PC:G:PC:0:0:1:20:0:

EqIC EqPh EqDC EqSurf EqGen 26/03/2020, 15:49

	Na	O	S	Si	Zz		
88119	0.012175895	4.2621004	0.02925007	0.34393204	0		
e-012	0.0016890444	0.73681839	9.9699668e-006	7.552195e-007	3.4895545e-018	a	aq_gen
0	0	0.0062923754	0	0	0	g	gas_gen
0	0	0.4892394	0	0.034246758	0	s	C3(AF)S0.84H
0	0.012175895	2.0118444	0	0.30968528	0	s	CSHQ
0	0	0	0	0	0	s	ettringite-AlFe

$bXa[{\text{CSHQ}}][{\text{Na}}]$

$bXa[{\text{CSHQ}}][{\text{Si}}]$

Syntax for use in process calculations

Summary C-S-H solid solution :

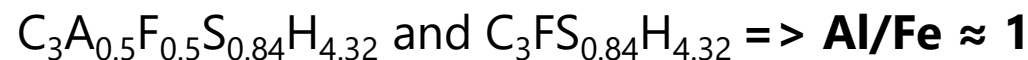
C-S-H solid solution: 0.022 K₂O · 0.020 Na₂O · 1.582 CaO · 1 SiO₂ · 2.875 H₂O
Ca/Si = 1.58, K/Si = 0.044, Na/Si = 0.040 (K/Ca = 0.028, Na/Ca = 0.025)

Single file - hydration of Portland cement

Presence of hydrogarnet

Input: System Definition		Results: Equilibrium State				
Phase/species	L	T	Amount (mol)	logSI/Activity	Concentration	Activity coeff
⊕ a aq_gen	69	a	0.74137655	1.182e-08		
⊕ g gas_gen	6	g	0.0031839843	-1.857e-08		
⊖ s C3(AF)S0.84H	2	s	0.04076995	5.09e-09		
C3AFS0.84H4.32		I	0.040539285	0.994342	0.99434228	1
C3FS0.84H4.32		I	0.00023066497	0.00565771	0.0056577202	1
⊕ s CSHQ	6	s	0.44660884	8.212e-09		

Iron-containing siliceous hydrogarnet is modelled as a solid solution with the following end members:



Al/Fe ratios > 1 are not considered due to experimental findings on hydrated cement pastes with «normal» curing times (up to a few years). The data for $C_3AS_{0.42}H_{5.16}$ and $C_3AS_{0.84}H_{4.32}$ are deactivated but would be available in the database.

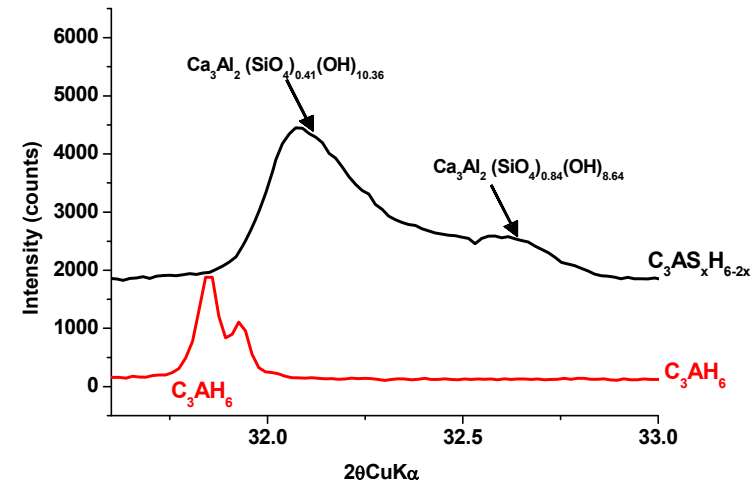
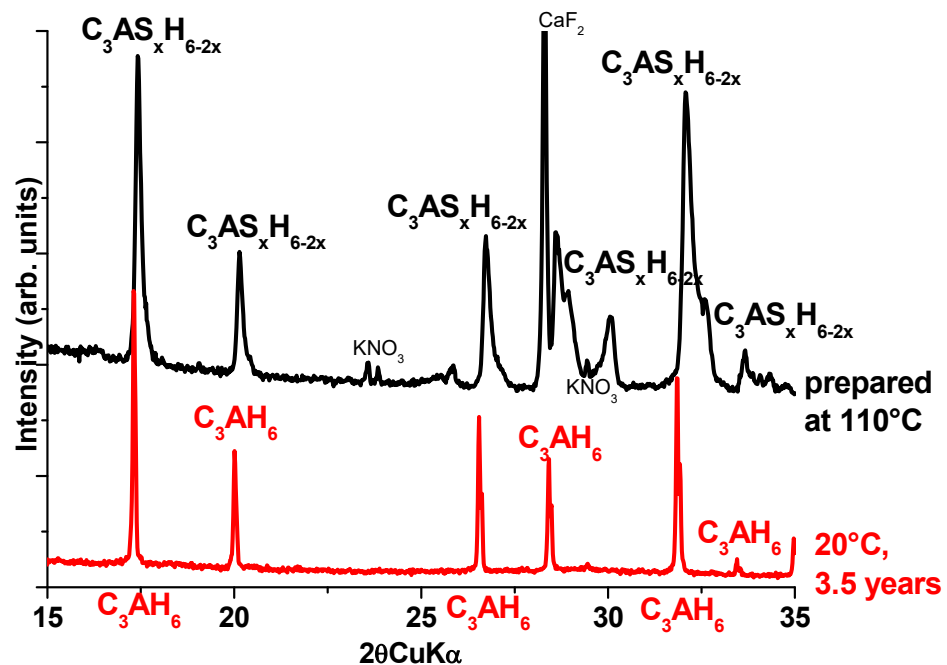
B.Z. Dilnesa, B. Lothenbach, G. Renaudin, A. Wichser, D. Kulik, Synthesis and characterization of hydrogarnet

$Ca_3(Al_xFe_{1-x})_2(SiO_4)_y(OH)_{4(3-y)}$, Cem Concr Res 59 (2014) 96-111.

B.Z. Dilnesa, E. Wieland, B. Lothenbach, R. Dähn, K. Scrivener, Fe-containing phases in hydrated cements, Cem. Concr. Res. 58 (2014) 45-55.

Single file - hydration of Portland cement

Presence of hydrogarnet

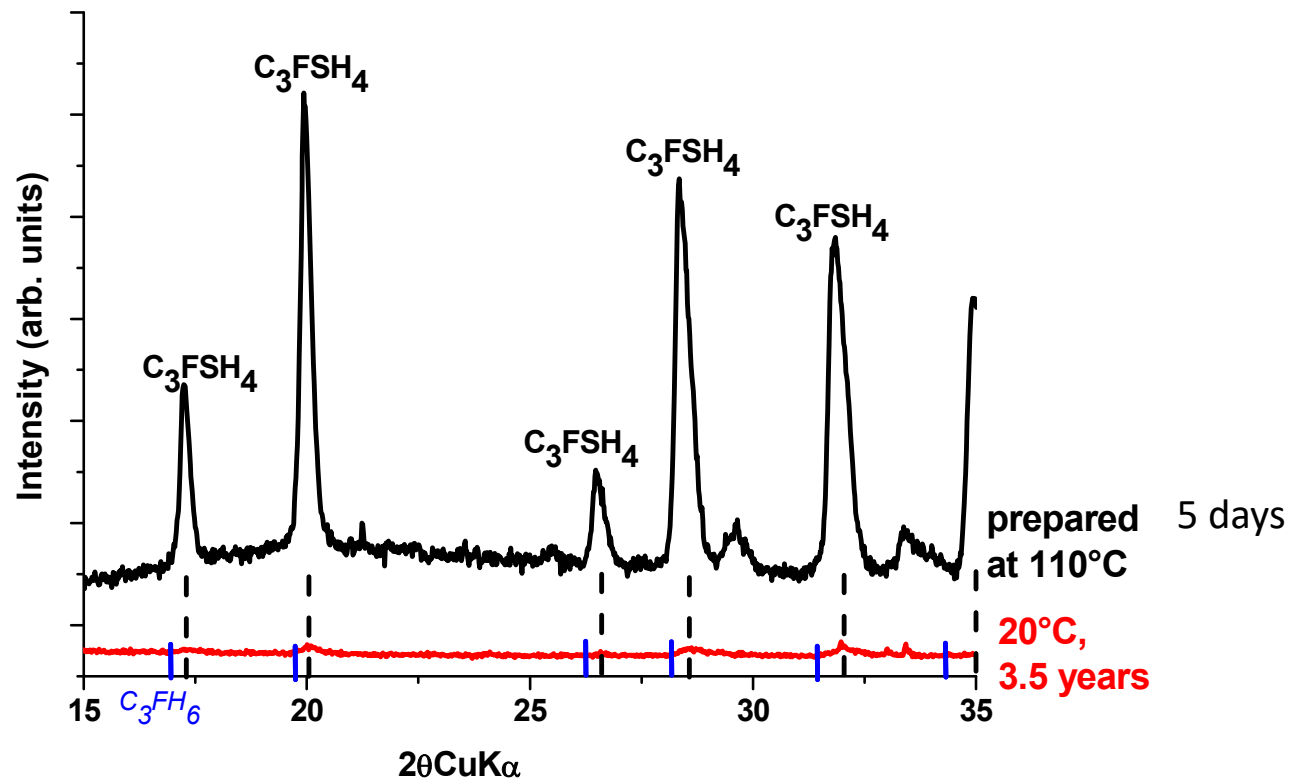


Room temperature: only C_3AH_6 and $C_3FS_xH_{6-2x}$ forms, but no $C_3AS_xH_{6-2x}$
 $C_3AS_xH_{6-2x}$ forms only at 110°C, although stable at 20°C

However, mixed $C_3A_{0.5}F_{0.5}S_xH_{6-2x}$ form

Single file - hydration of Portland cement

Fe- siliceous hydrogarnet in hydrated PC

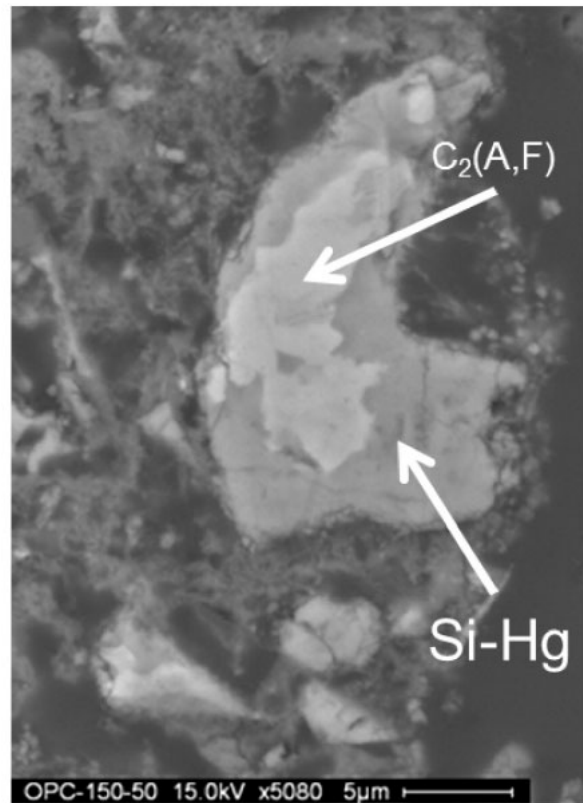


*Low temperature Fe-siliceous hydrogarnet poorly crystalline
=> difficult to detect by XRD => selective extraction*

Dilnesa ea 2014

Single file - hydration of Portland cement

Si-hydrogarnet in hydrated PC



20°C

50°C

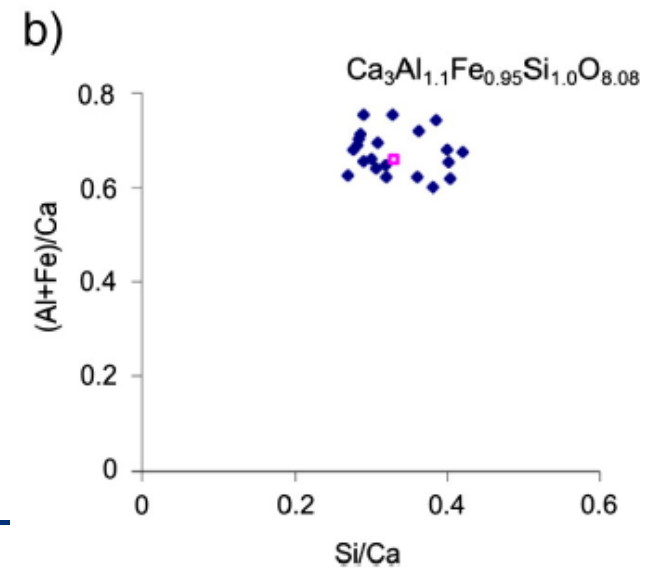
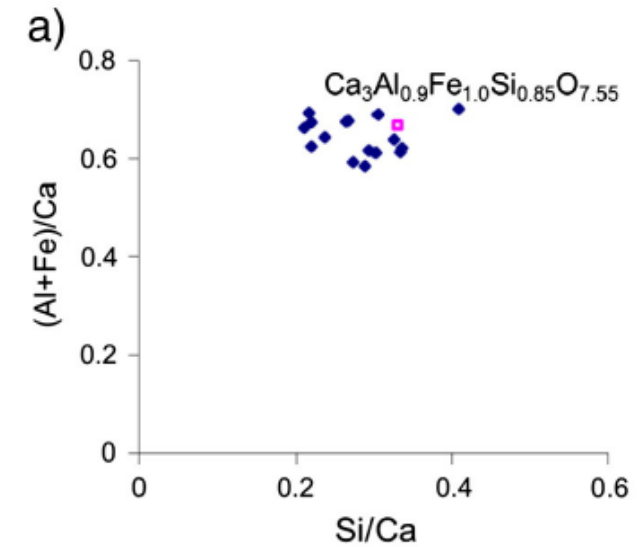


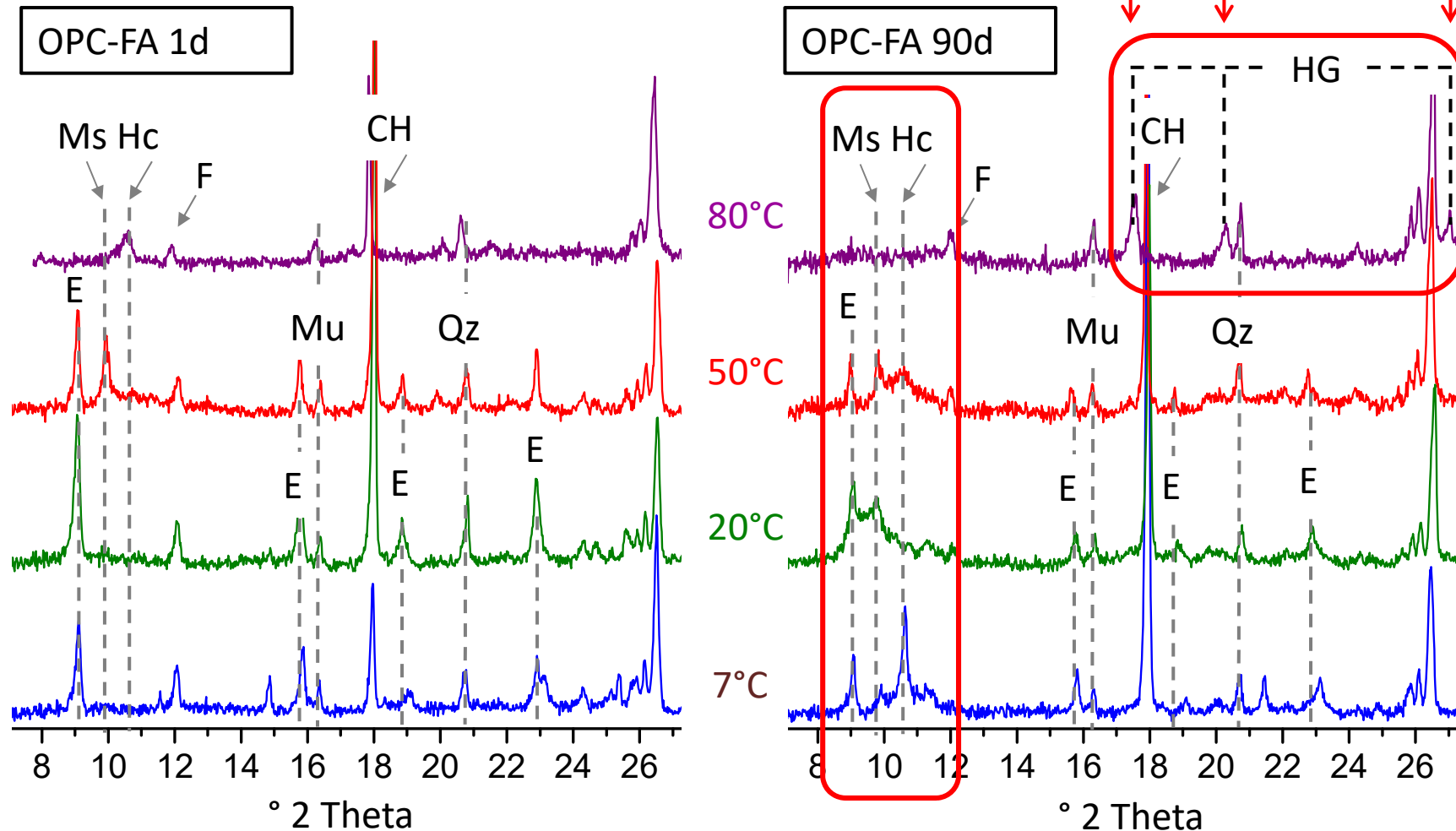
Fig. 8. SEM of ferrite clinker surrounded by hydration products after selective extraction.

B.Z. Dilnesa, E. Wieland, B. Lothenbach, R. Dähn, K. Scrivener, Fe-containing phases in hydrated cements, *Cem. Concr. Res.* 58 (2014) 45–55.

Single file - hydration of Portland cement

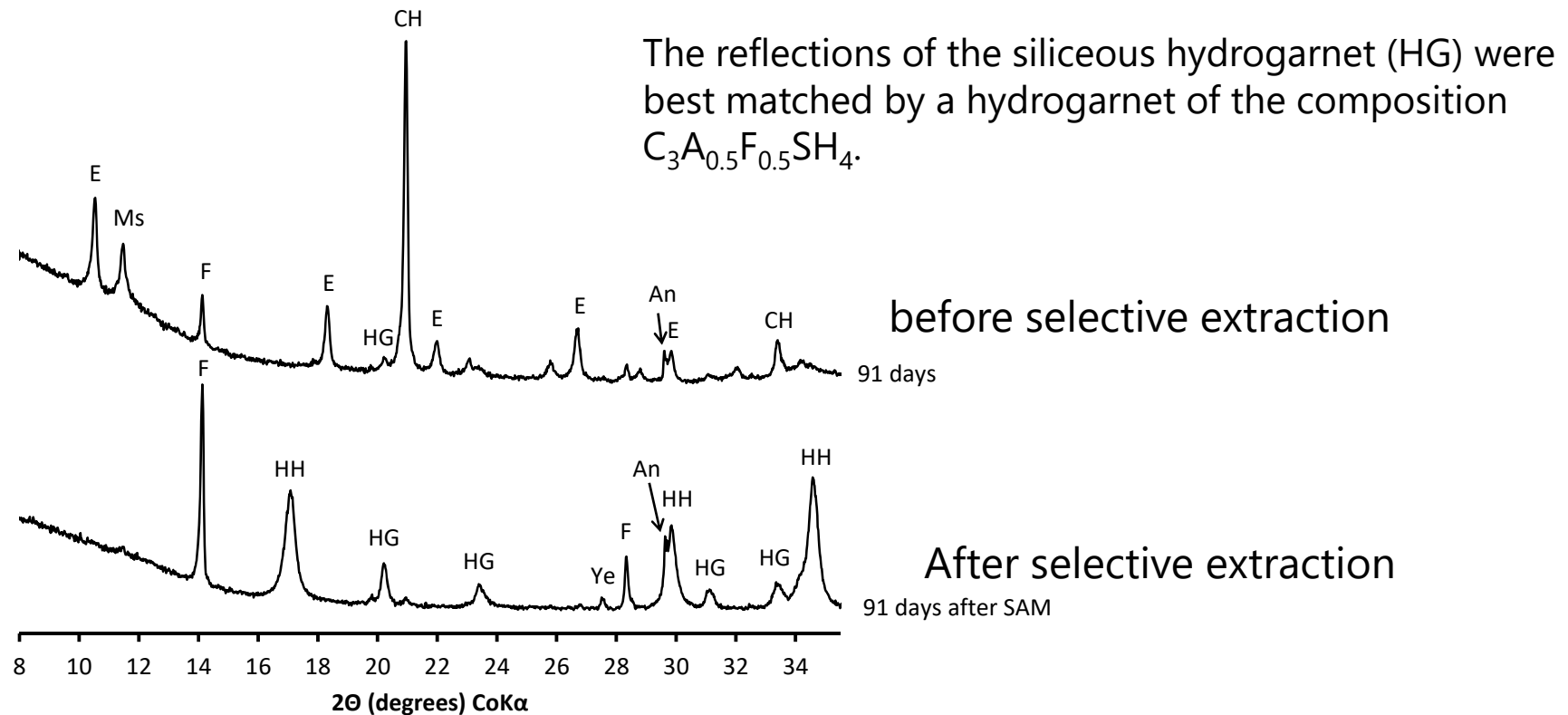
Siliceous hydrogarnet (PC blended with fly ash)

Deschner F., Lothenbach L., Winnefeld F., Neubauer J.: Effect of temperature on the hydration of Portland cement blended with siliceous fly ash, Cement and Concrete Research 52 (2013), 169-181.



Single file - hydration of Portland cement

Si-hydrogarnet in hydrated ACSA



Chitvoranund N., Winnefeld F., Hargis C.W., Sinthupinyo S., Lothenbach B.: Synthesis and hydration of alite-calcium sulfoaluminate cement, *Advances in Cement Research* 29 (2017), 101-111.

Single file - hydration of Portland cement

Hydrated cement composition – summary

- possibility to apply GEMS to simulate hydrated cement
- use metastability constraints (e.g. goethite suppressed)
- use either oxide composition or phase composition as input
- iron and alkalis present in real “PC”

Thus to improve accuracy of the calculation one has to consider:

- Iron containing phases (mainly hydrogarnet important
(Möschner et al. Geoch. Cosm. Acta 2007, Dilnesa et al. CCR 2014a+b
included in the cement database)
 - Sorption of alkalis on C-S-H , good proxy, not perfect
(*experimental data*: Hong and Glasser CCR 1999, included in the database)
 - Sorption of sulfate on C-S-H
(*experimental data*: Divet et al. CCR 1998, Barbarulo et al. 2002, Skapa PhD Thesis U. Aberdeen, 2009) not included
 - Substitution of alumina (Richardson CCR 1994, Chen et al. ICC 2007,
Pardal et al. CCR 2009 & Inorg. Chem. 2012, ongoing work based on CASH I+II projects at Empa,
for alkali activated slags use CNASH_ss model by Myers et al., CCR 2014, provided separately as
aam for GEMS)
- kinetics can be taken into account as function of clinker reactivity over time
(e.g. Lothenbach et al. CCR 2006 & 2008)

Tutorial – process: hydration of Portland cement

Hydration of Portland cement

- 1) Hydration of PC - single system
- 2) Influence of limestone on hydration of PC – process file
 - a) Mass based output
 - b) Volume based output
 - c) Composition of aqueous phase
- 3) Influence of fly ash on hydration of PC – process file

Process file - hydration of PC + limestone

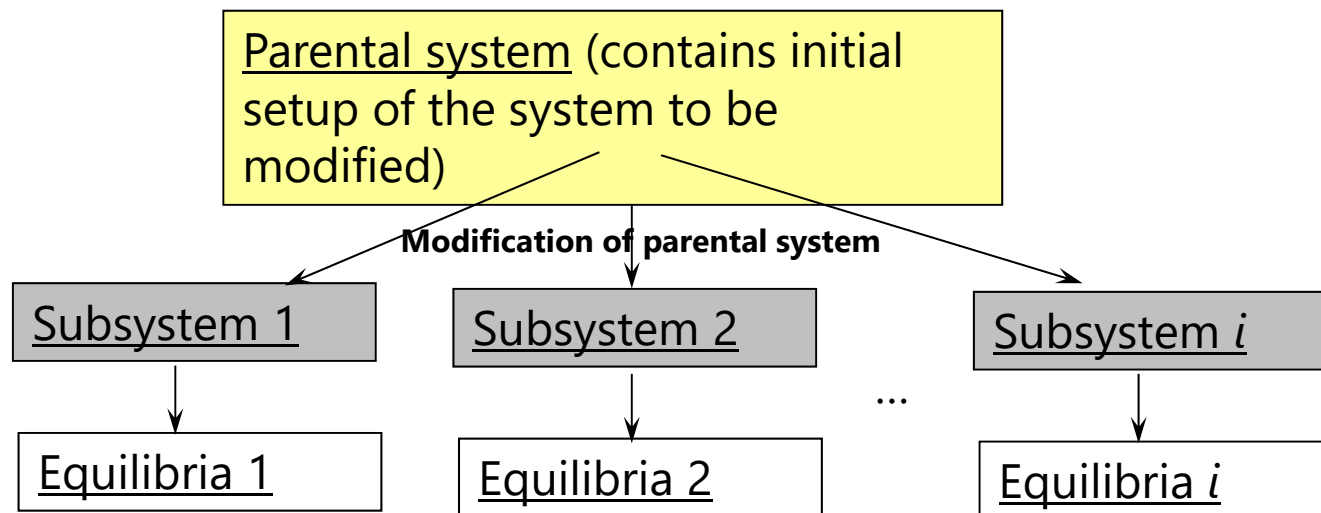
Description of analytical problem

- Addition of increasing amounts of limestone to OPC
- We want to assess the chemical and mineralogical consequences of the addition of increasing amounts of limestone, as calcite, in a systematic way.
- Related phase changes
 - a) mass changes
 - b) volume changes
 - c) changes in the aqueous phase composition

Process file - hydration of PC + limestone

Process simulations - Short introduction

- simulation of stepwise processes, e.g. dissolution, incremental addition, mixing, titration
- especially useful if a regular change of the bulk composition occurs in the process
- simulation of incremental temperature changes

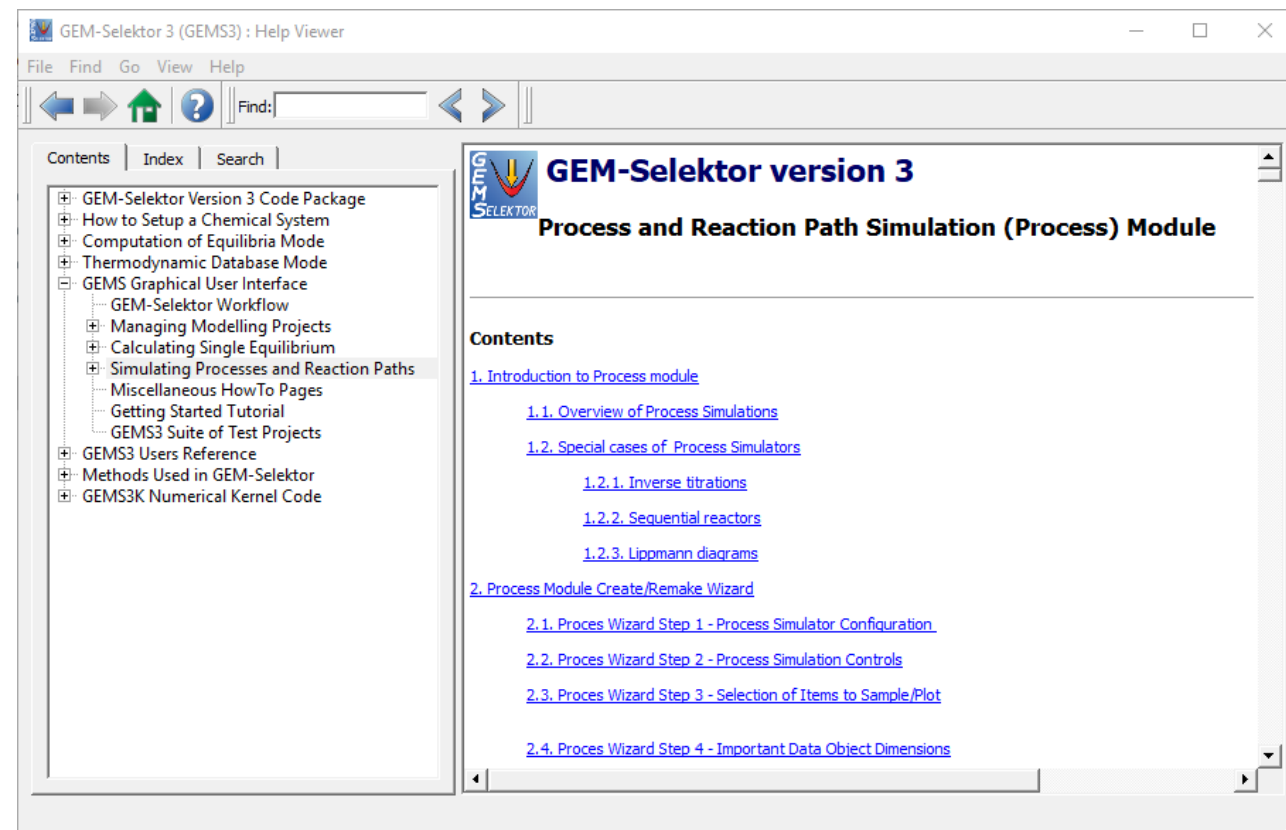


Structure of process simulator

Process file - hydration of PC + limestone

Process simulations - Short introduction

- GEMS uses a built in math script interpreter to execute process simulations and other functions (similar to the macros in Excel)
- a description of the math script interpreter and used expressions can be found in the related GEMS help file



Process file - hydration of PC + limestone

Experimental problem:

Blending of the **hydrated cement** from the previous example ...

Table 1
 Composition of the cement and the limestone used

	PC
<i>Chemical analysis [g/100 g]^a</i>	
CaO	63.9
SiO ₂	20.2
Al ₂ O ₃	4.9
Fe ₂ O ₃	3.2
CaO (free)	0.93
MgO	1.8
K ₂ O	0.78
Na ₂ O	0.42
CO ₂	0.26
SO ₃	2.29
K ₂ O _{soluble} ^b	0.72
Na ₂ O _{soluble} ^b	0.09
Ignition loss	0.37

Parental system

... with various amounts of
limestone

Process file - hydration of PC + limestone

Experimental problem:

Addition of increasing amounts of limestone to PC up to 10% in steps of 0.2%)

Assumptions:

- initial amount of cement constant = 100 g
"cement" = PC + limestone (= 100% CaCO_3)
- w/b ratio = 0.50 (50 g water), constant
- addition of 0.1 g O_2 , constant
- 100% hydration

Process file - hydration of PC + limestone

We use the single file created previously now as parent file for the process simulation.

Single calculations →

Process calculations →

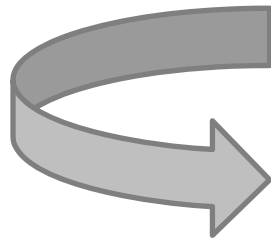
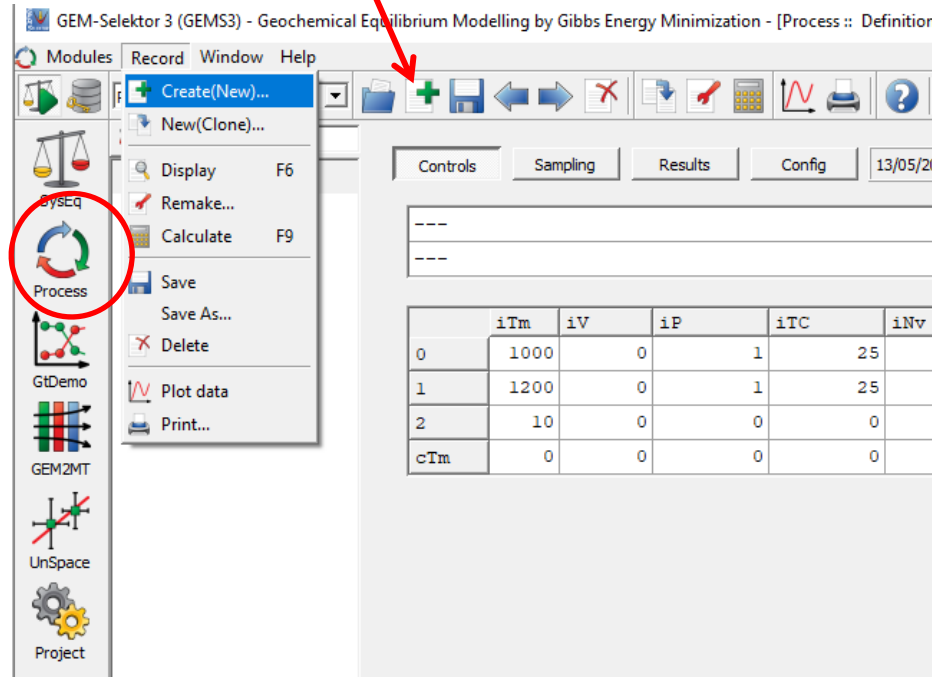
Phase/species	L	T ₃	On/Off
aq_gen	75	a	+
gas_gen	6	g	+
C3 (AF) S0.84H	2	s	+
CSHQ	6	s	+
ettringite-AlFe	2	s	-
ettringite-FeAl	2	s	-
monosulph-AlFe	2	s	-
monosulph-FeAl	2	s	-
straetlingite	2	s	+
ettringite	2	s	+
SO4_OH_AFm	2	s	+
OH_SO4_AFm	2	s	+
SO4_CO3_AFt	2	s	+
CO3_SO4_AFt	2	s	+
hydrotalc-pyro	2	s	+
MSH	2	s	+
Al (OH) 3am	1	s	+
Al (OH) 3mic	1	s	+
Gibbsite	1	s	-

Process file - hydration of PC + limestone

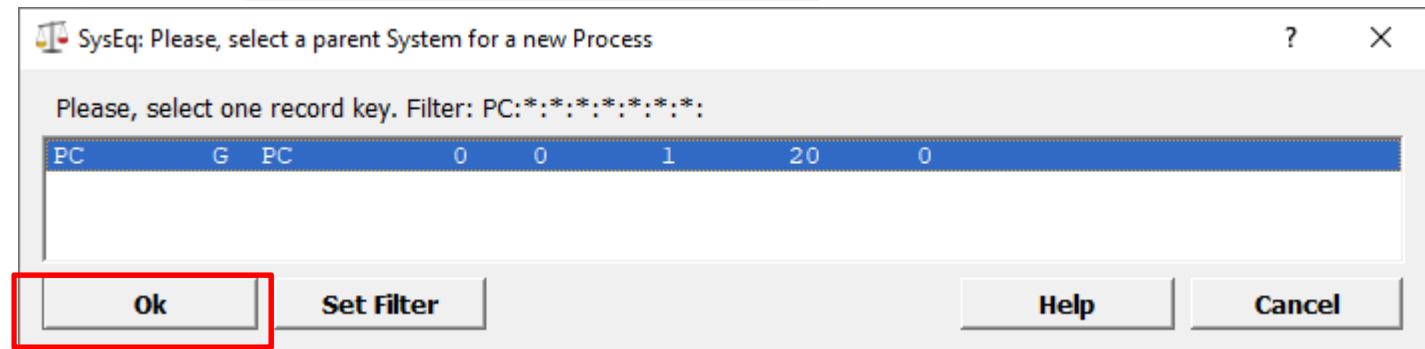
Create new process file

1.

or click here



Select parent file



Process file - hydration of PC + limestone

Process: Please, set a new record key

PC:G:PC:0:0:1:20:0:LS_mass:S

PC	Name of the modeling project
G	Thermodynamic potential to minimize {G}
PC	Name of the parent chemical system definition (CSD)
0	CSD (recipe) variant number <integer>
0	Volume of the system, dm3
1	Pressure, bar, or 0 for Psat(H2O)g
20	Temperature, C
0	Variant number for additional constraints
LS_mass	Name of this process simulation task
S	Process simulation mode code {P, S, L, G, T, R}

Ok Reset From List Help Cancel

project name

pressure

temperature

file name of process simulation

simulation type

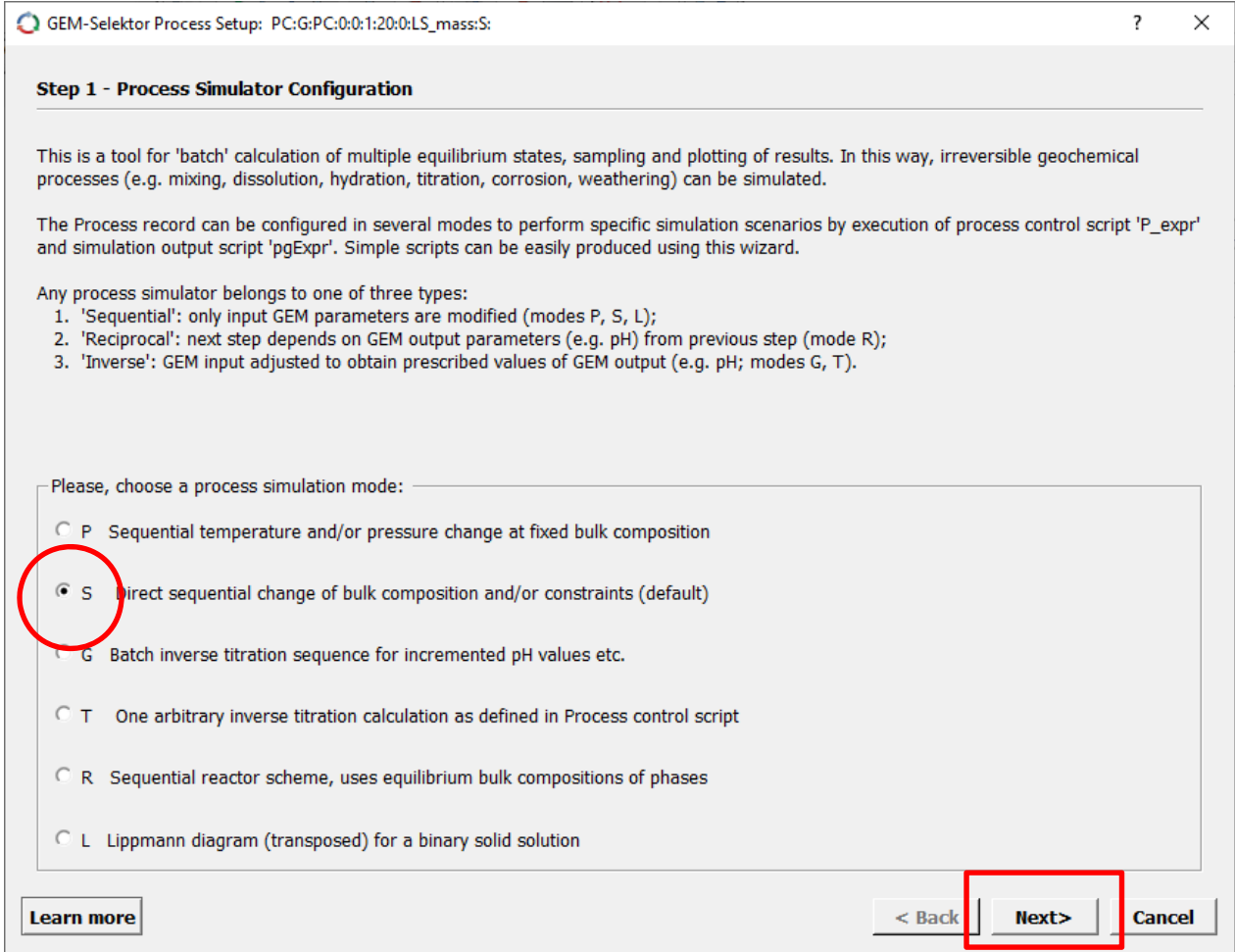
user input

Process file - hydration of PC + limestone

Choice of simulation type:

In the case of incremental limestone addition we directly change the bulk composition

→ **Sequential change of bulk composition**



GEM-Selektor Process Setup: PC:G:PC:0:0:1:20:0:LS_mass:S

Step 1 - Process Simulator Configuration

This is a tool for 'batch' calculation of multiple equilibrium states, sampling and plotting of results. In this way, irreversible geochemical processes (e.g. mixing, dissolution, hydration, titration, corrosion, weathering) can be simulated.

The Process record can be configured in several modes to perform specific simulation scenarios by execution of process control script 'P_expr' and simulation output script 'pgExpr'. Simple scripts can be easily produced using this wizard.

Any process simulator belongs to one of three types:

1. 'Sequential': only input GEM parameters are modified (modes P, S, L);
2. 'Reciprocal': next step depends on GEM output parameters (e.g. pH) from previous step (mode R);
3. 'Inverse': GEM input adjusted to obtain prescribed values of GEM output (e.g. pH; modes G, T).

Please, choose a process simulation mode:

- P Sequential temperature and/or pressure change at fixed bulk composition
- S Direct sequential change of bulk composition and/or constraints (default)
- G Batch inverse titration sequence for incremented pH values etc.
- T One arbitrary inverse titration calculation as defined in Process control script
- R Sequential reactor scheme, uses equilibrium bulk compositions of phases
- L Lippmann diagram (transposed) for a binary solid solution

[Learn more](#) < Back Next > Cancel

Process file - hydration of PC + limestone

Wizard available for process files

1. Adapt temperature and step size for stored individual calculations
2. Select PC and CaCO_3 (as we want to vary their relative amounts)
3. Select Aqua and O_2

GEM-Selektor Process Setup: PC:G:PC:0:0:1:20:0:LS-mass:S: ? X

Step 2 - Process Simulation Controls (click 'Next' to retain the old script)

	iTm	iV	iP	iTC	iNv	iTau	ipXi	iNu	ipH	ipe
From	1000	0	1	20	0	0	0	0.1	0	0
Until	1200	0	1	20	0	0	0	3.1	0	0
Start	1	0	0	0	0	0	0	0.1	0	0

Titration cNu (linear)
 Diagram logD vs x (linear)
 Titration cpXi logarithmic
 Diagram logKd vs log(m)

Linear titration and logD diagrams use the iNu iterator; logarithmic titration and logKd diagrams use ipXi. Titrations: select required titrants as items from 'Compos', 'DComp', 'IComp' or 'Phase' lists, optionally also select items from 'DC-lower' or 'DC-upper' to change metastability constraints.

To plot logD vs linear x (mole fraction) scale: (i) select minor then host end member from the 'DComp' list, (ii) select trace then host ion from the 'Molality' list. To plot logKd and isotherms vs log(molality) scale: (i) select trace then host compositions from the 'Compos' list; (ii) select trace then host elements from the 'Sorbed' list. In both cases, skip the next wizard page.

Compos	CaSO4	H2S	Mg3Si2O5(OH)4	NaOH
DComp	CaSO4_05H2O	H2SO4	MgCO3	O2
IComp	CaSiO3	HCl	MgCl2	PC
Phases	Fe2O3	HClO4	MgO	SO3
DC-lower	FeCO3	K2CO3	MgSO4	SWsaltSimp
DC-upper	FeO	K2O	Na2CO3	SiO2
Molality	FeOOH	K2SO4	Na2O	
Sorbed	FeS	KCl	Na2SO4	
	Gypsum	KOH	NaCl	
	H2	Mg(OH)2	NaClO4	

```
modC[J] =: cNu;
xa_{CaCO3} =: cNu * 1;
xa_{PC} =: cNu * 1;
```

We need to edit this later

Learn more < Back **Next>** Cancel

Process file - hydration of PC + limestone

Wizard available for GEM-Selektor Process Setup: PC:G:PC:0:0:1:20:0:LS_Mass:S: ?

1. Select solids: choose
2. **phM => mass (in g);**
=> we can adapt skript later

Step 3 - Selection of items to sample/plot (click "Next" without selecting anything to retain the old script)

Property	Item Selection		Sampling Script
Scalars	aq_gen	Ferrite C6AsH9	<pre> xp[J] =: J; yp[J][0] =: phM[{{CSHQ}}]; yp[J][1] =: phM[{{Portlandite}}]; yp[J][2] =: phM[{{C3(AF)S0.84H}}]; yp[J][3] =: phM[{{ettringite}}]; yp[J][4] =: phM[{{SO4_CO3_Aft}}]; yp[J][5] =: phM[{{CO3_SO4_Aft}}]; yp[J][6] =: phM[{{C4AsH16}}]; yp[J][7] =: phM[{{SO4_OH_AFm}}]; yp[J][8] =: phM[{{OH_SO4_AFm}}]; yp[J][9] =: phM[{{C4Ac0.5H12}}]; yp[J][10] =: phM[{{C4AcH11}}]; yp[J][11] =: phM[{{Calcite}}]; yp[J][12] =: phM[{{OH-hydrotalcite}}]; yp[J][13] =: phM[{{aq_gen}}]; </pre>
u	gas_gen	CA Aragonite	
ue	C3(AF)S0.84H	CA2 Calcite	
b	CSHQ	C2AH75 C3FH6	
Cb	straetlingite	C3AH6 C4FH13	
m_t	ettringite	CAH10 C3FS0.84H	
lgm_t	SO4_OH_AFm	C4AsH105 C3FS1.34H	
icM	OH_SO4_AFm	C4AsH12 C4Fc05H10	
Xa	SO4_CO3_Aft	C4AsH14 C4FcH12	
Xwa	CO3_SO4_Aft	C4AsH16 Dolomite-c	
phVol	hydrotalc-pyro	C4AsH9 Dolomite-c	
phM	MSH	Chabazite lime	
Fa	Al(OH)3am	ZeoliteP Portlandite	
bXa(aq_gen)	Al(OH)3mic	C2ASH55 Anhydrite	
bXa(gas_gen)	Kaolinite	C4AcH9 Gypsum	
bXa(C3(AF)S)	Graphite	C4Ac0.5H105 hemihydra	
bXa(CSHQ)	Mayenite	C4Ac0.5H12 Iron	
bXa(straetlin)	Belite	C4Ac0.5H9 Fe-carbona	
bXa(ettringit)	Aluminate	C4AcH11 Siderite	
bXa(SO4_OH)	Alite	C6AsH13 Magnetite	
bXa(SO4_AFm)			
bXa(OH_SO4)			
bXa(SO4_CC)			
bXa(CO3_SC)			

Masses of phases (in grams) in equilibrium

Learn more < Back **Next>** Cancel

We need to edit this later

Process file - hydration of PC + limestone

Numerical settings of process simulation

GEM-Selektor Process Setup: PC:G:PC:0:0:1:20:0:LS_mass:S

Step 4 - Important data object dimensions

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

Number of steps

2 columns for input constituents of bulk composition (PC components, limestone)

number of y columns in output file (here = total amount of expected phases = 14)

number of x columns in output file (here = amount of limestone)

Optional entries of experimental data possible to compare with calculations

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

Allocation of optional data vectors

CSD variant # ('vTm') Volume V, l ('vV') Pressure P, bar ('vP')

Temperature T ('vT') Constraints # ('vNV')

Process extent pXi ('vpXi')

Kinetic parameters ('vKin')

Time Tau ('vTau')

Learn more < Back **Next>** Cancel

Convenient to «overestimate» because maybe more phases occur than expected

Process file - hydration of PC + limestone

Additional settings

GEM-Selektor Process Setup: PC:G:PC:0:0:1:20:0:LS_mass:S: ? X

Step 5 - Additional options

On this page, some options of the Process simulator operation can be changed (for specific cases).

Optional modes of operation

- Use 'P_expr' simulation control script (can be turned off in P simulation mode)
- Save generated SysEq records to the project data base (always saved in G and T modes)
- Use time dependent calculations and plotting mode (for kinetics simulations, reserved)
- Use Smart Initial Approximation of GEM IPM algorithm for faster calculations (on your discretion)
- Use a stepwise mode of Process simulation (for troubleshooting purposes)

The 'P_expr' simulation control script must be used in most cases except the P mode (e.g., if temperature is changed using ITC iterator, but the system recipe remains constant).

Saving process-generated SysEq records may be necessary for subsequent sampling of results by GtDemo module or for troubleshooting, but may dramatically increase the size of project database. This flag has no effect on reciprocal and inverse titrations, where optimized SysEq records are always saved.

[Learn more](#)

Save the equilibria of each step independently

⇒ **Good to check each calculations**

⇒ **But can make files big**

⇒ **Can also be turned off**

Process file - hydration of PC + limestone

Additional settings

GEM-Selektor Process Setup: PC:G:PC:0:0:1:20:0:LS_mass:S: ? X

Step 6 - Final settings and comments

Optional

Set here the number of links to SDref source of data and bibliography records (default 0)

After you click "Finish":

- (1) 'Controls' page of the Process window will appear. Fill out comments in 'PName' and 'PNote' lines. Check the process iterators for correct ranges and increments.
- (2) Modify the simulation control script 'P_expr', if necessary. Some example scripts can be found in help pages or via the 'Help' 'Scripts' menu command. Check also the sampling script in 'Sampling' page of the process window.
- (3) Click on 'Calculate' toolbar button to start the simulation; for the first time, do not use the graphic output. If error messages appear, check and fix the scripts or iterators and try the calculation again. After the simulation has finished, look at sampled results in 'xp' and 'yp' fields on 'Results' page (can be copy-pasted to commercial spreadsheets).
- (4) Check and edit the axis and ordinate (plot) names, and click on the 'Plot data' toolbar button to see a customizable Graph Dialog. To plot experimental data over simulated curves (for visual fitting), close the Graph dialog, enter data into xEp and yEp fields on 'Results' page, then open the Graph dialog again and customize the plot.

[Learn more](#) < Back **Finish** Cancel

Process file - hydration of PC + limes

cNu: running number
 can be used for various calculation:
 here: fraction CaCO_3

The screenshot shows the GEMS software interface. At the top, there's a toolbar and a status bar. Below that, there are tabs for 'Controls', 'Sampling', 'Results', and 'Config'. The 'Controls' tab is active, showing a text area with 'addition of limestone to PC' and 'GEMS tutorial'. Below this is a table of control parameters:

	iTm	iV	iP	temp	iTC	iNv	iTau	ipXi	iNu	ipH	ipe
0	1000	0	0	1	20	0	0	0	* -0.6	0	0
1	1200	0	0	1	20	0	0	0	10	0	0
2	1	0	0	0	0	0	0	0	0.2	0	0
cTm	1053	0	0	1	20	0	0	0	10	0	0

Below the table is a text editor with the following content:

```

$ amount of limestone, PC contains already 0.6 g CaCO3,
$ will written in 1st column; cNu = calculated number
modC[J][0] =: cNu;
xa_{{CaCO3}} =: modC[J][0];

$ amount of PC
xa_{{PC}} =: 100-modC[J][0];

$PC written in 2nd column;
modC[J][1] =: 100-modC[J][0];
    
```

On the right side of the text editor, there is a table with columns 'modC[0]' and 'mo'.

	modC[0]	mo
7		0
8		0
9		0
10		0
11		0
12		0
13		0
14		0
15		0

Start value
 End value
 Step size
 of indices for the stored
 individual single files

Modify text to
 (\$ = comment)

When finished
Click somewhere
(outside active box)
 => Else GEMS might ignore changes

project description

pressure temp

Start value
 End value
 Step size
 cNu

* We start at -0.6 as our cement contains already 0.6% CaCO_3 , and we also want to model in this example the hydrates without any limestone

Process file - hydration of PC + limestone

describes output of calculated data as table and graph

Controls | **Sampling** | Results | Config | 13/05/2019, 13:41

NeIt 9999 0 Next 1 I 0 J 0 Jp 0

pSTkey

cTau 0 cpXi 0 cXi

cpH 0 cpe 0 cEh

```

$ x-axis: fraction of calcite in cement
$ PC contains already 0.6% CaCO3
xp[J] =: xa_{{CaCO3}}+0.6;
$
$ y-axis in g per 100g unhydrated cement
yp[J][0] =: phM[{{CSHQ}}];
yp[J][1] =: phM[{{Portlandite}}];
yp[J][2] =: phM[{{C3(AF)S0.84H}}];
yp[J][3] =: phM[{{ettringite}}]+phM[{{SO4_CO3_AfT}}]+phM[{{CO3_SO4_AfT}}];
yp[J][4] =: 0;
yp[J][5] =: 0;
yp[J][6] =: phM[{{C4AsH16}}]+phM[{{SO4_OH_AfM}}]+phM[{{OH_SO4_AfM}}];
yp[J][7] =: 0;
yp[J][8] =: 0;
yp[J][9] =: phM[{{C4Ac0.5H12}}];
yp[J][10] =: phM[{{C4AcH11}}];
yp[J][11] =: phM[{{Calcite}}];
yp[J][12] =: phM[{{OH-hydrotalcite}}];
yp[J][13] =: phM[{{aq_gen}}];
    
```

**Columns yp[J][0], yp[J][1], ...
if you change order, change also the headings below**

pX_Nam limestone

pLnam	CSHQ	Portlandite	C3(AF)S0.84H	ettringite	--	---
-------	------	-------------	--------------	------------	----	-----

Definition of x-axis: 2 equivalent options

$xp[J] =: xa_{\{CaCO3\}}+0.6;$

$xp[J] =: modC[J][1]+0.6;$

Definition of output on a mass basis, e.g. C-S-H

$yp[J][0] =: phM[{{CSHQ}}];$

Ettringite (summarized):

$yp[J][3] =: phM[{{ettringite}}]$
 $+ phM[{{CO3_SO4_AfT}}] +$
 $phM[{{SO4_CO3_AfT}}];$

Mass pore solution:

$yp[J][13] =: phM[{{aq_gen}}];$

Process file - hydration of PC + limestone

In case the convergence error occurs ...

GEM-Selektor 3 (GEMS3) - Geochemical Equilibrium Modelling by Gibbs Energy Minimization - [Project :: Numerical and Configuration Settings]

Modules Record Window Help

EqDemc

PC:*

1 PC

PLists Controls Settings Config 27/03/2020, 09:40

Pa_SPP Tolerances and controls: GEMSGUI v.3.7.0 and GEMS3K v.3.7.0

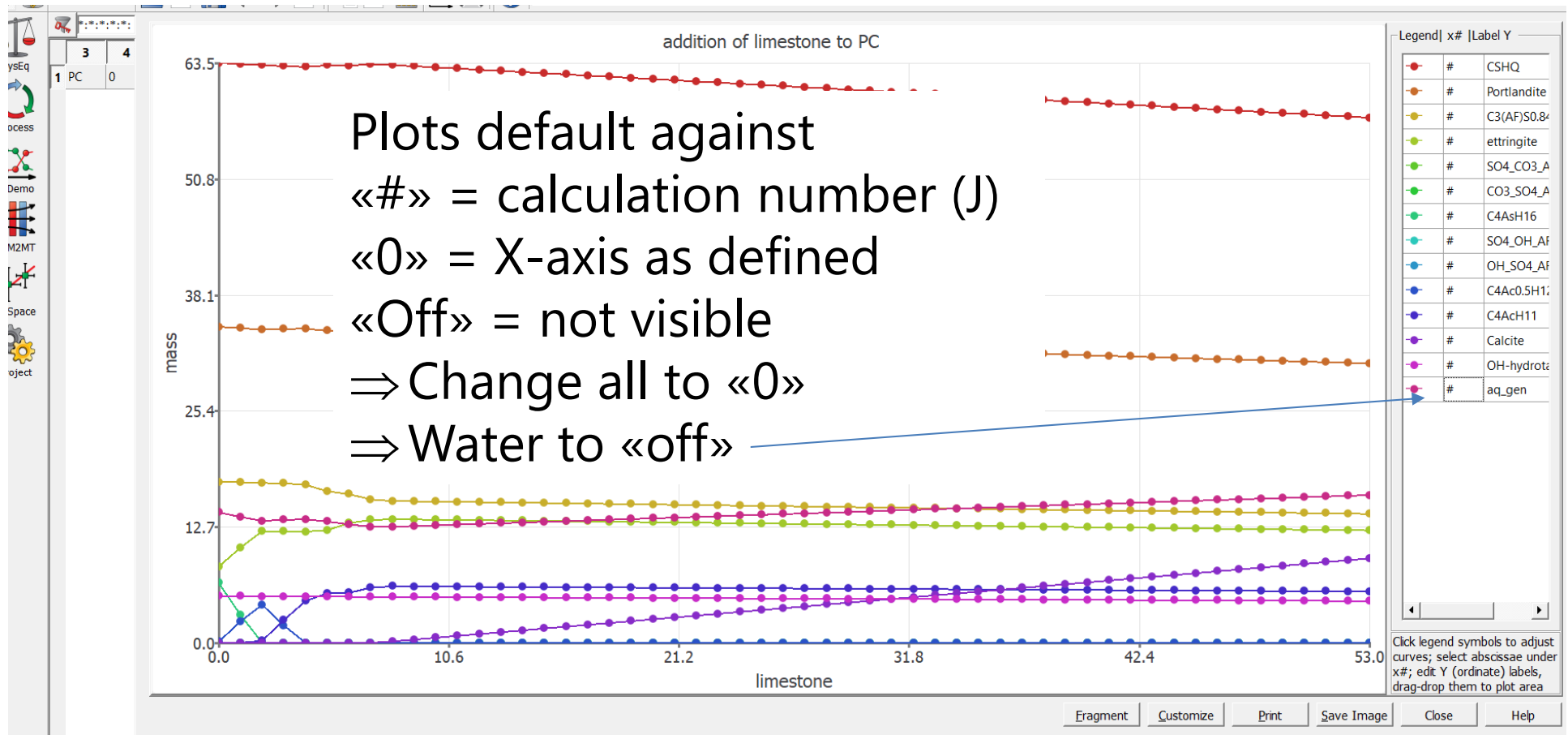
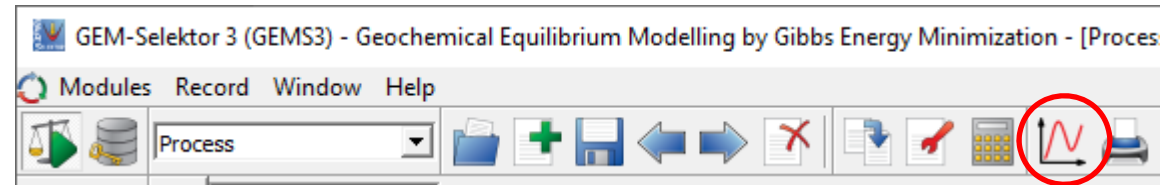
Pa_DK	1e-005	Pa_IIM	7000	Pa_LLG	30000	Pa_AG	1	Pa_DGC	0.01
Pa_DHB	1e-013	Pa_DFY	1e-005	1e-005	1e-005	1e-005	1e-005	1e-005	1e-006
Pa_DB	1e-017	Pa_DS	1e-020	Pa_XMI	1e-013	1e-013	1e-033	1e-020	1e-005
Pa_EPS	1e-010	0.001	Pa_GAN	1	1000	0.001	Pa_DG	1000	
Pa_DPV	130	1	0	Pa_DF	0.01	0.01	Pa_DNS	12.05	
Pa_PE	1	Pa_PC	2	Pa_PRD	2	-5	1	Pa_DKI	1e-010

Project

Process file - hydration of PC + limestone

1. open graph

2. label graph



Process file - hydration of PC + limestone

Modify the graph as you prefer: example

Customize Graph: addition of limestone to PC

Graph

0 - Lines/Symbols

addition of limestone to PC

Axis Setup

Abscissa grid 5 limestone Add unit of x-axis

Ordinate grid 5 mass Add unit of y-axis

Graph x: 0 10

y: 0 0

Fragment x: 0 0

y: 0 0

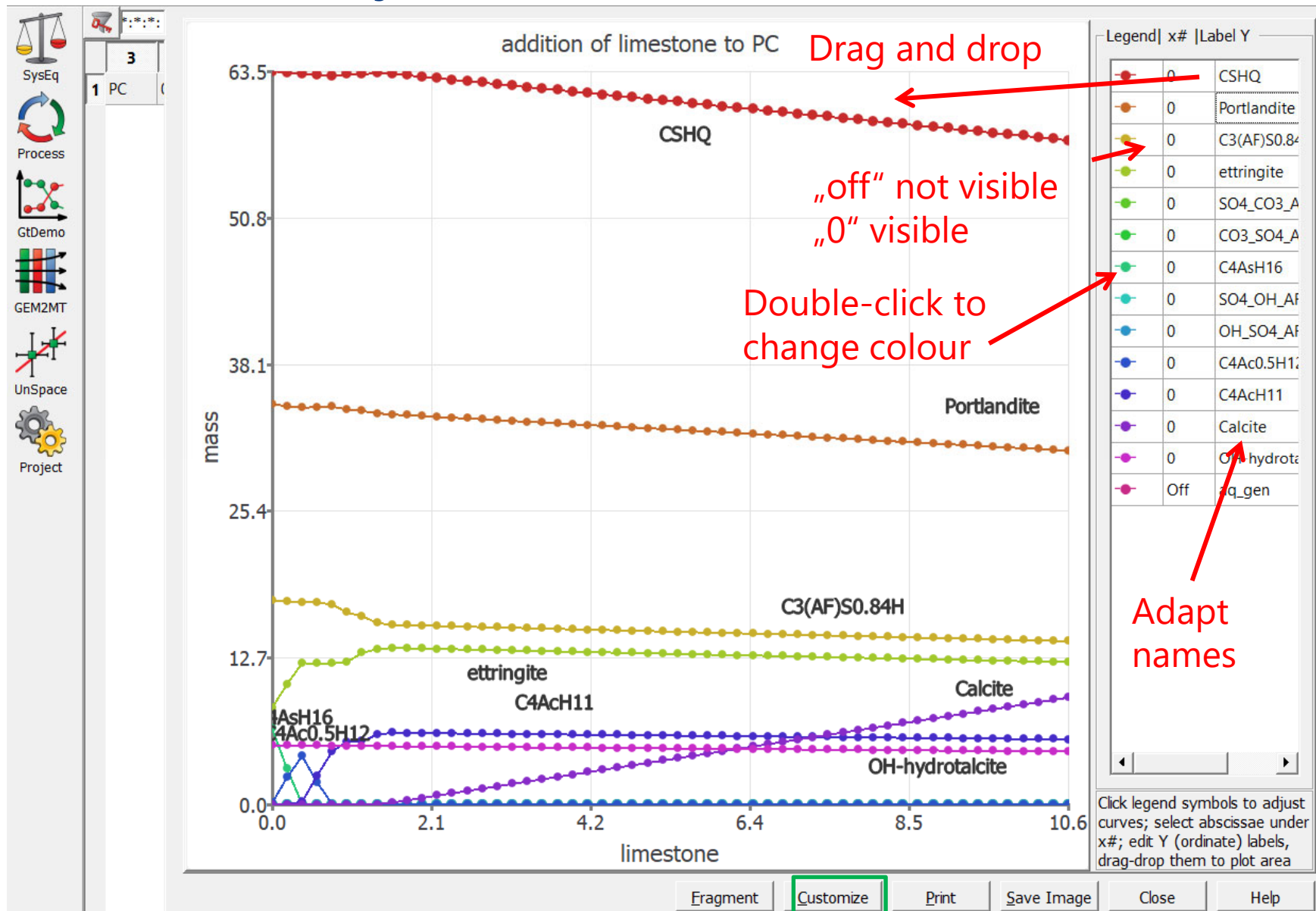
Label font: Change Font... Sans Serif, 14, -1, 5, 50, 0, 0, 0, 0

Background Change Color...

OK Cancel Apply Help

Min - max
0 - 0: autoscale

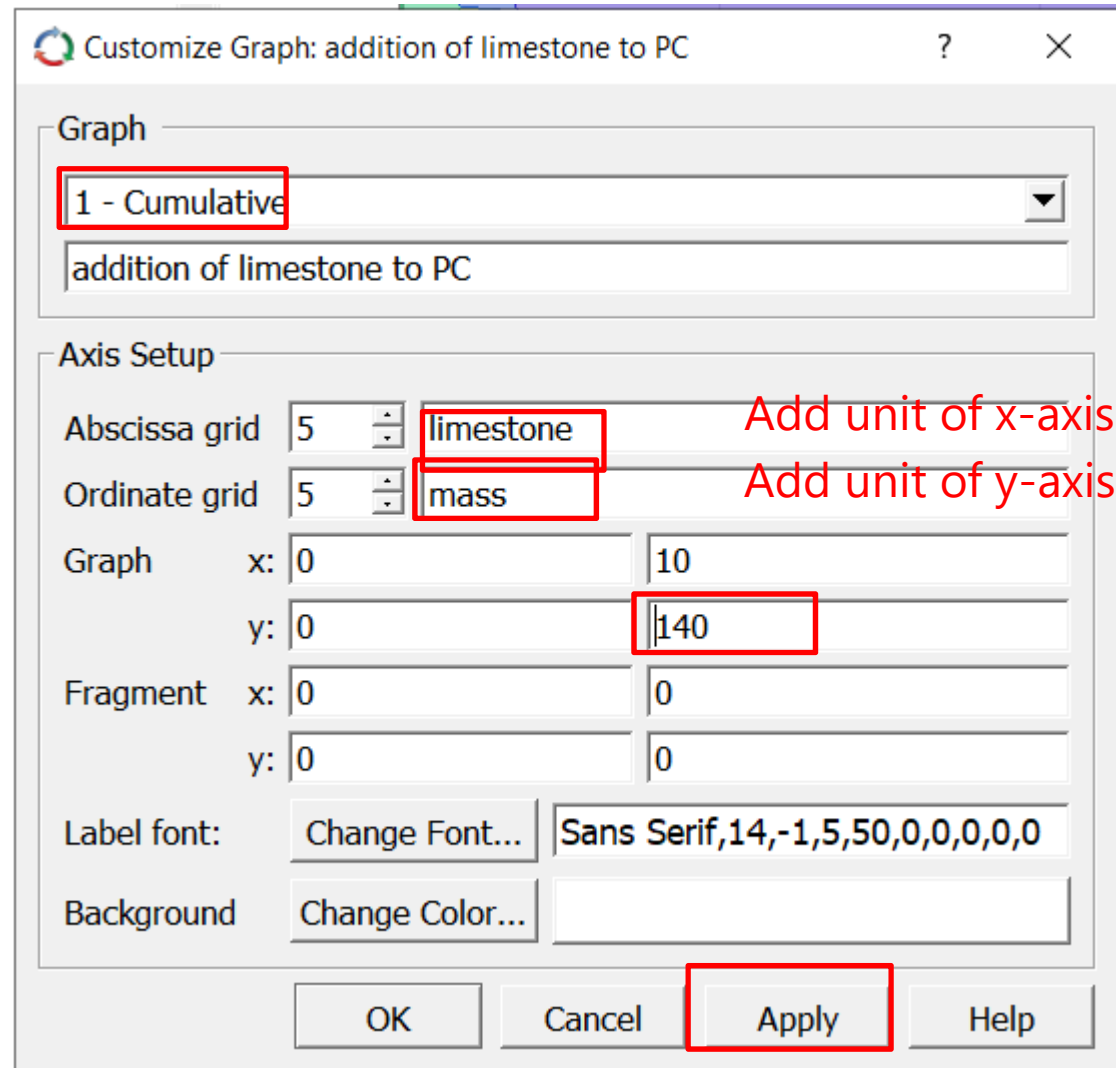
Process file - hydration of PC + limestone



To adapt scale / axis-labelling

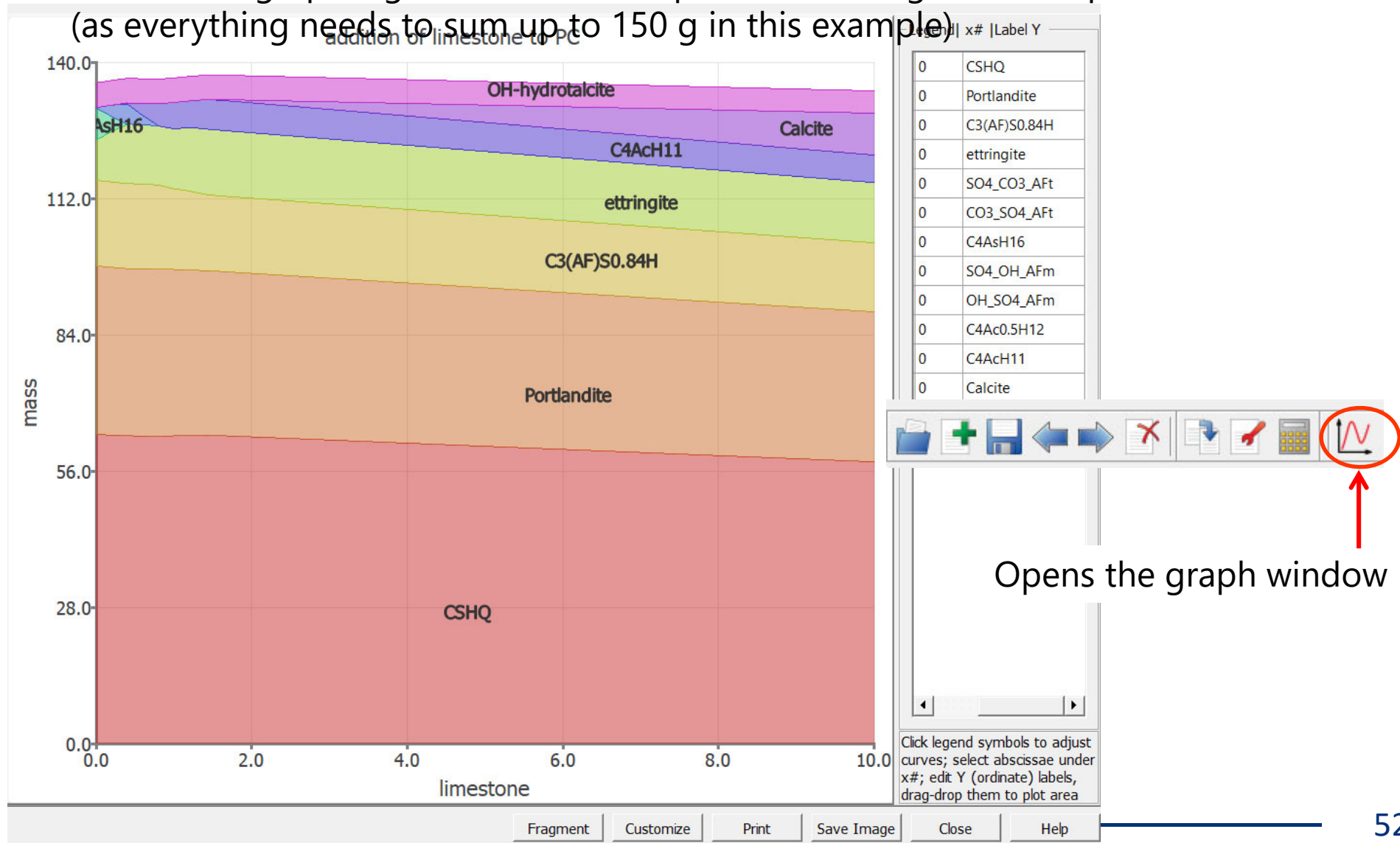
Process file - hydration of PC + limestone

Modify the graph as you prefer: example



Process file - hydration of PC + limestone

Cumulative graph – good to check if a phase is missing in the output (as everything needs to sum up to 150 g in this example)



Process file - hydration of PC + limestone

Numerical output

Possibility of simple copy and paste of the data into other programs e.g. Excel or Origin

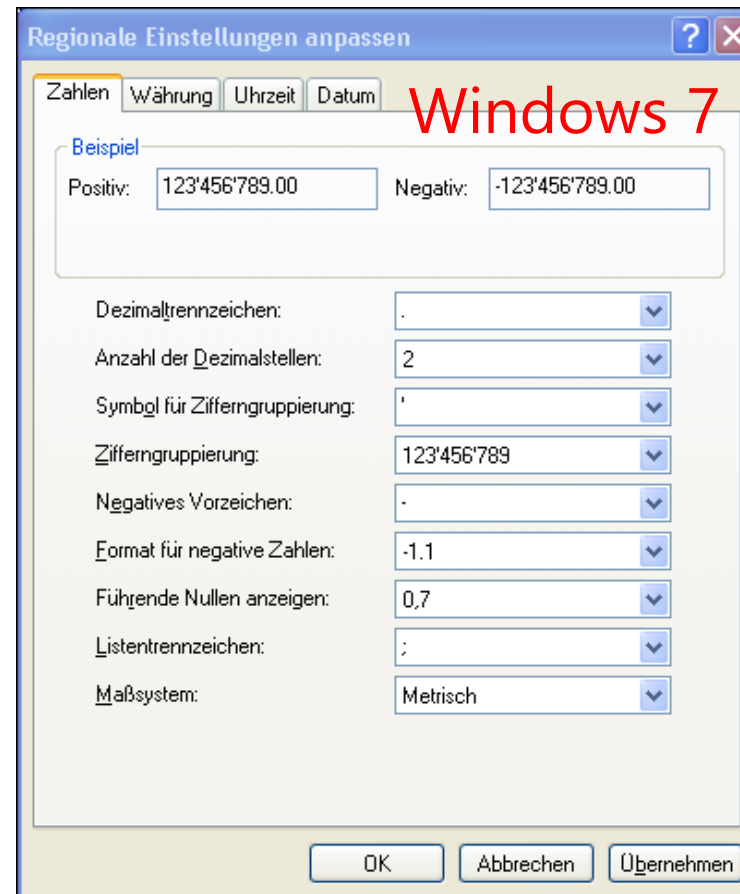
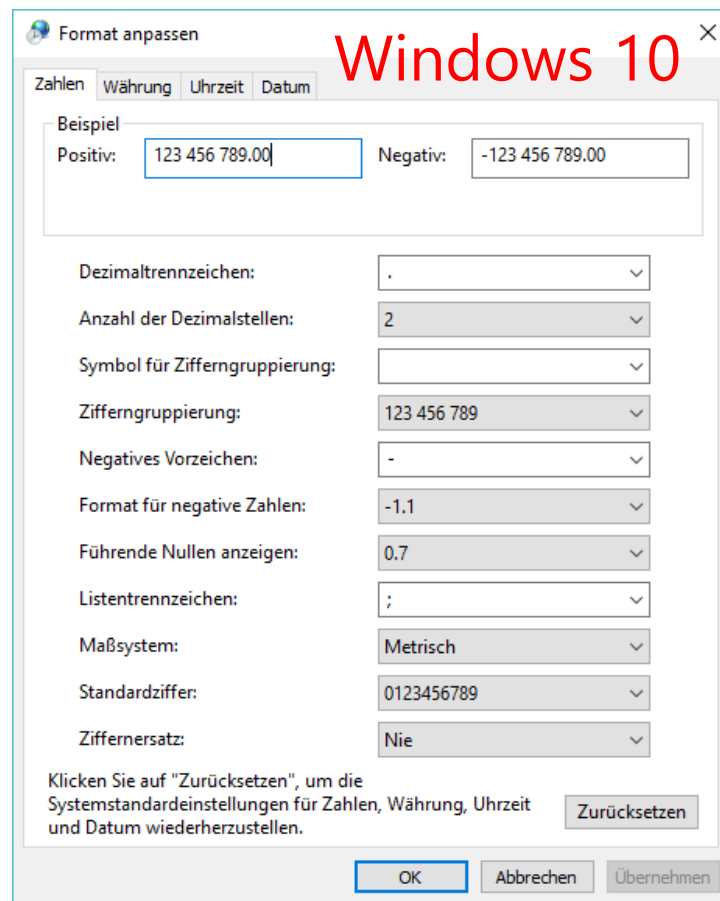
Controls		Sampling		Results		Config		27/03/2020, 13:22		
addition of limestone to PC						pY_Nam	mass			
pX_Nam	limestone	CSHQ	Portlandite	C3 (AF) S0.84H	ettringite	SO				
0	0	63.479529	34.639764	17.577815	8.3255595					
1	0.2	63.354146	34.477327	17.542837	10.388585					
2	0.4	63.247179	34.325451	17.464707	12.194956					
3	0.6	63.120692	34.402836	17.429852	12.170592					
4	0.8	63.049524	34.424192	17.266221	12.144797					
5	1	63.2112	34.1883	16.56103	12.313768					
6	1.2	63.205746	34.052285	16.245849	13.082729					
7	1.4	63.312215	33.848959	15.669432	13.424362					
8	1.6	63.246478	33.743932	15.493466	13.502994					
9	1.8	63.118507	33.674382	15.462198	13.475827					
10	2	62.990537	33.604835	15.430939	13.448654					
11	2.2	62.862567	33.535293	15.399679	13.421481					
12	2.4	62.734593	33.465758	15.368418	13.39431					
13	2.6	62.606625	33.396221	15.337159	13.367136					
14	2.8	62.478656	33.326691	15.305898	13.339964					
15	3	62.350689	33.257162	15.274641	13.31279					
16	3.2	62.222721	33.187638	15.24338	13.285618					
17	3.4	62.094754	33.118119	15.21212	13.258446					
18	3.6	61.966785	33.048604	15.180861	13.231273					
19	3.8	61.838819	32.979092	15.149598	13.204102					
20	4	61.710855	32.909582	15.118339	13.176928					
21	4.2	61.582892	32.840076	15.087077	13.149757					

Process file - hydration of PC + limestone

Copying data to or from Excel files

We need **decimal points**,
not commas !

*Change your excel to use „ . “
as a decimal point
in the control panel of Windows*



Process file - hydration of PC + limestone

GEM-Selektor 3 (GEMS3) - Geochemical Equilibrium Modelling by Gibbs Energy Minimization - [EqStat: Single Thermodynamic System in Project PC]

Modules Record Data Calculate View Print Window Help

SingleSystem

PC:****:****:

	3	4	5	6	7	8
1	PC	0	0	1	20	0
2	PC	1000	0	1	20	000
3	PC	1001	0	1	20	000
4	PC	1002	0	1	20	000
5	PC	1003	0	1	20	000
6	PC	1004	0	1	20	000
7	PC	1005	0	1	20	000
8	PC	1006	0	1	20	000
9	PC	1007	0	1	20	000
10	PC	1008	0	1	20	000
11	PC	1009	0	1	20	000
12	PC	1010	0	1	20	000
13	PC	1011	0	1	20	000
14	PC	1012	0	1	20	000
15	PC	1013	0	1	20	000
16	PC	1014	0	1	20	000
17	PC	1015	0	1	20	000
18	PC	1016	0	1	20	000
19	PC	1017	0	1	20	000
20	PC	1018	0	1	20	000

Input: System Definition | Results: Equilibrium State

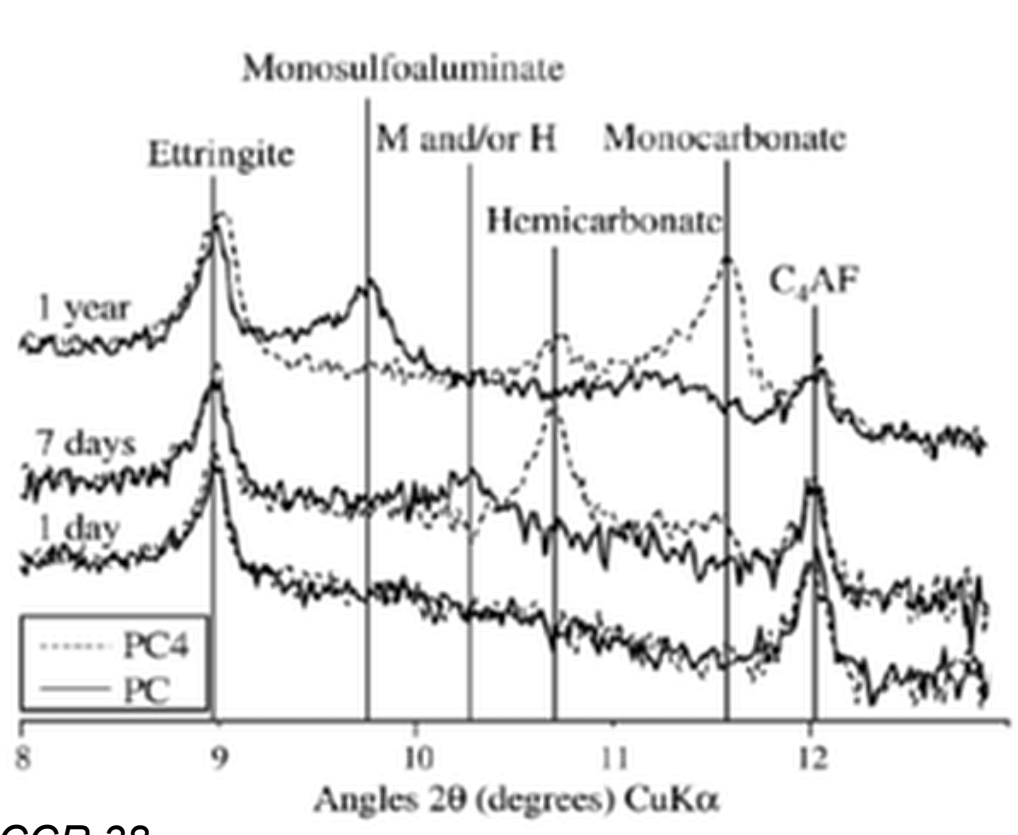
Phase/species	L	T	On/	UC	Add to BC	UG	G0
aq_gen	75	a	+	g	0	J	0
gas_gen	6	g	+	g	0	J	0
C3 (AF) S0.84H	2	s	+	g	0	J	0
CSHQ	6	s	+	g	0	J	0
ettringite-AlFe	2	s	-	g	0	J	0
ettringite-FeAl	2	s	-	g	0	J	0
monosulph-AlFe	2	s	-	g	0	J	0
monosulph-FeAl	2	s	-	g	0	J	0
straetlingite	2	s	+	g	0	J	0
SO4_OH_AFm	2	s	+	g	0	J	0
OH_SO4_AFm	2	s	+	g	0	J	0
SO4_CO3_AFt	2	s	+	g	0	J	0
CO3_SO4_AFt	2	s	+	g	0	J	0
MSH	2	s	+	g	0	J	0
Al(OH)3mic	1	s	+	g	0	J	0
Gibbsite	1	s	-	g	0	J	0
Kaolinite	1	s	+	g	0	J	0
Graphite	1	s	+	g	0	J	0
Mayenite	1	s	+	g	0	J	0
Belite	1	s	+	g	0	J	0
Aluminate	1	s	+	g	0	J	0

a record of the equilibrium phase assemblage at each step is automatically saved

it can be assessed individually (e.g. to search for "missing phases" in the output)

Background: Limestone addition to PC

Formation of monosulfoaluminate in carbonate free paste, whereas monocarboaluminate+Aft are predominant in calcite blended paste

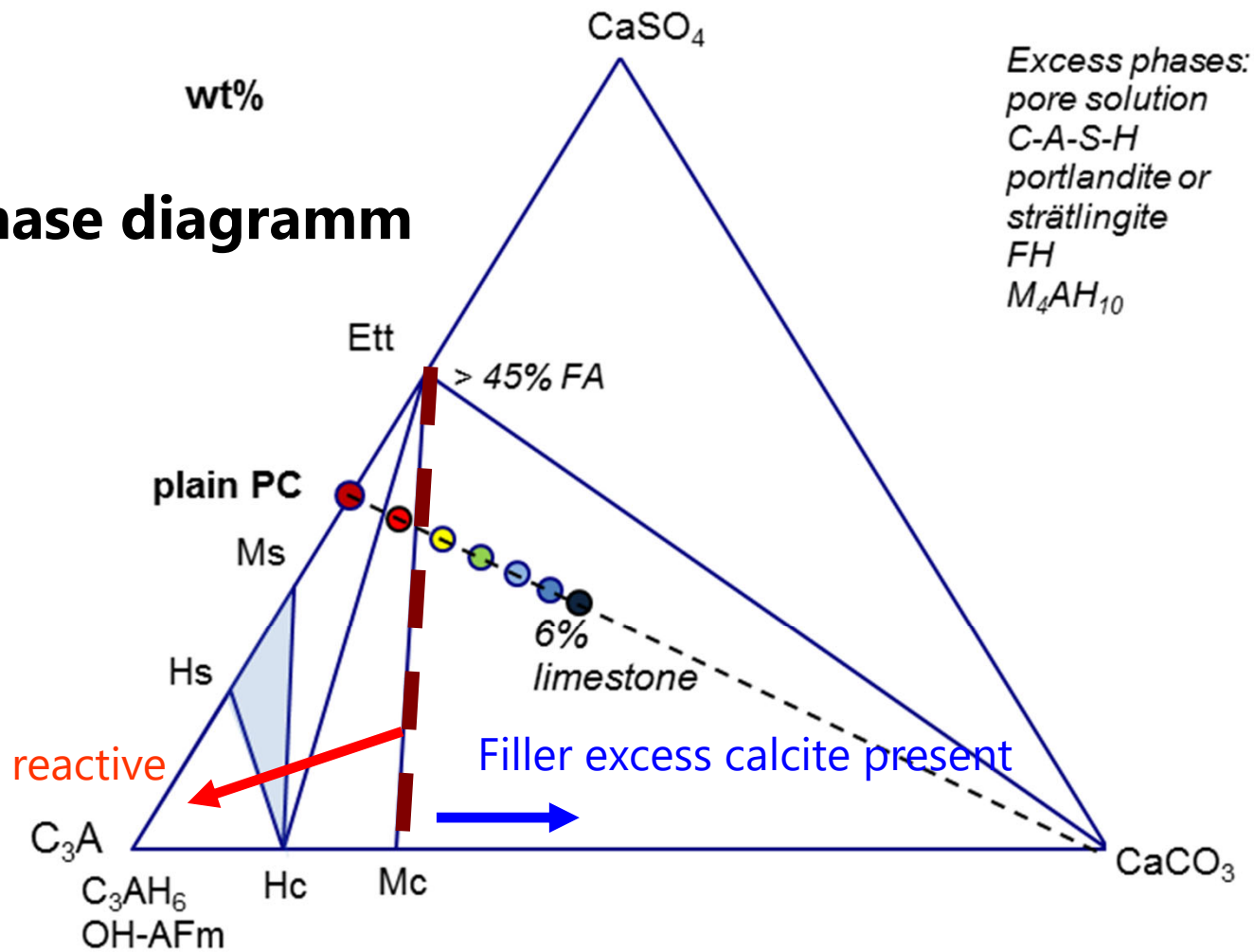


Lothenbach et al 2008, CCR 38

Good agreement between experiments and calculations

Background: Limestone addition to PC

Phase diagramm



Tutorial – process: hydration of Portland cement

Hydration of Portland cement

- 1) Hydration of PC - single system
 - 2) Influence of limestone on hydration of PC – process file
 - 3) Mass based -> volume based output
 - 4) Influence of fly ash on hydration of PC – process file
- Guided tutorial
- Individual work

Process file - hydration of PC + limestone

The past example has shown that adding limestone causes significant mineralogical changes during cement hydration.

While these changes affect the qualitative composition of the phase assemblages they also affect the quantities of phases present.

Thus an influence on the specific volumes of the hydrated phases in dependence of the limestone content is likely.



Modification of the existing process to plot specific volumes of the individual phases present in the chosen example

Process file - hydration of PC + limestone

Example calculation of volume changes:

Modification of the existing process to plot specific volumes of the individual phases present in the chosen example

Calculation of volumes is based on individual molar volumes of each phase included in the database

Ettringite	
Ca6Al2(SO4)3(OH)12(H2O)26	
MO	1255.11
Zz	0
ab	---
V0d	70.703
G0d	-15205936.09
H0d	-17535007.5
S0d	1900
Cp0d	2174.36
PrTr	1
LamST	---
BetAlp	---
Lothenbach_ea:2007:pap:	logK -44.9; S
Ederova_ea:1979:pap:	Cp
Taylor:1997:book:	V0 (dens 1775 kg/m3)

V0d [0,0] : Molar volume V0 of Dependent Component at standard state (J/bar)

For example ettringite:

Theor. density: 1.775 g/cm³ (derived from fitted unit cell size)

Molar volume

$$= 1255.11 \text{ g/mol} / 1.775 \text{ g/cm}^3 = 707 \text{ cm}^3/\text{mol}$$

$$1 \text{ cm}^3/\text{mol} = 10^{-1} \text{ J/bar} \rightarrow \underline{70.7 \text{ J/bar}}$$

Process file - hydration of PC + limestone

Modification of the existing process to plot specific volumes of the individual phases present in the chosen example

Hints:

- Clone “old” process (ensure that you are in process mode) and save it under a different name (suggested name: LS_Vol).
- Select same parent system.
- Only change the output part of the process file to calculate volume instead of mass.
example:

mass:

`yp[J][0] =: phM[{{CSHQ}}];`

volume:

`yp[J][0] =: phVol[{{CSHQ}}];`

- **Efficient: copy to word and use “replace”** `yp[J][0] =: Xa[{{CSHQ}}]; => Moles`
- Change y-axis labelling to cm³/100g and make a cumulative plot.

Process file - hydration of PC + limestone

PC:G:PC:0:0:1:20:0:LS_Vol:S:

Controls	Sampling	Results	Config	13/05/2019, 15:59
----------	----------	---------	--------	-------------------

NeIt	9999	54	Next	0	I	0	J	53	Jp	53
------	------	----	------	---	---	---	---	----	----	----

pSTkey	PC:G:PC:0:0:1:20:0:	cTm	1053	cNV	0
--------	---------------------	-----	------	-----	---

cTau	0	cpXi	0	cXi	1	cNu	10
------	---	------	---	-----	---	-----	----

cpH	0	cpe	0	cEh	0	cT	293.15
-----	---	-----	---	-----	---	----	--------

```

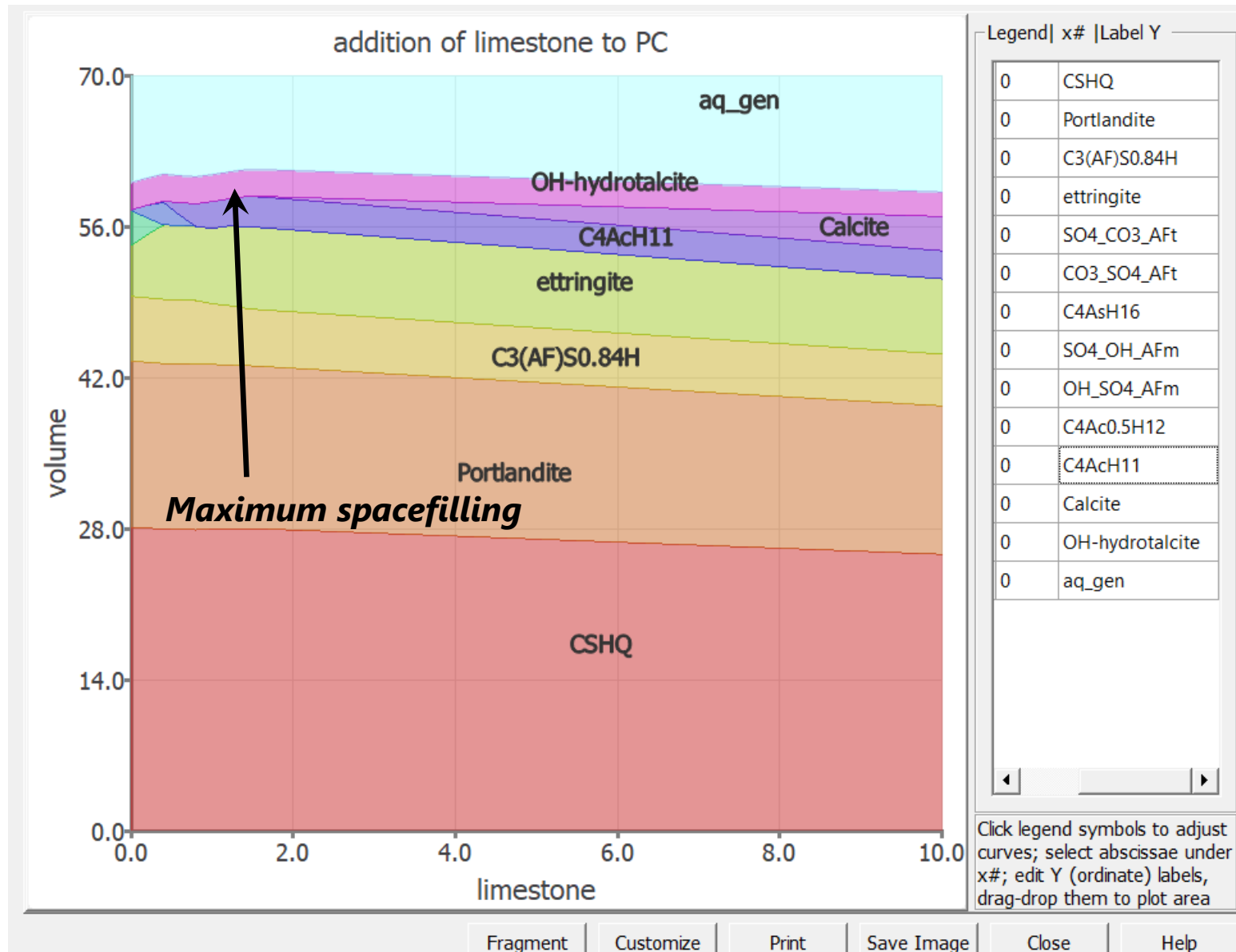
$ x-axis: fraction of calcite in cement
$ PC contains already 0.6% CaCO3
xp[J] =: xa_{{CaCO3}}+0.6;
$
$ y-axis in g per 100g unhydrated cement
yp[J][0] =: phVol[{{CSHQ}}];
yp[J][1] =: phVol[{{Portlandite}}];
yp[J][2] =: phVol[{{C3(AF)S0.84H}}];
yp[J][3] =: phVol[{{ettringite}}]+phVol[{{SO4_CO3_AFt}}]
+phVol[{{CO3_SO4_AFt}}];
yp[J][4] =: 0;
yp[J][5] =: 0;
yp[J][6] =: phVol[{{C4AsH16}}]+phVol[{{SO4_OH_AFm}}]+phVol[{{OH_SO4_AFm}}];
yp[J][7] =: 0;
yp[J][8] =: 0;
yp[J][9] =: phVol[{{C4Ac0.5H12}}];
yp[J][10] =: phVol[{{C4AcH11}}];
yp[J][11] =: phVol[{{Calcite}}];
yp[J][12] =: phVol[{{OH-hydrotalcite}}];
yp[J][13] =: phVol[{{aq_gen}}];

```

yp[J][0] =: phVol[{{CSHQ}}];

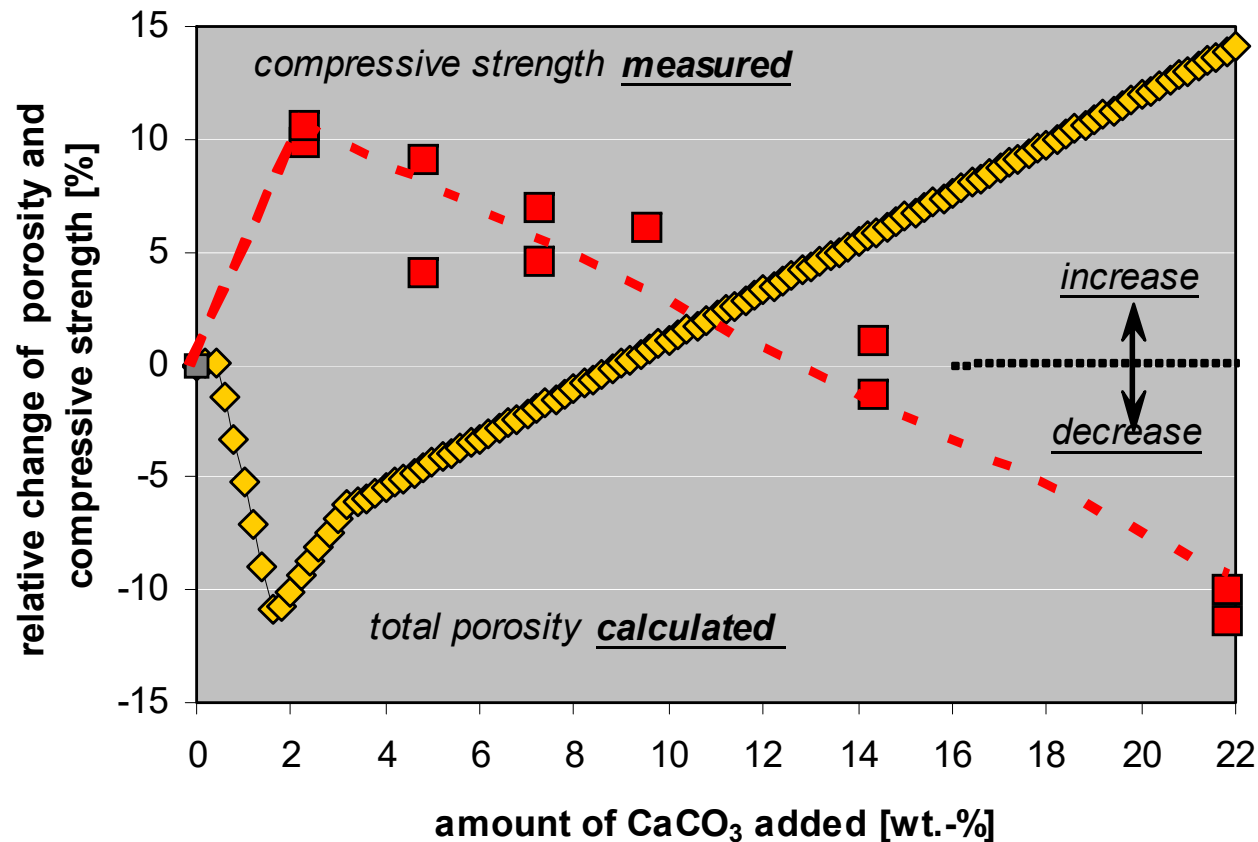
Efficient:
copy to word and
use "replace"
Copy back

Process file - hydration of PC + limestone



Process file - hydration of PC + limestone

Possible Links: Thermodynamics vs. engineering properties



one example of a good correlation between predicted changes of relative porosity and measured compressive strength

Process file - hydration of PC + limestone

Example calculation of pore solution composition:

- Clone “old” process (ensure that you are in process mode) and save it under a different name (suggested name: LS_sol).
- Select same parent system.
- Only change the output part of the process file to calculate ionic concentrations. Use the recipe wizard.
- Plot aqueous composition as total molality [mmol/kg] and pH

Aqueous composition:

this example 

yp[J][0] =: **m_t**{Ca}; *total concentration (as measured e.g. by ICP-OES or IC)*

yp[J][0] =: **lgm_t**{Ca}; *log total concentration (as measured e.g. by ICP-OES or IC)*

yp[J][0] =: **my**{Ca+2}; *species concentrations*

yp[J][0] =: **10^lga**{Ca+2}; *species activity (as measured by ion selective electrode)*

yp[J][0] =: **pH**; *gives pH ! Very sensitive to temperature*

yp[J][0] =: **IS**; *ionic strength*

yp[J][0] =: **my**{OH-}; *hydroxide concentration (molal)*

Process file - hydration of PC + limestone

Controls		Sampling		Results		Config		27/03/2020, 13:55		
NeIt	9999	0	Next	1	I	0	J	0	Jp	0
pSTkey	PC:G:PC:0:0:1:20:0:							cTm	10	
cTau	0		cpXi	0		cXi	1		cNu	
cpH	0		cpe	0		cEh	0		cT	


```

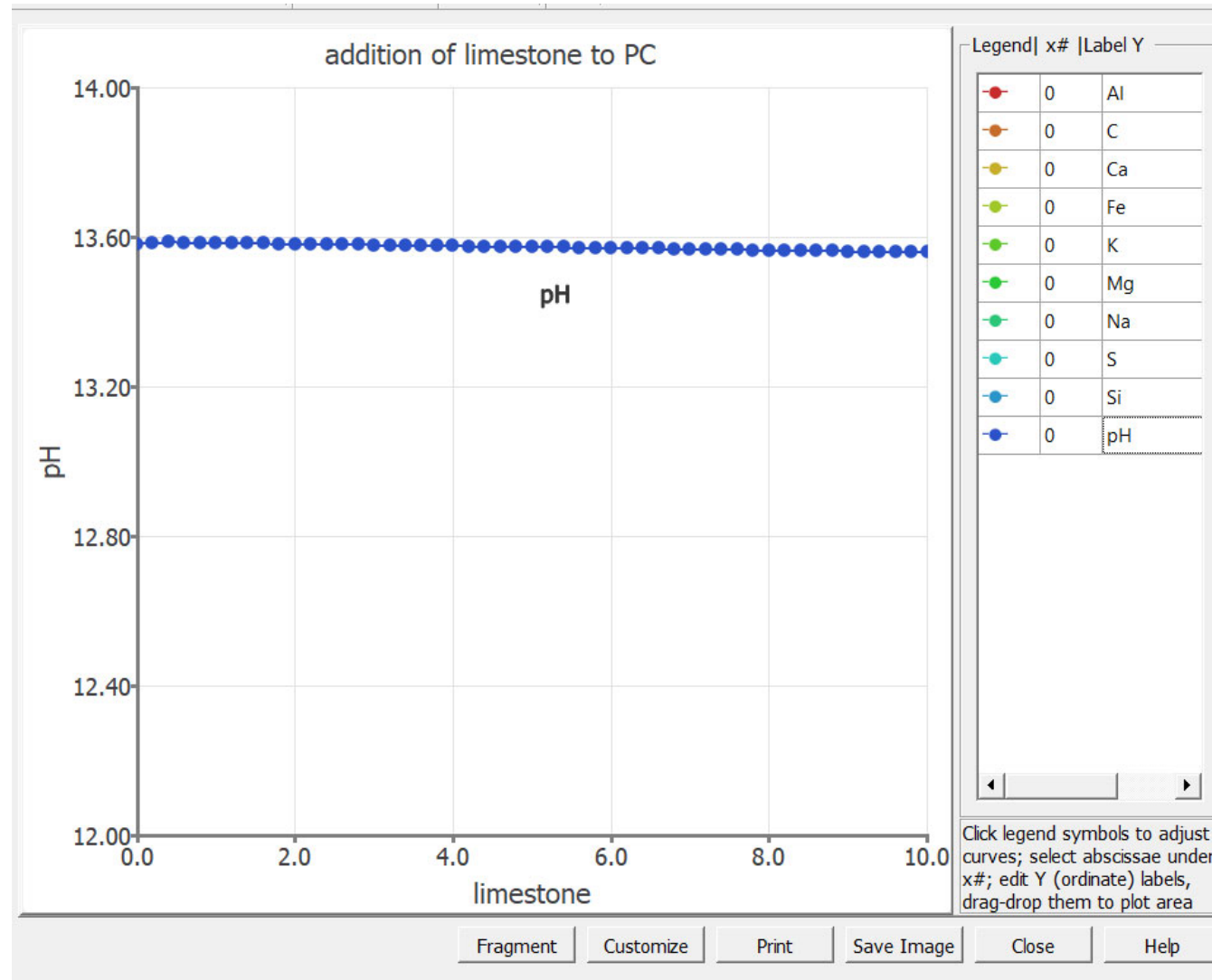
$$x axis: total fraction of CaCO3 in cement
$PC contains already 0.6 wt%
xp[J] =: xa_{{CaCO3}}+0.6;

yp[J][0] =: lgm_t{{Al}};
yp[J][1] =: lgm_t{{C}};
yp[J][2] =: lgm_t{{Ca}};
yp[J][3] =: lgm_t{{Fe}};
yp[J][4] =: lgm_t{{K}};
yp[J][5] =: lgm_t{{Mg}};
yp[J][6] =: lgm_t{{Na}};
yp[J][7] =: lgm_t{{S}};
yp[J][8] =: lgm_t{{Si}};
yp[J][9] =: pH;
  
```

yp[J][0] =: lgm_t{{Al}};
log total concentration
(as measured e.g. by ICP-OES or IC)

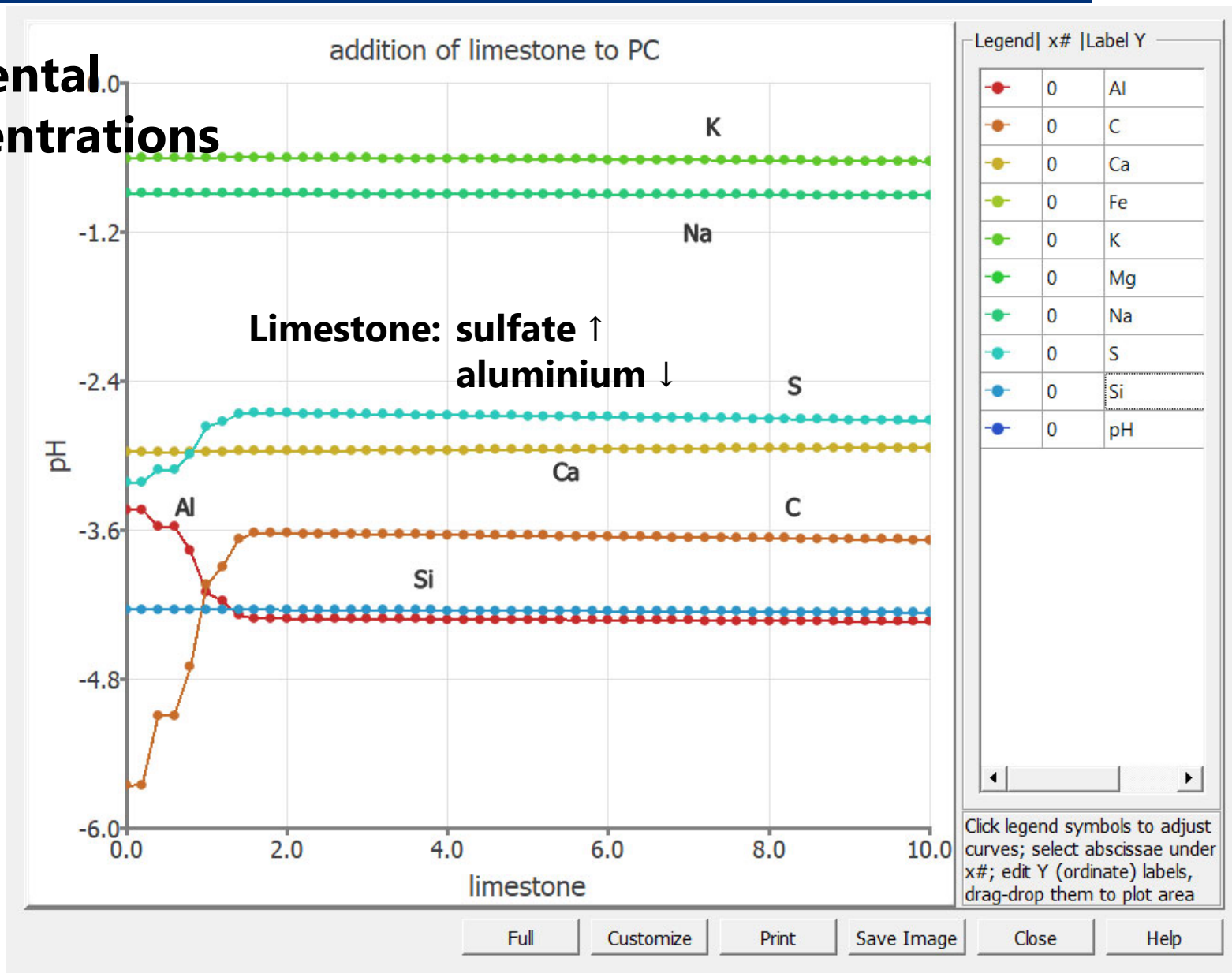
Process file - hydration of PC + limestone

pH - value

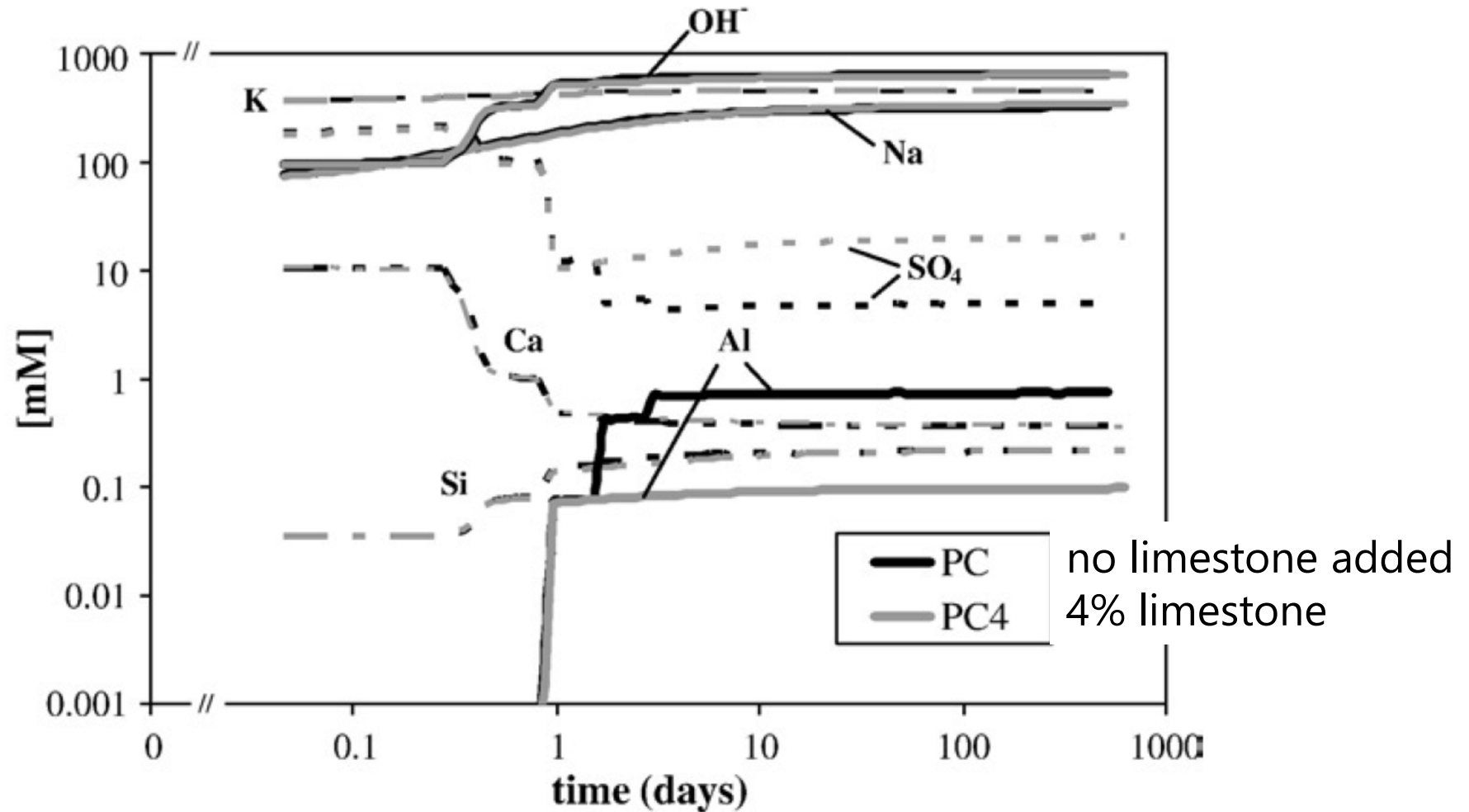


Process file - hydration of PC + limestone

Elemental concentrations



Process file - hydration of PC + limestone



Lothenbach et al 2008, CCR 38

**Limestone: sulfate ↑
aluminium ↓**

Process file - hydration of PC + limestone

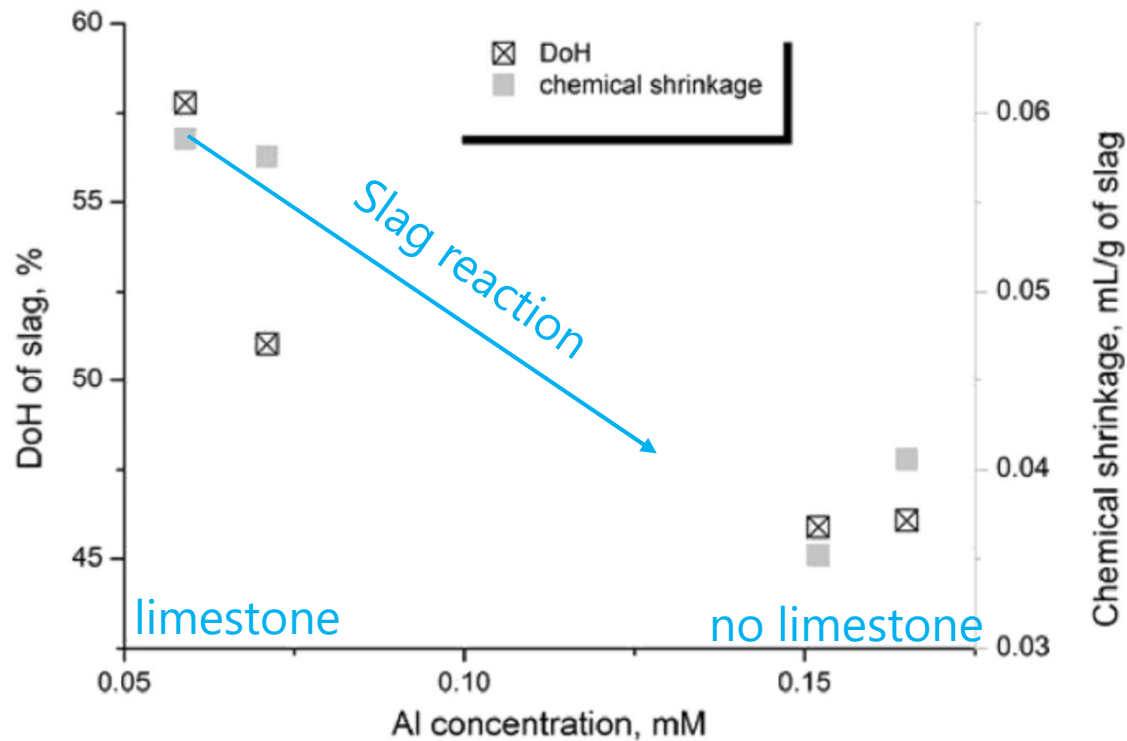


Fig. 21. The relationship between Al concentration in the pore solution and chemical shrinkage and degree of hydration of slag at 28 days. Note, there is $\pm 2\%$ error associated with the method for measuring the DoH of slag.

Adu-Amankwah et al 2017, CCR 100

**Limestone: sulfate \uparrow
aluminium \downarrow**

**\Rightarrow High Al suppresses slag and alite reaction
 \Rightarrow Limestone accelerates**

Tutorial – process: hydration of Portland cement

Hydration of Portland cement

- 1) Hydration of PC - single system
- 2) Influence of limestone on hydration of PC – process file
 - a) Mass based output
 - b) Volume based output
 - c) Composition of aqueous phase
- 3) Influence of fly ash on hydration of PC – process file

Process file - hydration of PC + fly ash

Example:

- **Modification of the existing process to plot a) masses and b) specific volumes of the individual phases present in the chosen example**
- **Use an “artificial fly ash” with 100% glass content and simplified composition**
- **Assume 100% hydration of the fly ash and congruent dissolution**
- **Vary fly ash content between 0 and 20% in steps of 0.4%**
- **Create a predefined composition for fly ash (FA)**

Hints:

- **Clone the project with limestone addition (mass-based), name it e.g. FA_mass**
- **Modify the input part:**
 - **Vary fly ash content: $\text{modC}[J][0] =: cNu*0.4;$**
 - **Fly ash quantity as $x_{a_}\{FA\} =: \dots$**
 - **Remember that there is no limestone in the fly ash**
- **Check for missing phases (look at the calculated single files). Add them to the output part. Label the graph correctly.**
- **When the mass-based file runs smoothly, clone the file, name it e.g. FA_Vol and modify the output part to display specific volumes**

Process file - hydrated of PC + fly ash

Composition of fly ash

XRF-analysis ^a [wt%]		Mineralogical phase composition ^b [wt%]		Glass composition [wt%]	
F1		F1		F1	
SiO ₂	50.9	Mullite	8.2	SiO ₂	54.4
Al ₂ O ₃	24.7	Quartz	7.0	Al ₂ O ₃	24.8
Fe ₂ O ₃	7.3	Hematite	0.7	Fe ₂ O ₃	5.7
CaO	3.7	Magnetite	0.8	CaO	4.6
MgO	1.8	Anhydrite		MgO	2.1
K ₂ O	3.9	Periclase		K ₂ O	4.9
Na ₂ O	0.9	Lime		Na ₂ O	1.1
TiO ₂	1.1	Amorphous	83.3	TiO ₂	1.4
Mn ₂ O ₃	0.1			Mn ₂ O ₃	0.1
P ₂ O ₅	0.8			P ₂ O ₅	0.9
SO ₃	0.4 ^c			SO ₃	0.0
SrO					
LOI	3.5				
C	2.7 ^d				
Sum	99.1		100.0		100.0

average glass composition

We only consider the «big four»

Process file - hydrated PC + fly ash

Two options for input:

Glass composition [wt%]

F1

SiO ₂	54.4
Al ₂ O ₃	24.8
Fe ₂ O ₃	5.7
CaO	4.6
MgO	2.1
K ₂ O	4.9
Na ₂ O	1.1
TiO ₂	1.4
Mn ₂ O ₃	0.1
P ₂ O ₅	0.9
SO ₃	0.0

Option 1: Input in g oxide

recalculation in mol-%

	in glass g/100g	normalised g/100g	molar mass g/mol	normalised mol/100g
SiO ₂	54.4	60.6	60.08	1.00943076
Al ₂ O ₃	24.8	27.6	101.96	0.27116236
Fe ₂ O ₃	5.7	6.4	159.69	0.03979282
CaO	4.8	5.4	56.08	0.0954203
total	89.7	100		

recalculation in atom-%

	normalised mol/100g
Si	1.00943
Al	0.54232
Fe	0.07959
Ca	0.09542
O	3.04715

=> Different options for input in predefined composition

Option 2: Input in mol elements

Process file - hydrated PC + fly ash

Make a predefined composition for fly ash

GEM-Selektor 3 (GEMS3) - Geochemical Equilibrium Modelling by Gibbs Energy Minimization - [EqStat: Single Thermodynamic System in Project PC]

Modules Record Data Calculate View Print Window Help

SingleSystem

PC:*****:***:

Input: System Definition Results: Equilibrium State

Phase/species	L	T	Amount (mol)	logSI/Activity	C
⊕-a aq_gen	69	a	0.74137657	-6.317e-10	
⊕-g gas_gen	6	g	0.0031839841	-1.115e-9	
⊕-s C3 (AF) S0.84H	2	s	0.040769951	-1.148e-9	
⊕-s CSHQ	6	s	0.44660885	-5.789e-10	
⊕-s ettringite-AlFe	2	s	0	-1	
⊕-s ettringite-FeAl	2	s	0	-1	
⊕-s monosulph-AlFe	2	s	0	-1	
⊕-s monosulph-FeAl	2	s	0	-1	
⊕-s straetlingite	2	s	0	-1.43	
⊕-s ettringite	2	s	0.0097500224	8.224e-9	
⊕-s SO4_OH_AFm	2	s	0	-1	
⊕-s OH_SO4_AFm	2	s	0	-1	
⊕-s SO4_CO3_Aft	2	s	0	-1	
⊕-s CO3_SO4_Aft	2	s	0	-1	
⊕-s hydrotalc-pyro	2	s	0	-9.748	
⊕-s MSH	2	s	0	-4.257	
⊕-s Al (OH) 3am	1	s	0	-3.33	
⊕-s Al (OH) 3mic	1	s	0	-2.466	
⊕-s Gibbsite	1	s	0	-1.943	
⊕-s Kaolinite	1	s	0	-13.82	
⊕-s Graphite	1	s	0	-85.21	
⊕-s Mavenite	1	s	0	-135.1	

Click here to access copy of the database associated with this project

Make a predefined composition for fly ash

The screenshot shows the GEM-Selektor 3 (GEMS3) software interface. The main window displays a predefined composition object (PCO) for 'PC with limestone'. The composition is defined by the following table:

svmlC	PCO	svmlC	CIc	CI	
0	Al ...	0.05907926	0	Al ... M	0
1	C ...	0.0036313673	1	C ... M	0
2	Ca ...	0.70041792	2	Ca ... M	0
3	Fe ...	0.024634934	3	Fe ... M	0
4	K ...	0.010179733	4	K ... M	0
5	Mg ...	0.027451387	5	Mg ... M	0
6	Na ...	0.0083306518	6	Na ... M	0
7	O ...	1.3359998	7	O ... M	0
8	S ...	0.017580691	8	S ... M	0
9	Si ...	0.20664962	9	Si ... M	0

Click here to assess the list of predefined compositions and to create a new one

Use «Record – New(Clone)» from the pull-down menu or click here («Record – Remake» allows you to change an existing record)

The screenshot shows the GEM-Selektor 3 (GEMS3) software interface. The main window is titled 'Compos :: Predefined composition objects (PCO)'. The left sidebar contains a list of chemical species under the 'Compos' category. The main area displays a table of data for the 'PCO' entry.

Toolbar Annotations: A red circle highlights the 'New(Clone)' icon (a document with a downward arrow) in the toolbar. A red arrow points from the text above to this icon.

List Annotations: A red box highlights the '45 PC' entry in the 'Compos' list on the left. A red arrow points from the text below to this entry.

Main Window Content:

Page 1 Settings 01/02/2018, 09:11

PC with limestone

Composition from Lothenbach_ea_b:2008:pap:

0.0600843	0	0	0	0	0	0
-----------	---	---	---	---	---	---

	svmIC	PCO		svmIC	CIc	CI		
0	Al	...	0.05907926	0	Al	...	M	0
1	C	...	0.0036313673	1	C	...	M	0
2	Ca	...	0.70041792	2	Ca	...	M	0
3	Fe	...	0.024634934	3	Fe	...	M	0
4	K	...	0.010179733	4	K	...	M	0
5	Mg	...	0.027451387	5	Mg	...	M	0
6	Na	...	0.0083306518	6	Na	...	M	0
7	O	...	1.3359998	7	O	...	M	0
8	S	...	0.017580691	8	S	...	M	0
9	Si	...	0.20664962	9	Si	...	M	0

To create a new entry, it is best to clone an existing one - we chose to clone the entry PC

Make a predefined composition for fly ash: option 1, add g oxides

Compos: Please, set a new record key

FA:MIN:Fly-ash:

FA Name of predefined composition object (PCO)

MIN Code of PCO type { AQ RO GA FL HC PM MIN }

Fly-ash Comment to PCO description

Ok Reset From List Help Cancel

Can be used to add g oxides
4 as CaO, Al₂O₃, SiO₂, Fe₂O₃

Will have to written manually

GEM-Selector Compos Setup: FA:MIN:Fly-ash:

Step 1 - Predefined Composition Object (PCO) configuration

Compos record contains data for a Predefined Composition Object (PCO), which describes a salt, the air, a mineral, a rock, a natural water, etc., treated as a single named entity in the chemical system recipe.

PCO can be configured according to the source data: as IC or DC amounts/concentrations; as user-defined formula (UDF) units; or as a large UDF entered into a text field.

Upon re-calculation, all given quantities will be added into a single IC mole amounts PCO vector, optionally scaled to a given total mass (in kg) or total number of moles.

PCO input data configuration

Use amounts of Independent Components (IComp) in this PCO definition (default)?

Use formulae of Dependent Components (from DComp/ReacDC records) in this PCO?

4 Set number of user-defined formula units for this PCO definition (0 by default)

Optional: Input user-defined formula (UDF) text

Use a user-defined formula text input field for this PCO definition?

M moles Select units of measurement for this UDF quantity (default: M)

0 Enter here the UDF quantity or amount in selected units (default: 1)

Learn more < Back Next> Cancel

GEM-Selector Compos Setup: FA:MIN:Fly-ash:

Step 2 - Additional settings and next actions

Optional

1 Set here the number of links to SDref bibliography records (default 0)

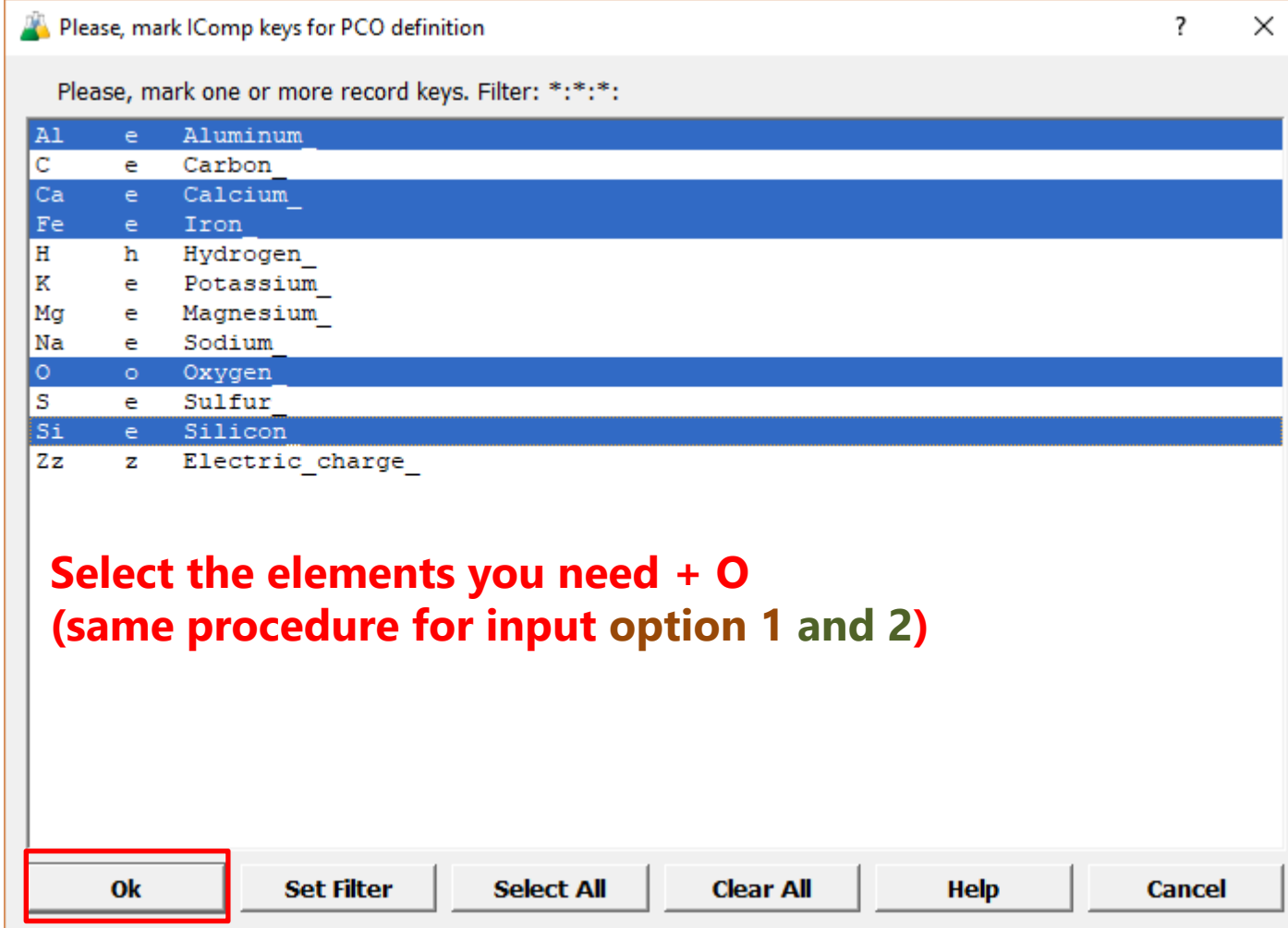
Use a vector of data uncertainties in this PCO definition

What will happen after you click "Finish"

- (1) For a PCO definition using IComp amounts, a list of available IComp records will be shown, asking you to mark the desired ones.
- (2) In a PCO definition using DC formulae, a list of available ReacDC/DComp records will be shown, asking you to mark the desired ones.
- (3) Page 1 of the 'Compos' window appears. Fill out Bcname field and (optionally) BCnote lines. Then enter data and formulae wherever needed, check units of amount/concentration.
- (4) Click on 'Calculate' toolbar button to compute the PCO vector. Check or enter the normalization values in MasVol[0] and MasVol[6] fields and calculate again, if needed. Setting both fields to zero disables the normalization of PCO to the total mass or total amount of moles, respectively.

Learn more < Back Finish Cancel

Make a predefined composition for fly ash: option 1 and 2



Please, mark IComp keys for PCO definition

Please, mark one or more record keys. Filter: *:*:*:

Al	e	Aluminum
C	e	Carbon
Ca	e	Calcium
Fe	e	Iron
H	h	Hydrogen
K	e	Potassium
Mg	e	Magnesium
Na	e	Sodium
O	o	Oxygen
S	e	Sulfur
Si	e	Silicon
Zz	z	Electric_charge

Select the elements you need + O
(same procedure for input option 1 and 2)

Ok Set Filter Select All Clear All Help Cancel

Make a predefined composition for fly ash: option 1, add g oxides

logy

Compos :: Calculation finished OK (elapsed time: 0 s).

Page 1 Settings 26/03/2020, 15:46

FA
Composition from Deschner_ea_b:2012:pap:

0.1	0	0	0	0	0	4.77219
-----	---	---	---	---	---	---------

	symIC	PCO		symIC	CIc	CI
0	Al ...	0.54138197	0	Al ... M		0
1	Ca ...	0.096295479	1	Ca ... M		0
2	Fe ...	0.080156203	2	Fe ... M		0
3	O ...	3.0457686	3	O ... M		0
4	Si ...	1.0085829	4	Si ... M		0

3) Once everything is entered, recalculate ...

1) ... and save new record.

⇒ Enter 0.1
Normalises everything to 100 g (0.1 kg)

2) Enter values
Composition normalised to 100g

Write CaO, Al₂O₃, SiO₂, Fe₂O₃

Case sensitive!

Page 1 Settings 05/02/2018, 09:53

+ - + - - M 5 0 4 1 0 0

Deschner_ea:2012:pap: FA composio

	formU	AUc	CA
0	CaO	g	5.4
1	SiO ₂	g	60.6
2	Al ₂ O ₃	g	27.6
3	Fe ₂ O ₃	g	6.4

Make a predefined composition for fly ash: option 2, mol elements

Compos: Please, set a new record key

FA:MIN:Fly-ash:

FA Name of predefined composition object (PCO)

MIN Code of PCO type { AQ RO GA FL HC PM MIN }

Fly-ash Comment to PCO description

Ok Reset From List Help Cancel

GEM-Selektor Compos Setup: FA1:MIN:Fly-ash

Step 1 - Predefined Composition Object (PCO) configuration

Compos record contains data for a Predefined Composition Object (PCO), which describes a salt, the air, a mineral, a rock, a natural water, etc., treated as a single named entity in the chemical system recipe.

PCO can be configured according to the source data: as IC or DC amounts/concentrations; as user-defined formula (UDF) units; or as a large UDF entered into a text field.

Upon re-calculation, all given quantities will be added into a single IC mole amounts PCO vector, optionally scaled to a given total mass (in kg) or total number of moles.

PCO input data configuration

Use amounts of Independent Components (IComp) in this PCO definition (default)?

Use formulae of Dependent Components (from DComp/ReacDC records) in this PCO?

0 Set number of user-defined formula units for this PCO definition (0 by default)

Optional: Input user-defined formula (UDF) text

Use a user-defined formula text input field for this PCO definition?

M moles Select units of measurement for this UDF quantity (default: M)

0 Enter here the UDF quantity or amount in selected units (default: 1)

Learn more < Back **Next>** Cancel

GEM-Selektor Compos Setup: FA:MIN:Fly-ash

Step 2 - Additional settings and next actions

Optional

1 Set here the number of links to SDref bibliography records (default 0)

Use a vector of data uncertainties in this PCO definition

What will happen after you click "Finish"

(1) For a PCO definition using IComp amounts, a list of available IComp records will be shown, asking you to mark the desired ones.

(2) In a PCO definition using DC formulae, a list of available ReacDC/DComp records will be shown, asking you to mark the desired ones.

(3) Page 1 of the 'Compos' window appears. Fill out Bcname field and (optionally) BCnote lines. Then enter data and formulae wherever needed, check units of amount/concentration.

(4) Click on 'Calculate' toolbar button to compute the PCO vector. Check or enter the normalization values in MasVol[0] and MasVol[6] fields and calculate again, if needed. Setting both fields to zero disables the normalization of PCO to the total mass or total amount of moles, respectively.

Learn more < Back **Finish** Cancel

Instead of g oxides we use mol of elements

Make a predefined composition for fly ash: option 2, mol elements

low Help

Page 1 Settings 05/02/2018, 10:50

FA, simplified, normalised to 100 g
Composition from Deschner_ea:2012:pap:

0.1 0 0 0 0 0 0 0

	svmIC	PCO		svmIC	CIc	CI
0	Al ...	0.54229563	0	Al ...	M	0.54232
1	Ca ...	0.095415713	1	Ca ...	M	0.09542
2	Fe ...	0.079586424	2	Fe ...	M	0.07959
3	O ...	3.0470131	3	O ...	M	3.04715
4	Si ...	1.0093846	4	Si ...	M	1.00943

**recalculation in
atom-%**

	normalised mol/100g
Si	1.00943
Al	0.54232
Fe	0.07959
Ca	0.09542
O	3.04715

=> Enter values

When everthing is entered, recalculate and save new record.

equivalent options, minor difference due rounding off (number of digits ...

Process file - hydration of PC + fly ash

The screenshot displays the GEM-Selektor software interface. On the left, the 'Modelling Projects' window lists various projects, with 'PC GEMS2019' highlighted in a red box. Below this window are several checkboxes for project configuration and two buttons: 'Open Project' (highlighted in a red box) and 'New Project'. On the right, the 'Compos' dialog box is open, showing a question mark icon and the text 'FA MIN Fly_ash_1M_ record to be inserted into project system.' Below this text are three buttons: 'Do it' (highlighted in a red box), 'Do it for All', and 'Cancel'. Below the 'Compos' dialog, the 'Input Recipe of Single Thermodynamic System: PC:G:PC:0:0:1:20:0:' window is visible. It features a 'tname' field with 'PC' entered. A table with 'Property' and 'Selection' columns is shown, with 'FA' highlighted in a red box in the 'Selection' column.

Property	Selection	
Compos (xa_)	Al(OH)3 CaCO3 H2SO4 PC	
DComp (xd_)	Al2O3 CaMg(CO3)2 K2CO3 SO3	
IComp (bi_)	Al2Si2O5(OH)4 CaO K2O SiO2	
Phase (xp_)	Aqua CaSO4 K2SO4	
Kin.lower (dll_)	C12A7 CaSO4_05H2O KOH	
Kin.upper (dul_)	G0 shift (gEx_)	CaSiO3 Mg(OH)2
Other Inputs	C3A FA Mg3Si2O5(OH)4	
	C3S Fe2O3 MgCO3	
	C4A3s FeCO3 MgO	
	C4AF FeO MgSO4	
	CA FeOOH Na2CO3	
	CA2 FeS Na2O	
	CH4 Gypsum Na2SO4	
	CO2 H2 NaOH	
	Ca(OH)2 H2S O2	

Then go back to your project

Process file - hydration of PC + fly ash

PC:G:PC:0:0:1:20:0:PC_FA:S:

Controls | Sampling | Results | Config | 27/03/2020, 13:29

Clone LS_mass (use number of steps = 51)

addition of FA to PC

GEMS tutorial

Change to 2000 to not overwrite PC-LS

change to 0% FA as start up to 20% FA change to 0.4 step size

	iTm	iV	iP	iTC	iNv	iTau	ipXi	iNu	ipH
0	2000	0	1	20	0	0	0	0	0
1	2100	0	1	20	0	0	0	20	0
2	1	0	0	0	0	0	0	0.4	0
cTm	1000	0	1	20	0	0	0	0	0

```

$ amount of FA,
$will written in 1st column; cNu = calculated number
modC[J][0] =: cNu;
xa_{{FA}} =: modC[J][0];

$ amount of PC
xa_{{PC}} =: 100-modC[J][0];

$PC written in 2nd column;
modC[J][1] =: 100-modC[J][0];

```

We have calcite only in the PC

We now add fly ash instead of limestone
`xa_{{FA}} =: modC[J][0];`

	modC[0]
0	
1	
2	
3	
4	
5	
6	

Process file - hydration of PC + fly ash

Controls	Sampling	Results	Config	27/03/2020, 14:40						
NeIt	9999	15	Next	1	I	0	J	14	Jp	14
pSTkey	PC:G:PC:0:0:1:20:0:							cTm	2014	cI
cTau	0		cpXi	0		cXi	1		cNu	
cpH	0		cpe	0		cEh	0		cT	

```
$x axis: total fraction of FA in cement
xp[J] =: xa_{{FA}};
```

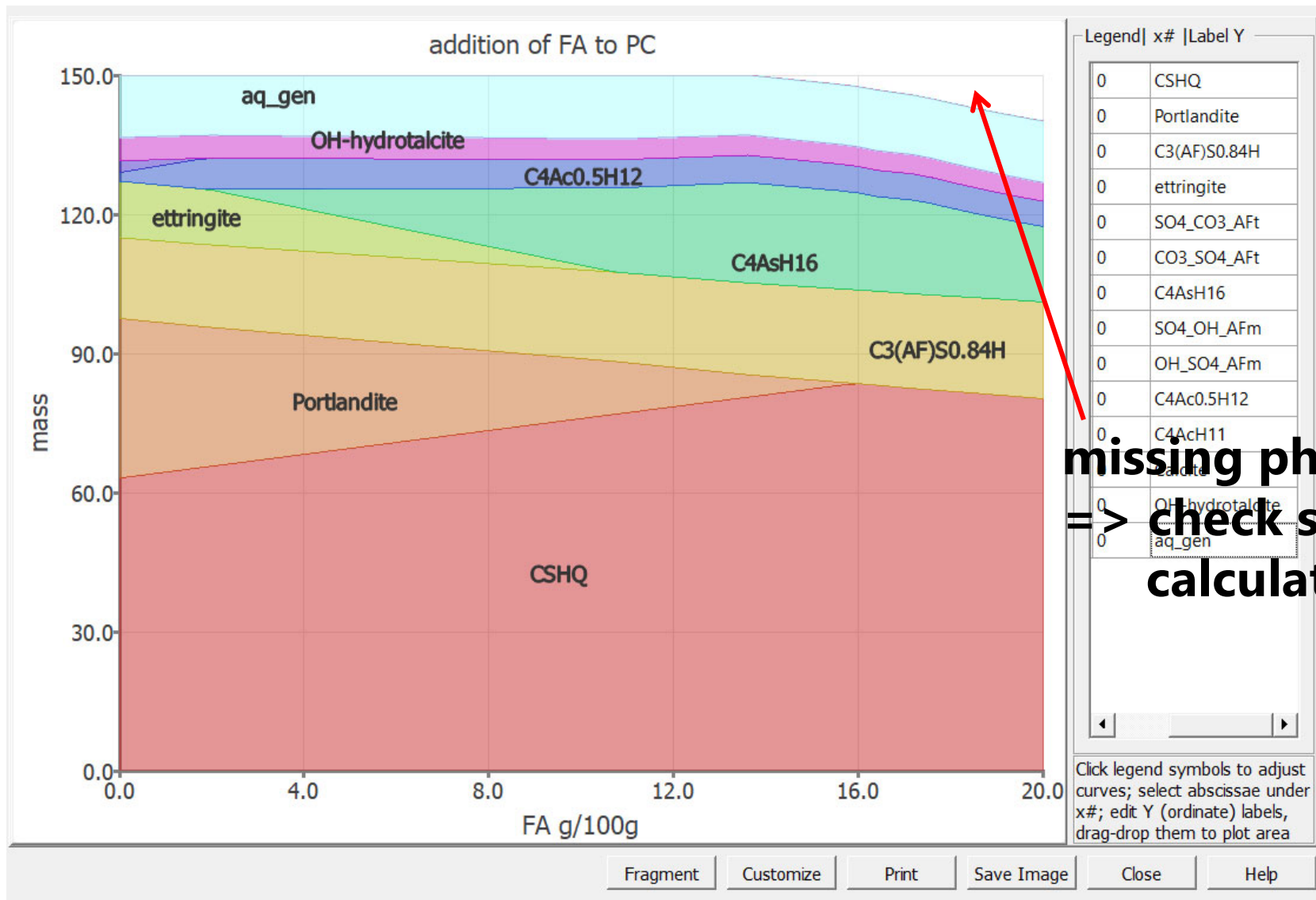
Change comment, change x-axis

```
$y-axis in g per 100 g unhydrated cement
```

```
yp[J][0] =: phM[{{CSHQ}}];
yp[J][1] =: phM[{{Portlandite}}];
yp[J][2] =: phM[{{C3(AF)S0.84H}}];
yp[J][3] =: phM[{{ettringite}}]+phM[{{SO4_CO3_Aft}}]+phM[{{CO3_SO4_Aft}}];
yp[J][4] =: phM[{{straetlingite}}];
yp[J][5] =: 0;
yp[J][6] =: phM[{{C4Ash16}}]+phM[{{SO4_OH_AFm}}]+phM[{{OH_SO4_AFm}}];
yp[J][7] =: 0;
yp[J][8] =: 0;
yp[J][9] =: phM[{{C4Ac0.5H12}}];
yp[J][10] =: phM[{{C4AcH11}}];
yp[J][11] =: phM[{{Calcite}}];
yp[J][12] =: phM[{{OH-hydrotalcite}}];
```

New phase: (CaO)₂Al₂O₃SiO₂(H₂O)₇₋₈

Process file - hydration of PC + fly ash



missing phase(s)
=> check single
calculations

Process file - hydration of PC + fly ash

Input: System Definition Results: Equilibrium State

Phase/species	L	T	Amount (mol)	logSI/Activity	Concentration	Act:
aq_gen	69	a	0.732848	-1.328e-08		
gas_gen	6	g	0.0031837365	-9.027e-10		
C3 (AF) S0.84H	2	s	0.048804933	-3.045e-10		
CSHQ	6	s	0.56117269	1.306e-09		
strätlingite	2	s	0.023842347	-1.534e-07		
ettringite	2	s	0	-0.5952		
SO4_OH_AFm	2	s	0.013212363	1.06e-07		
OH_SO4_AFm	2	s	0.013212363	1.06e-07		
SO4_CO3_AFt	2	s	0	-1		
CO3_SO4_AFt	2	s	0	-1		
hydrotalc-pyro	2	s	0	-10.41		
MSH	2	s	0	-7.114		
Al (OH) 3am	1	s	0	-2.561		
Al (OH) 3mic	1	s	0	-1.698		
Gibbsite	1	s	0	-1.175		
Kaolinite	1	s	0	-11.24		
Graphite	1	s	0	-85.78		
Mayenite	1	s	0	-128.2		
Belite	1	s	0	-2.062		
Aluminate	1	s	0	-36.91		
Alite	1	s	0	-14.64		
Ferrite	1	s	0	-37.64		
CA	1	s	0	-10.35		
CA2	1	s	0	-13.35		
C2AH75	1	s	0	-1.789		
C3AH6	1	s	0	-0.6313		
C4AH11	1	s	0	-3.17		
C4AH13	1	s	0	-1.339		
C4AH19	1	s	0	-1.034		
CAH10	1	s	0	-2.497		
C4AsH105	1	s	0	-1.483		

System: T = 293.15 K; P = 1.00 bar; V = 0.1509 L; Aqueous: built-in EDH(H); pH = 13.313; pe = 7.831; IS = 0.185 m

Check solids in single calculations

Process file - hydration of PC + fly ash

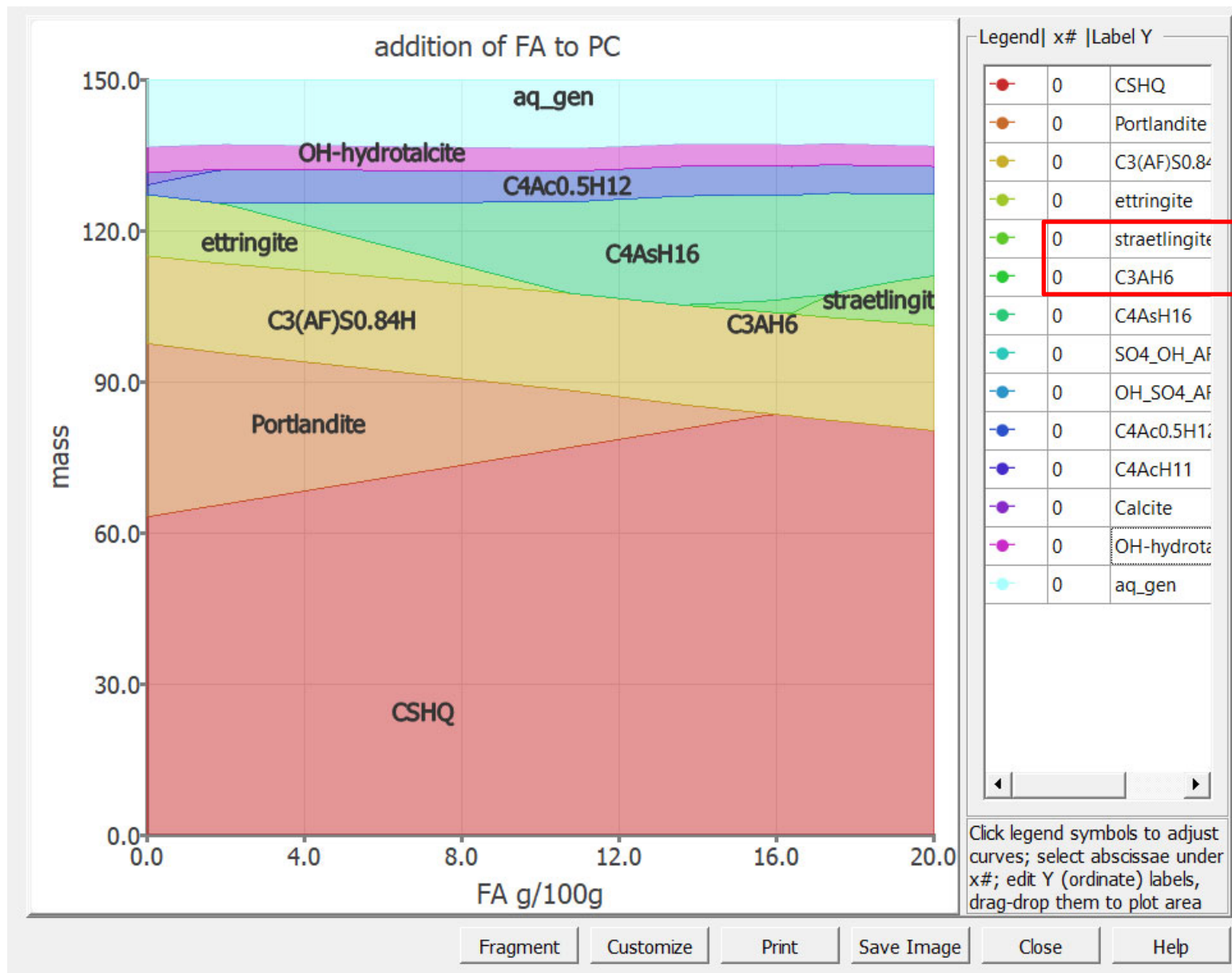
Controls		Sampling		Results		Config		27/03/2020, 15:11			
NeIt	9999	51	Next	0	I	0	J	50	Jp	50	
pSTkey	PC:G:PC:0:0:1:20:0:							cTm	2050		
cTau	0		cpXi	0		cXi	1		cNu		
cpH	0		cpe	0		cEh	0		cT		

```

$X axis: total fraction of FA in cement
xp[J] =: xa_{{FA}};

$y-axis in g per 100 g unhydrated cement
yp[J][0] =: phM[{{CSHQ}}];
yp[J][1] =: phM[{{Portlandite}}];
yp[J][2] =: phM[{{C3(AF)S0.84H}}];
yp[J][3] =: phM[{{ettringite}}]+phM[{{SO4_CO3_AfT}}]+phM[{{CO3_SO4_AfT}}];
yp[J][4] =: phM[{{straetlingite}}]; New phase: (CaO)2Al2O3SiO2(H2O)7-8
yp[J][5] =: phM[{{C3AH6}}]; katoite: (CaO)3Al2O3(H2O)6
yp[J][6] =: phM[{{C4AsH16}}]+phM[{{SO4_OH_AfM}}]+phM[{{OH_SO4_AfM}}];
yp[J][7] =: 0;
yp[J][8] =: 0; => Adapt also y-axis labels
yp[J][9] =: phM[{{C4Ac0.5H12}}];
yp[J][10] =: phM[{{C4Ach11}}];
yp[J][11] =: phM[{{Calcite}}];
yp[J][12] =: phM[{{OH-hydrotalcite}}];
  
```


Process file - hydration of PC + fly ash



Process file - hydration of PC + fly ash

What happens, when we replace 5% of PC by limestone?

Controls
Sampling
Results
Config
27/03/2020, 15:27

addition of FA to PC+Cc
 GEMS tutorial

	iTm	iV	iP	iTC	iNv	iTau	ipXi	iNu	ipH
0	2000	0	1	20	0	0	0	0	
1	2100	0	1	20	0	0	0	20	
2	1	0	0	0	0	0	0	0.4	
cTm	2000	0	1	20	0	0	0	0	

```

$ amount of FA,
$will written in 1st column; cNu = calculated number
modC[J][0] =: cNu;
xa_{{FA}} =: modC[J][0];

$ amount of PC
xa_{{PC}} =: 100-modC[J][0]-5;
xa_{{CaCO3}} =: 5;

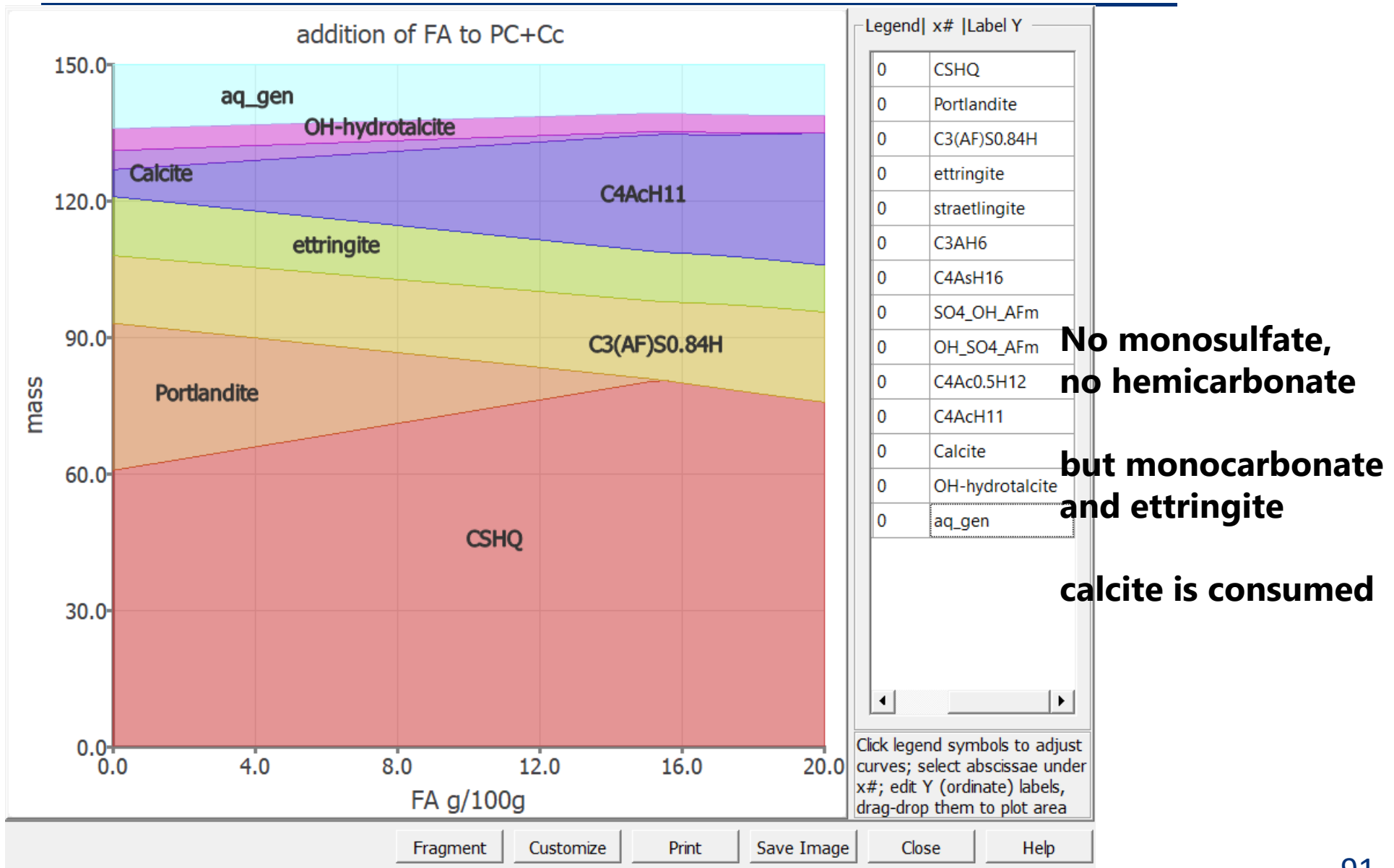
$PC written in 2nd column;
modC[J][1] =: 100-modC[J][0]-5;
          
```

	mo
0	
1	
2	
3	
4	
5	
6	
7	

We subtract the 5% LS from the PC ...

... and add 5% CaCO₃.

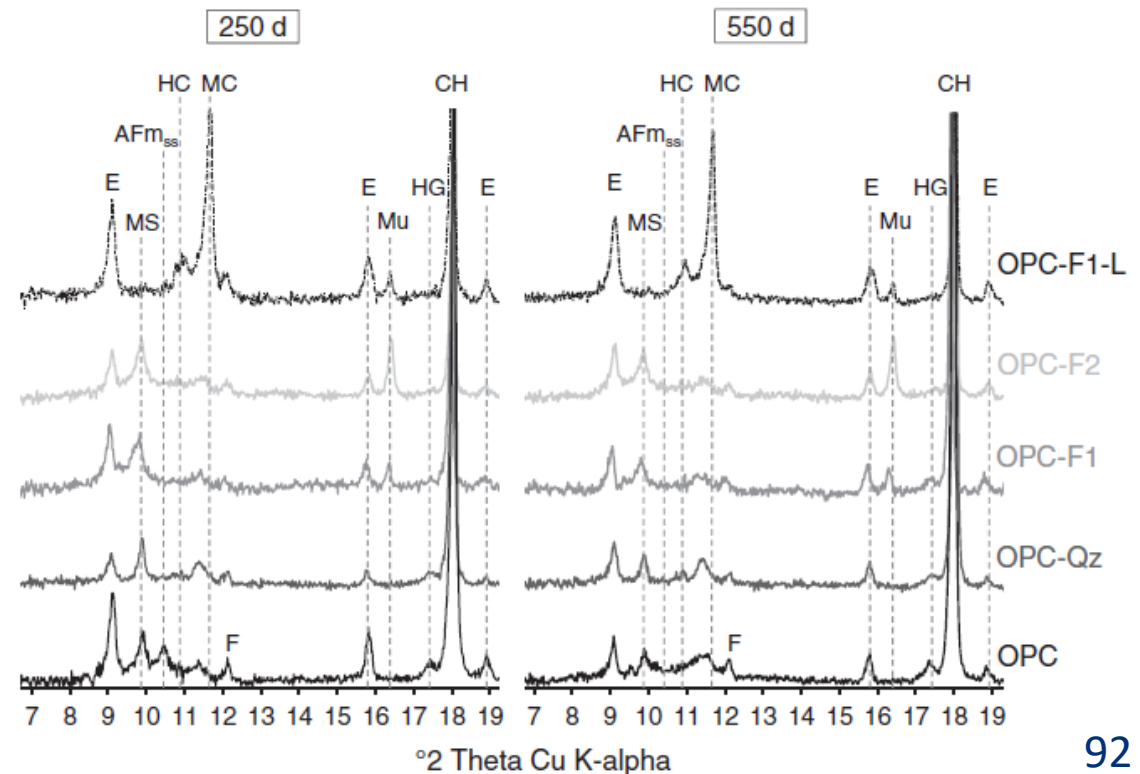
Process file - hydration of PC + fly ash



Process file - hydration of PC + fly ash

Addition of fly ash to PC:

- Less portlandite, more C-S-H (Ca/Si of C-S-H decreases, not shown)
- Ettringite destabilized, formation of monosulfate
=> ternary blends with fly ash and limestone favourable to stabilize ettringite (see e.g. de Weerd et al., Cem. Concr. Res. 41 (2011), 279-291)
- Strätlingite appears after consumption of portlandite



Deschner et al., Cem Concr Res. 52 (2013), 169-181.