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Materials Science and Technology

GEMS workshop 2020

Lecture 3

Process calculations – Hydrated Portland cement

Barbara Lothenbach, Frank Winnefeld, Bin Ma, Zhenguo Shi

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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

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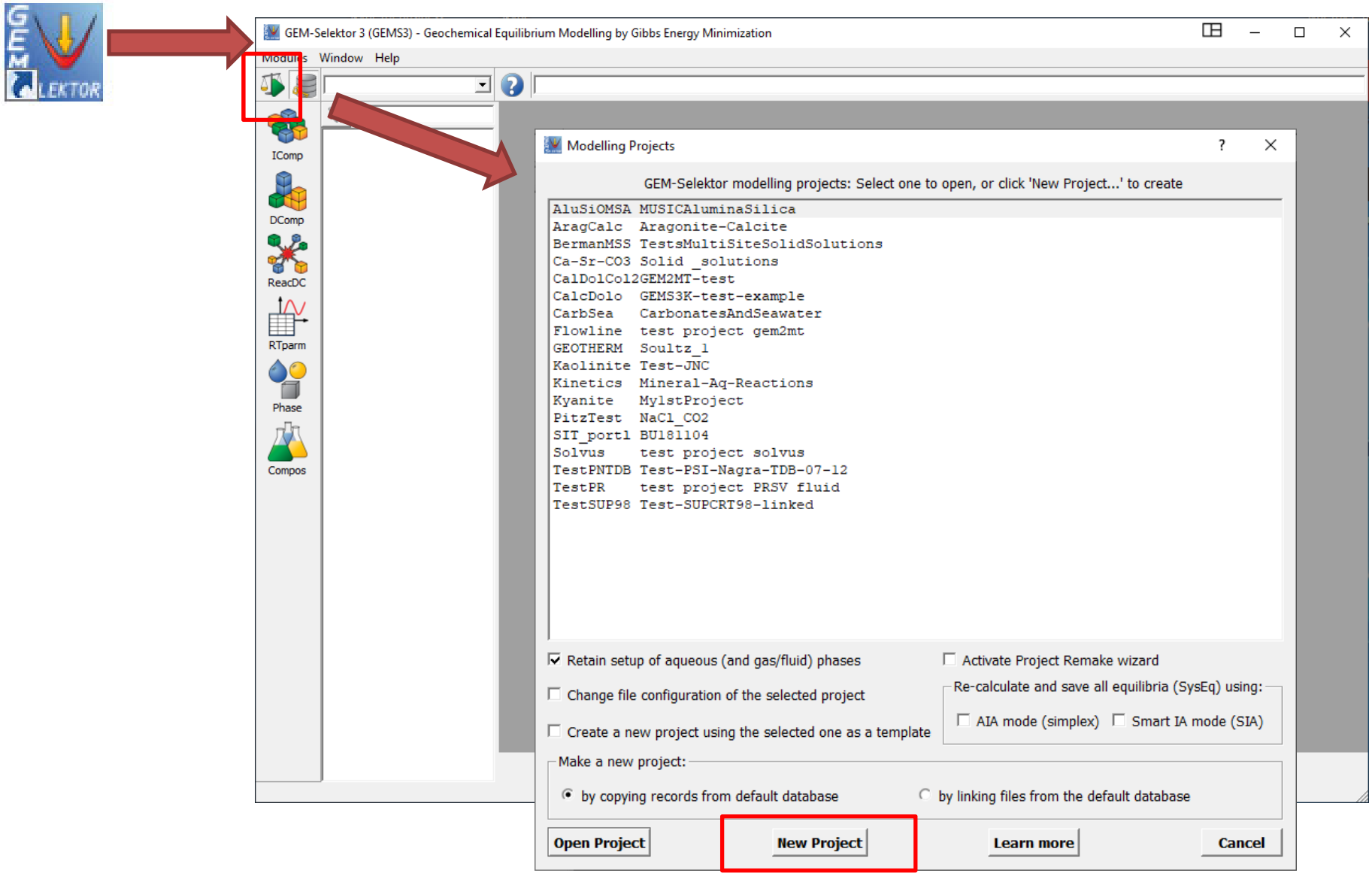
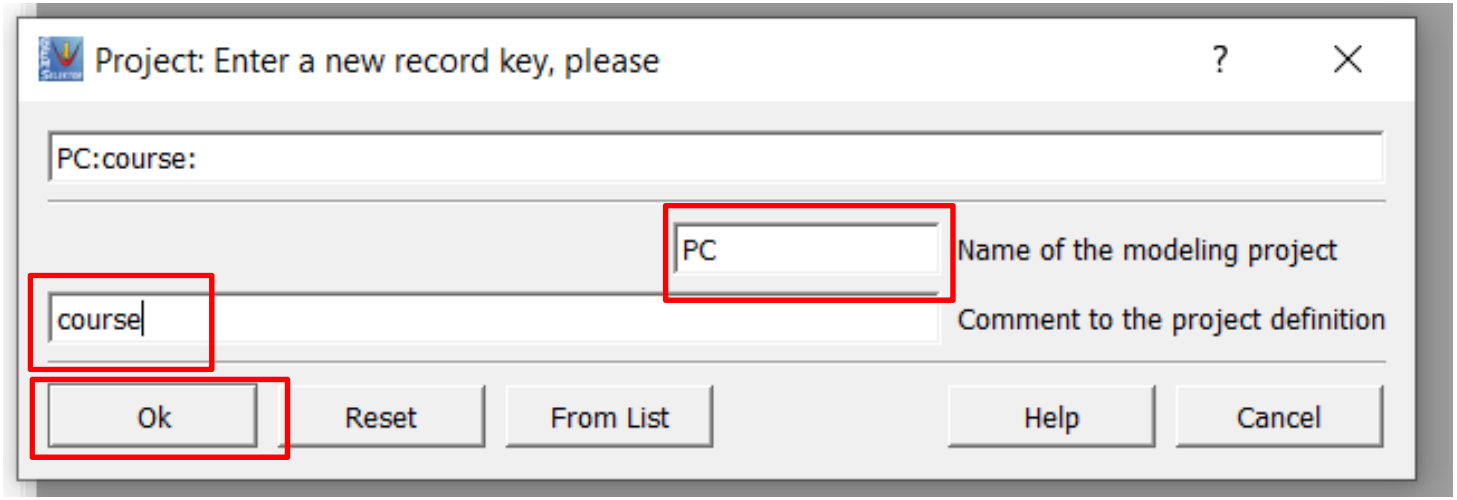
Hydration of a Portland cement

- 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

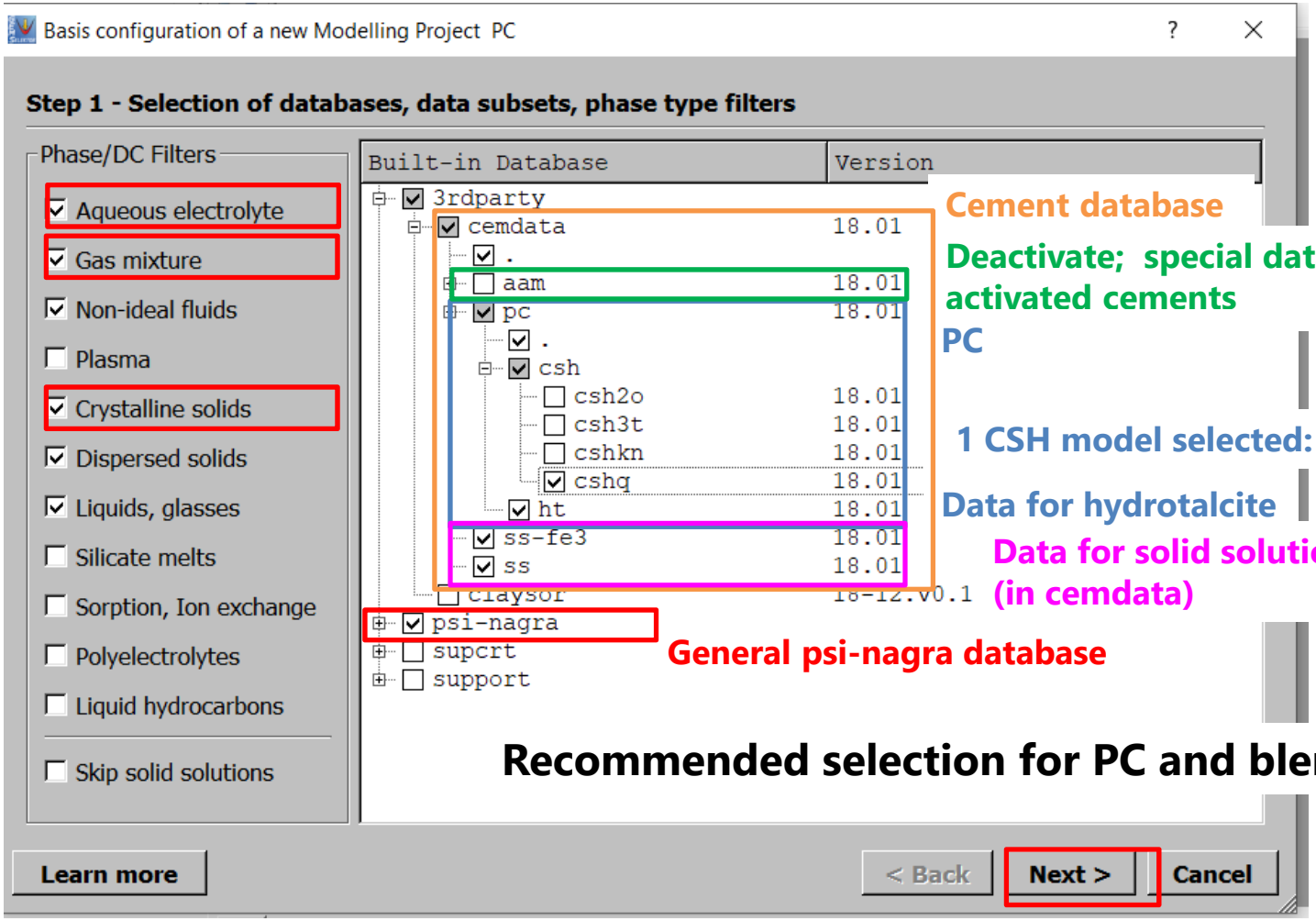


Single file - hydration of Portland cement



Single file - hydration of Portland cement

Select CEMDATA18 (3rd party data base)



Single file - hydration of Portland cement

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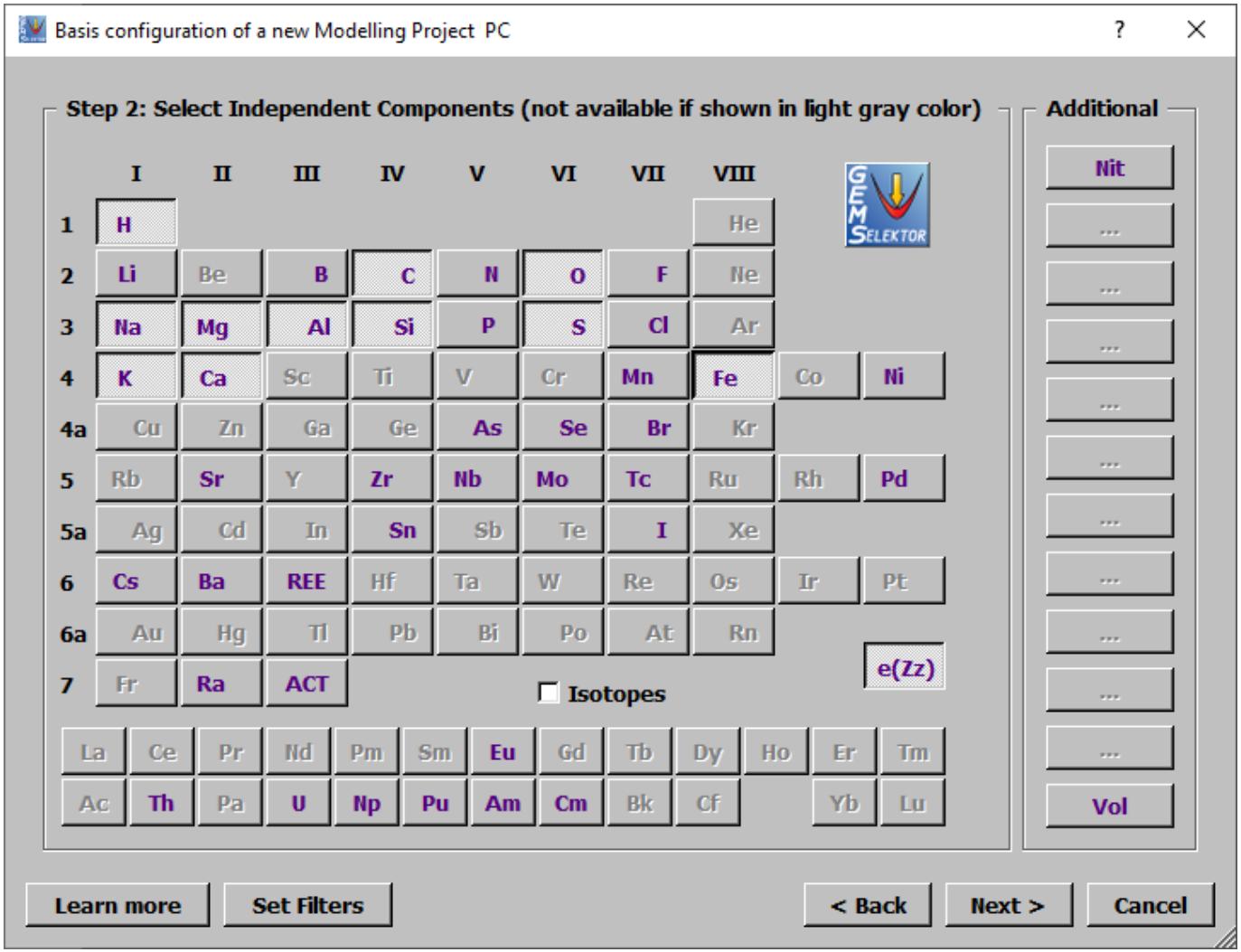
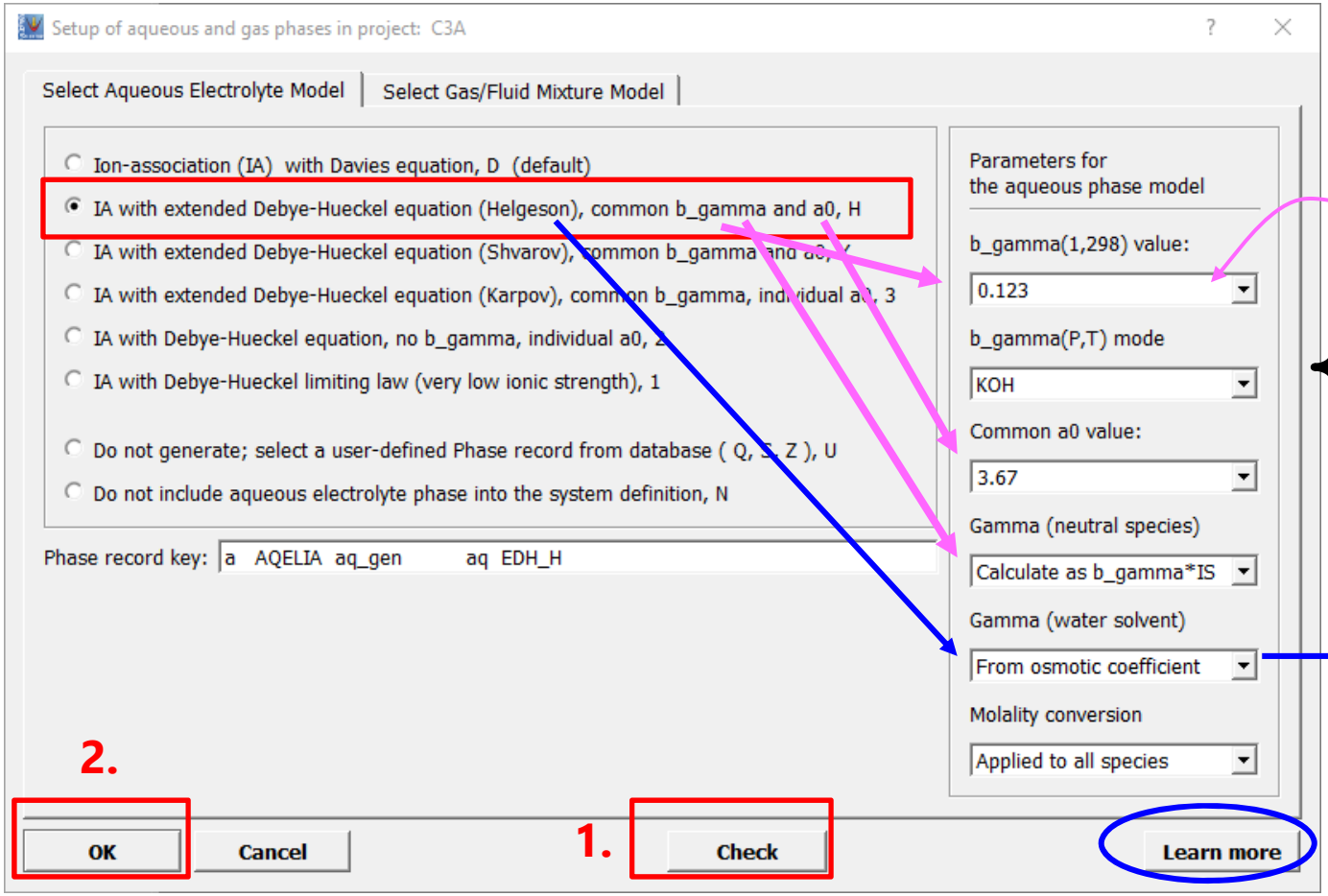
Select main elements present in PC



Single file - hydration of Portland cement

Select model for calculation of the aqueous phase



1) constant,
-> select at 298 K
2) f(pressure, temp)
-> electrolyte

a0=3.67 for KOH

Calculates activity of water

More details

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

$\{Ca^{2+}\} = [Ca^{2+}] \cdot \gamma_{Ca2+}$ ← Activity coefficicient

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

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

individual a, common b (Truesdell-Jones) I < 1 M

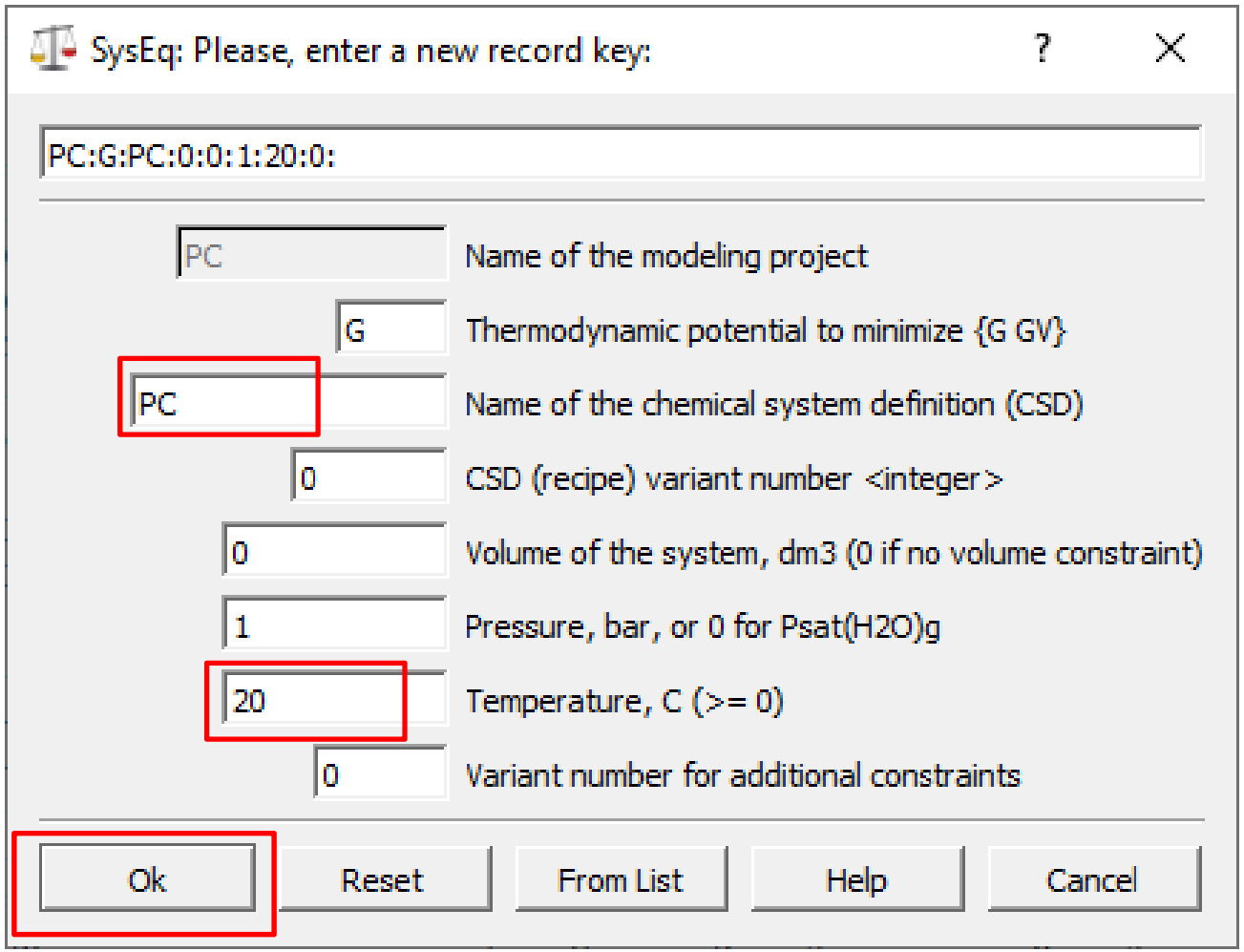
individual a, no b I < 0.3M

Davies $\log \gamma_{Ca^{2+}} = -AZ^2\left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.3I\right)$ 0.1 < I <0. 5 M

SIT $\log \gamma_{Ca^{2+}} = \frac{-AZ^2\sqrt{I}}{1+1.5\sqrt{I}} + \sum \varepsilon m_k$ I < 3 M

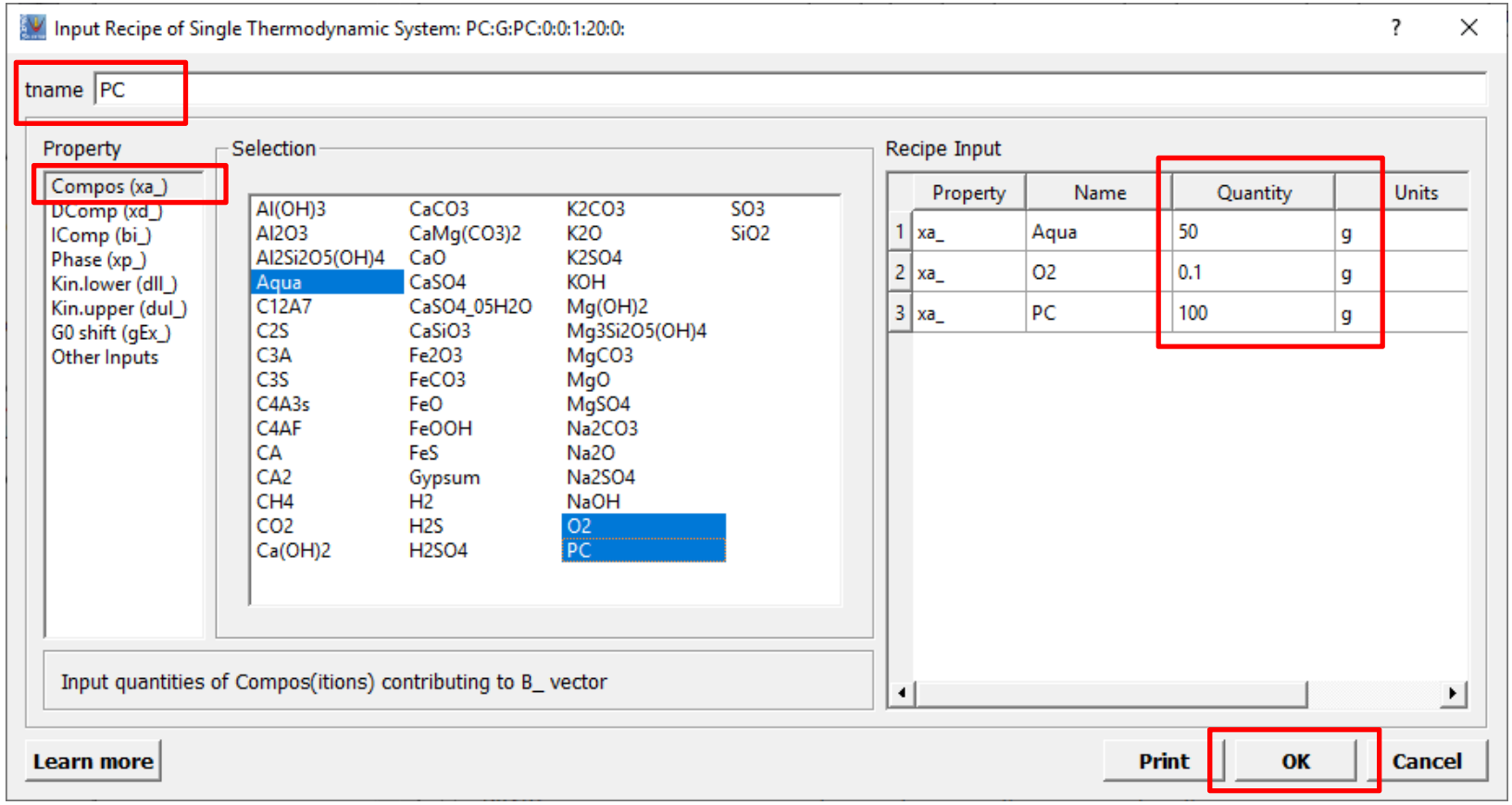
The calculation of activity coefficients is available as built-in function in the GEMS code.
For a detailed overview of different activity coefficients see:
C:\GEMS36\Gems3-app\Resources\doc\pdf\Activity-Coeffs.pdf and references therein

Single file - hydration of Portland cement



Single file - hydration of Portland cement

Use recipe wizard to enter PC composition



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
$CaSO_4 \cdot 2H_2O$ [d]	3.1
K_2SO_4 [b]	1.3
Na_2SO_4 [b]	0.21
Present as solid solution in the clinker phases	
K_2O [d]	0.054
Na_2O [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

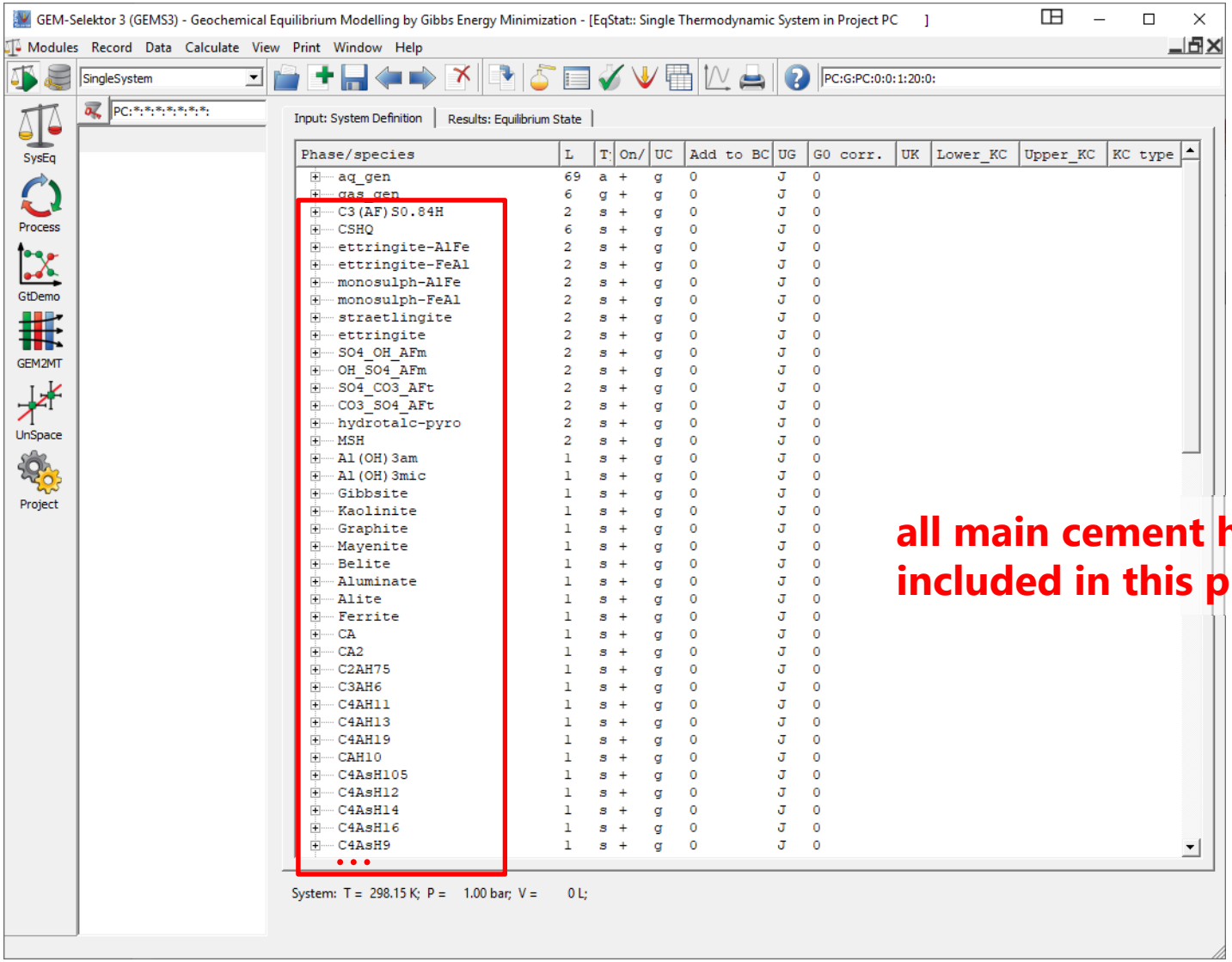
Lothenbach_ea_b:2008:pap: | OPC composition

	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»

B. Lothenbach et al. / Cement and Concrete Research 38 (2008) 848–860

Single file - hydration of Portland cement



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:

Input: System Definition | Results: Equilibrium State

Phase/species	L	T:	On/	UC	Add to BC	UG	G0 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

CSH-JenD = $(CaO)_{1.5}\cdot(SiO_2)_{0.6667}\cdot(H_2O)_{2.5}$

CSH-JenH = $(CaO)_{1.333}\cdot(SiO_2)_{1}\cdot(H_2O)_{2.1667}$

CSH-TobD = $[(CaO)_{1.25}\cdot(SiO_2)_{1}\cdot(H_2O)_{2.75}]_{0.6667}$

CSH-TobH = $(CaO)_{0.6667}\cdot(SiO_2)_{1}\cdot(H_2O)_{1.5}$ 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.

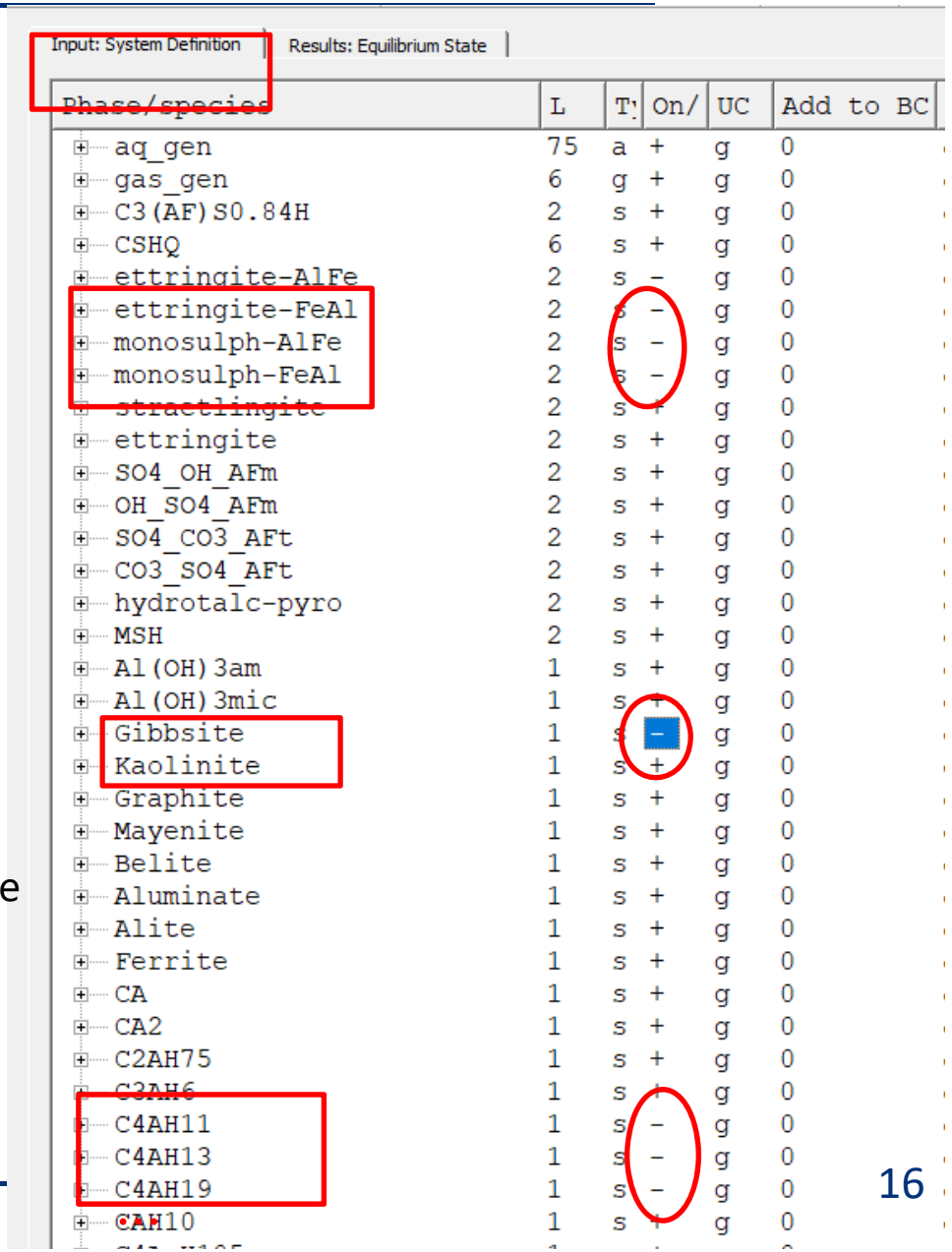
Single file - hydration of Portland cement

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), …
- Thaumasite (formation fast at low temp. Very slow at ambient temp and above)
- others:
  Etttringite Al/Fe ss
  Monosulfate Al/Fe ss
  C_4AH_{13}, C_4AH_{19}

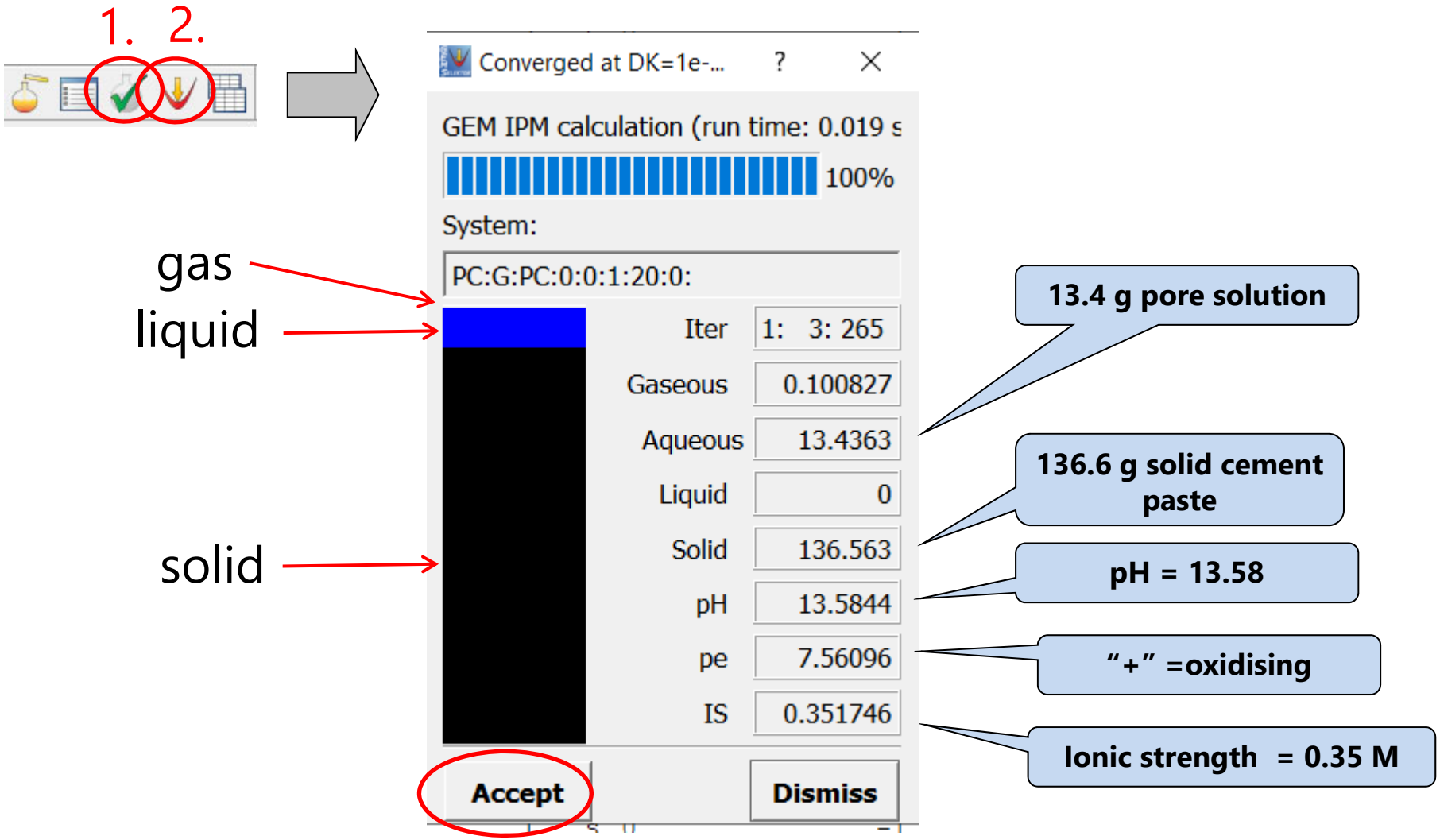
In general it is recommended:

- 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 !**

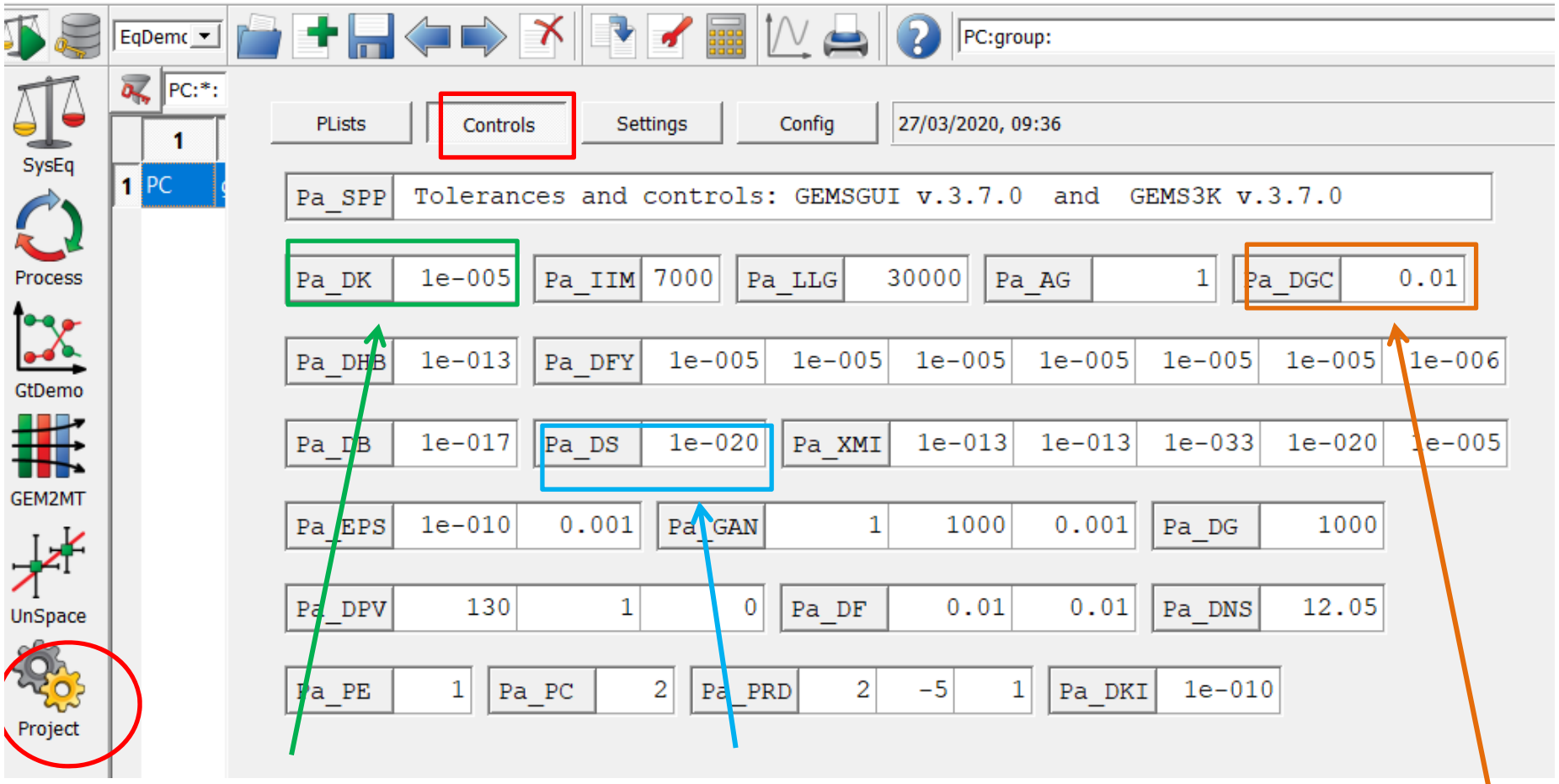


Single file - hydration of Portland cement

<u>Experimental conditions:</u> React 100 g PC with 50 g water (add 0.1 g air CO_2-free)



Convergence problem - workaround



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

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Predicted stable phase assemblage

Si-Hydrogarnet

C-S-H

ettringite

hemicarbonate

monocarbonate

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 = $(CaO)_{1.5}\cdot(SiO_2)_{0.6667}\cdot(H_2O)_{2.5}$

23.1 mol.-% CSH-JenH = $(CaO)_{1.333}\cdot(SiO_2)_1\cdot(H_2O)_{2.1667}$

27.3 mol.-% CSH-TobD = $[(CaO)_{1.25}\cdot(SiO_2)_1\cdot(H_2O)_{2.75}]_{0.6667}$

1.1 mol.-% CSH-TobH = $(CaO)_{0.6667}\cdot(SiO_2)_1\cdot(H_2O)_{1.5}$

6.1 mol.-% KSiOH = $[(KOH)_{2.5}\ SiO_2\ H_2O]_{0.2}$

5.5 mol.-% NaSiOH = $[(NaOH)_{2.5}\ SiO_2\ H_2O]_{0.2}$

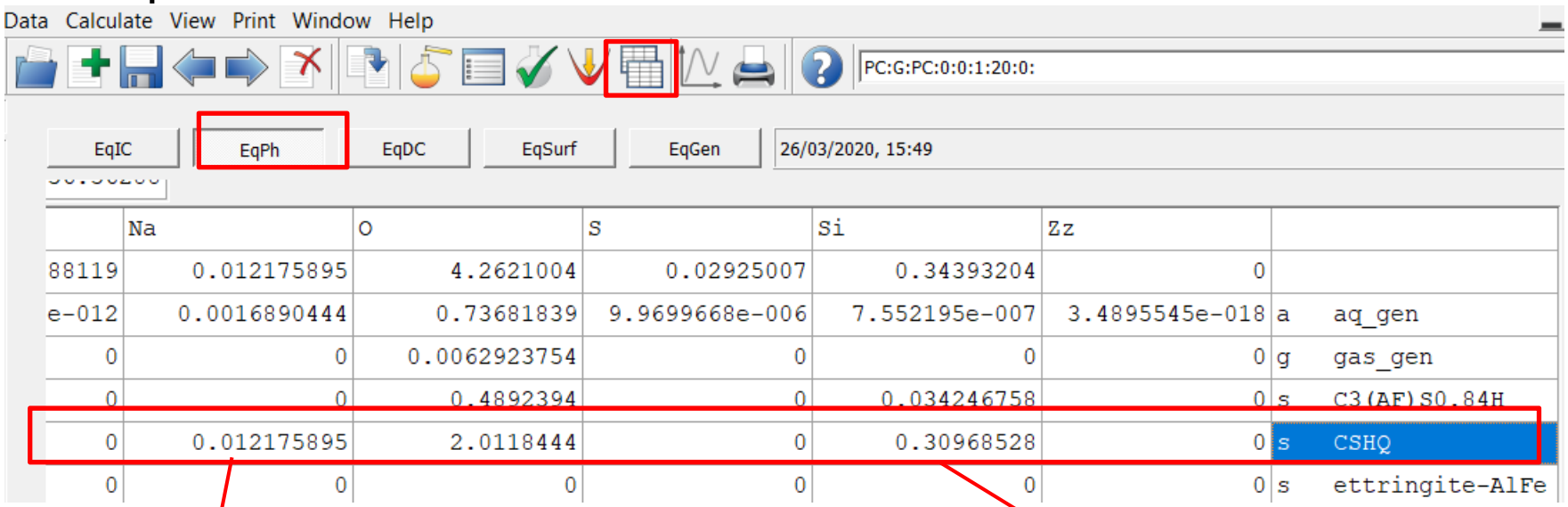
Al-intake in C-S-H: In preparation

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 K_2O · 0.020 Na_2O · 1.582 CaO · 1 SiO_2 · 2.874 H_2O
=> Ca/Si = 1.58

Single file - hydration of Portland cement

Composition of C-S-H



	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[{CSHQ}][{Na}]

bXa[{CSHQ}][{Si}]

Syntax for use in process calculations

Summary C-S-H solid solution :

C-S-H solid solution: 0.022 K_2O · 0.020 Na_2O · 1.582 CaO · 1 SiO_2 · 2.875 H_2O
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:

$C_3A_{0.5}F_{0.5}S_{0.84}H_{4.32}$ and $C_3FS_{0.84}H_{4.32}$ **=> Al/Fe ≈ 1**

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.

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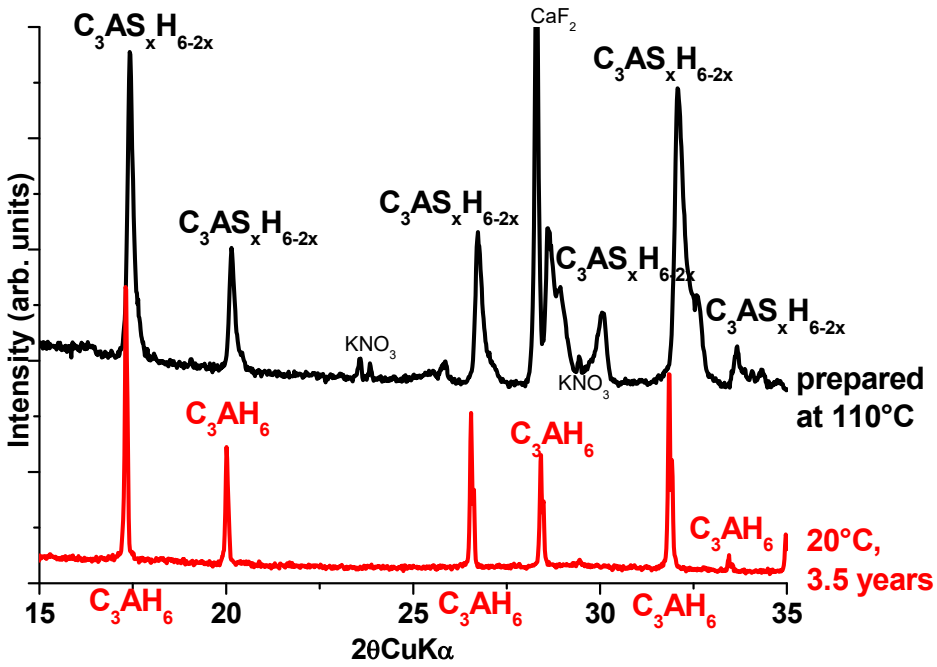
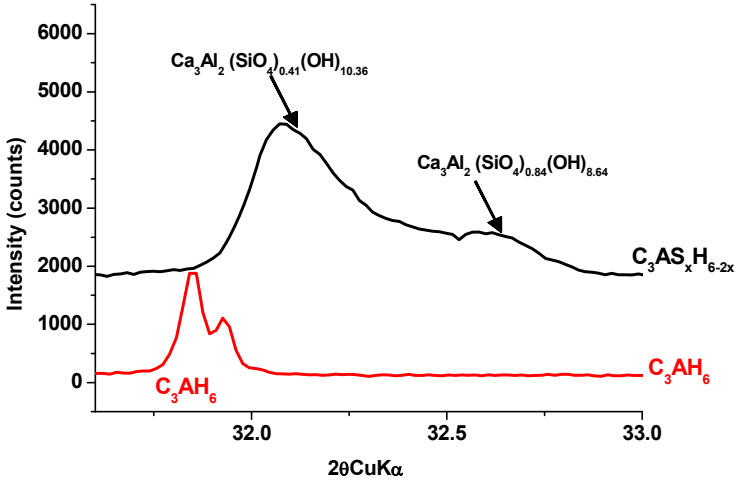
Presence of hydrogarnet



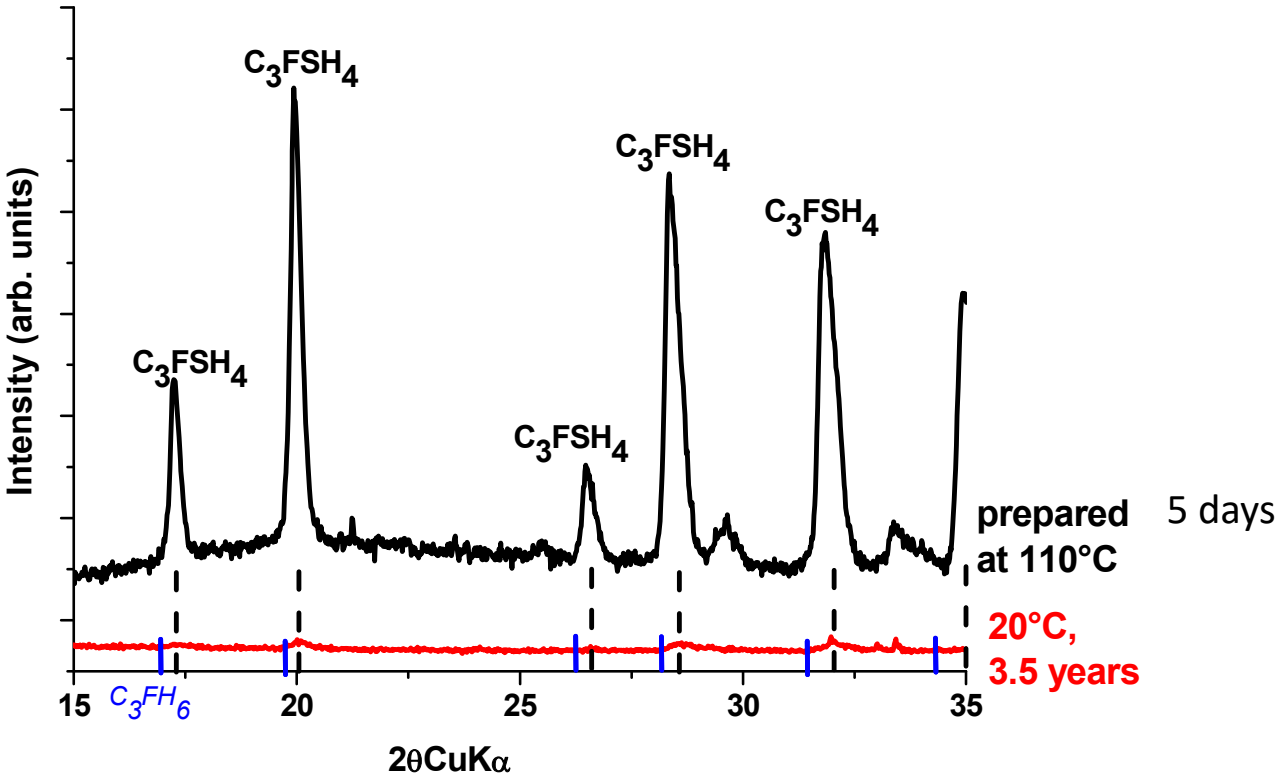


Room temperature: only C_3AH_6 and $C_3FS_xH_{6-2x}$ forms, *but no* $C_3AS_xH_{6-2x}$
$C_3AS_xH_{6-2x}$ *forms only at 110 C°, altough stable at 20 °C*

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

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Si-hydrogarnet in hydrated PC

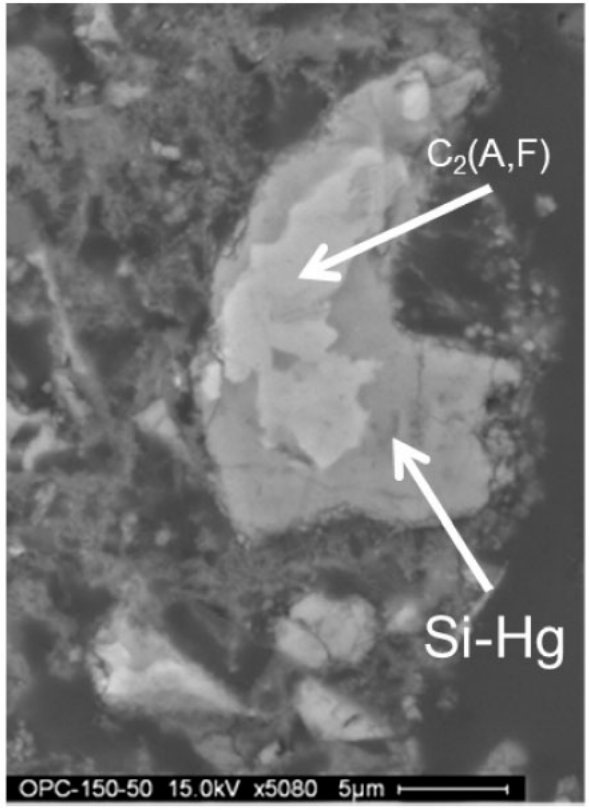
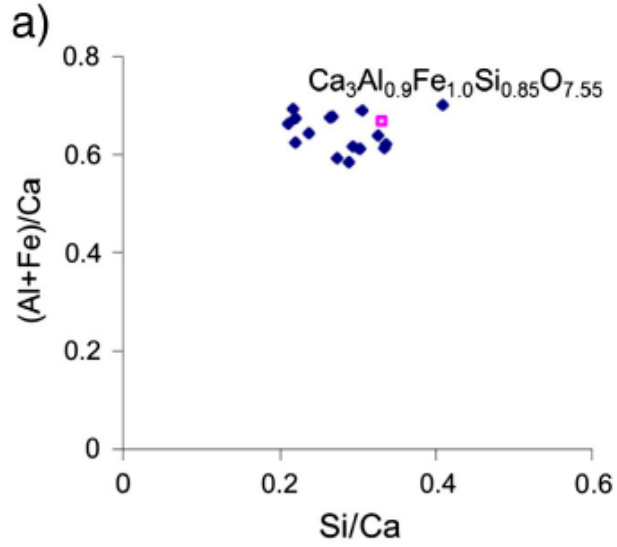
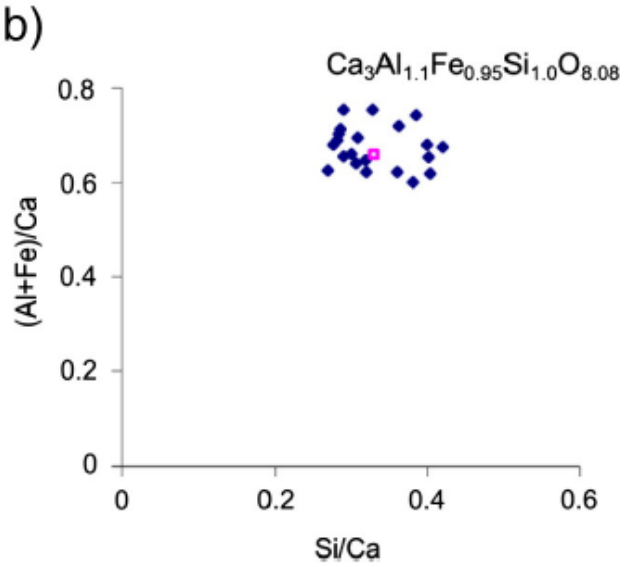


Fig. 8. SEM of ferrite clinker surrounded by hydration products after selective extraction.

20°C



50°C

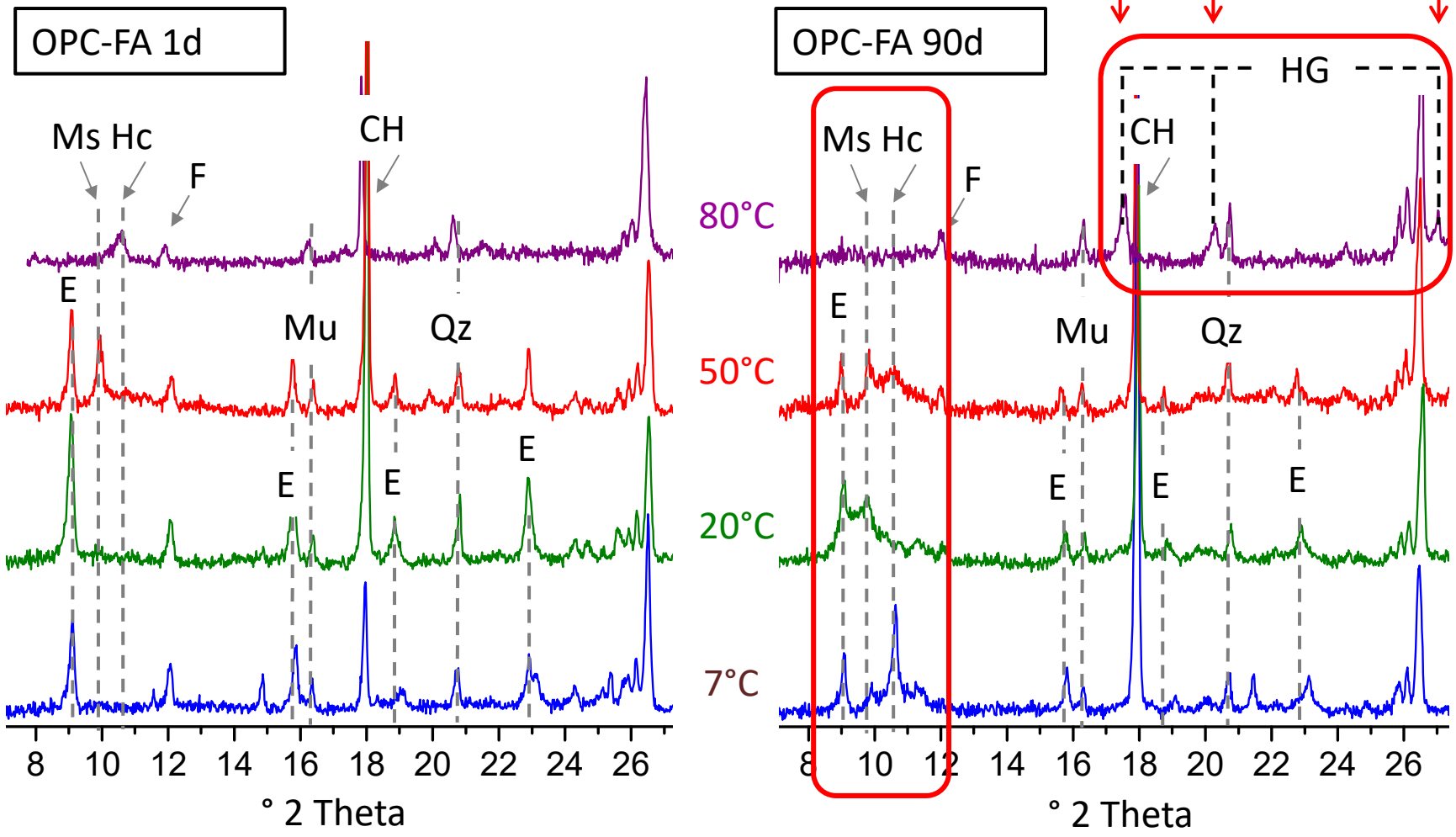


B.Z. Dilnesa, E. Wieland, B. Lothenbach, R. Dähn, K. Scrivener, Fe-containing phases in hydrated cements, Cem. Concr. Res. 58 (2014) 45–55.

Single file - hydration of Portland cement

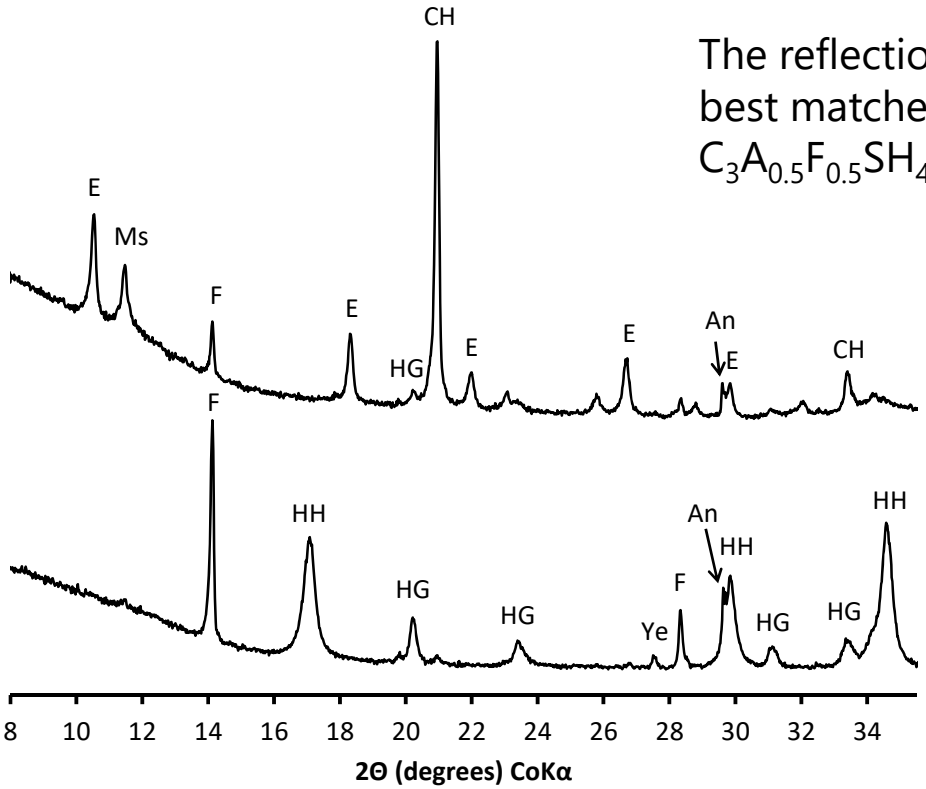
Siliceous hydrogarnet (PC blended with fly ash)

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



The reflections of the siliceous hydrogarnet (HG) were best matched by a hydrogarnet of the composition $C_3A_{0.5}F_{0.5}SH_4$.

before selective extraction

After selective extraction

91 days after SAM

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

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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 hydrogarent 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. ICCC 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)

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Materials Science and Technology

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

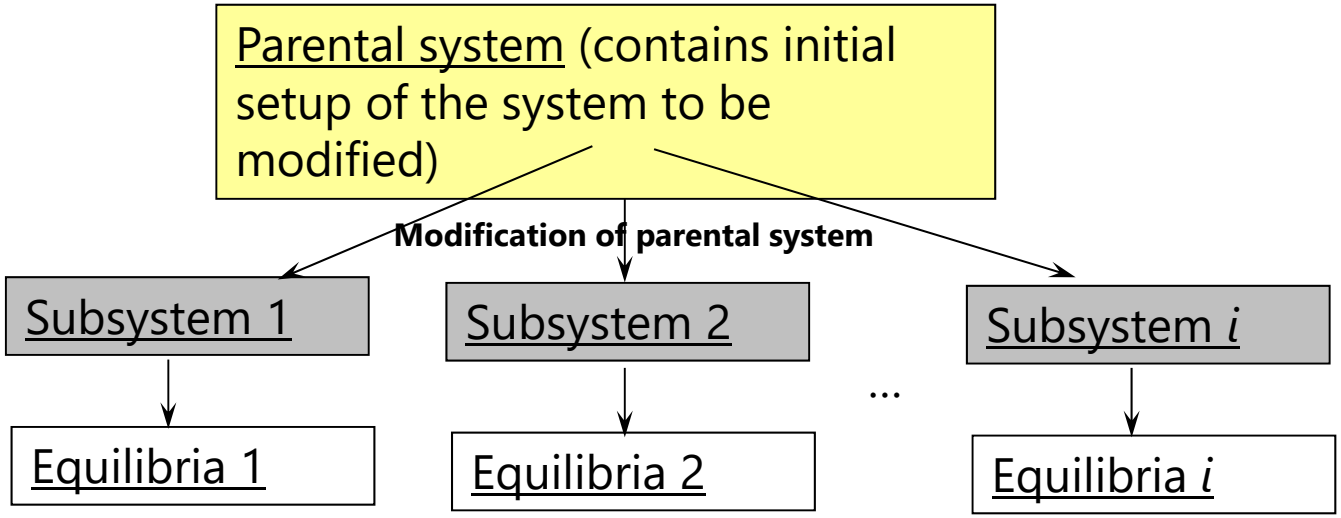
Description of analytical problem

- 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

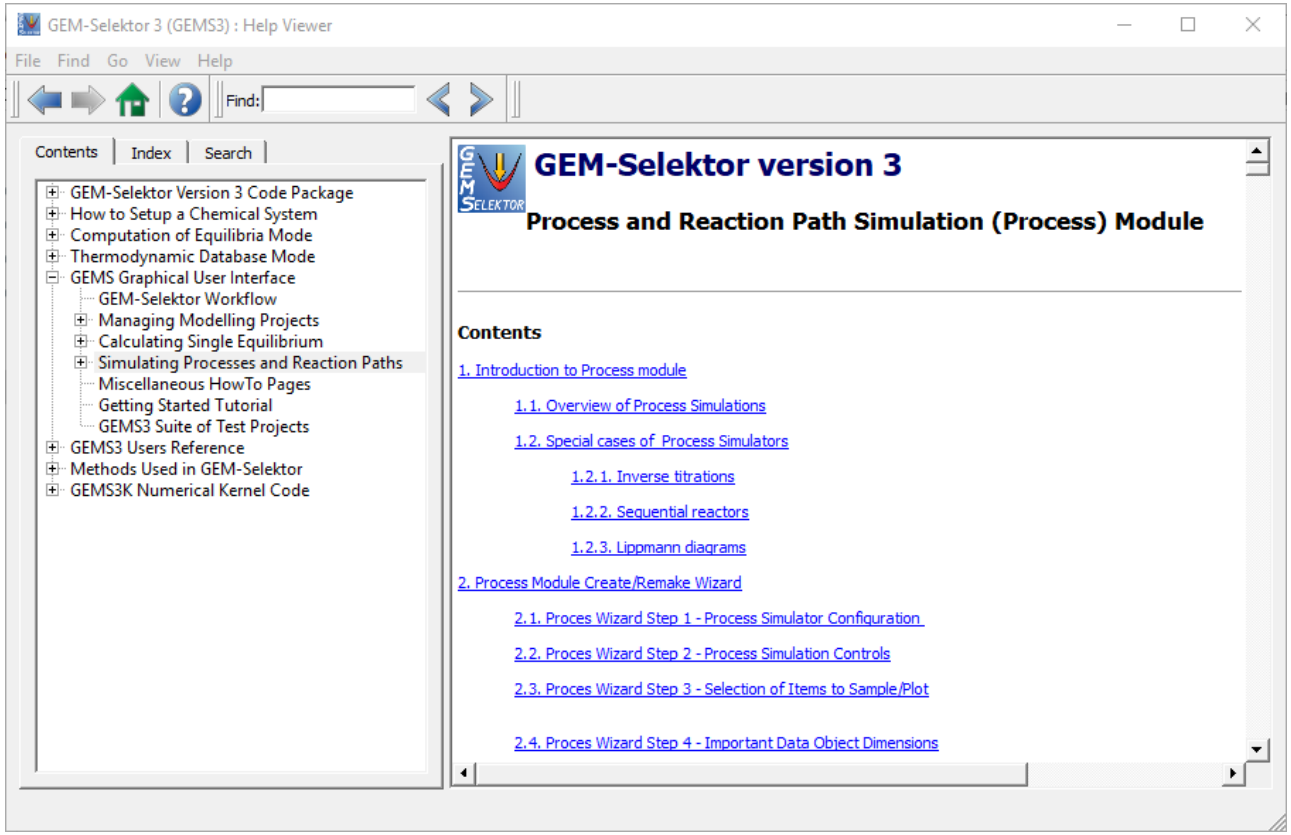


Structure of process simulator

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
Chemical analysis [g/100 g] [a]	
CaO	63.9
SiO_2	20.2
Al_2O_3	4.9
Fe_2O_3	3.2
CaO (free)	0.93
MgO	1.8
K_2O	0.78
Na_2O	0.42
CO_2	0.26
SO_3	2.29
$K_2O_{soluble}$ [b]	0.72
$Na_2O_{soluble}$ [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:

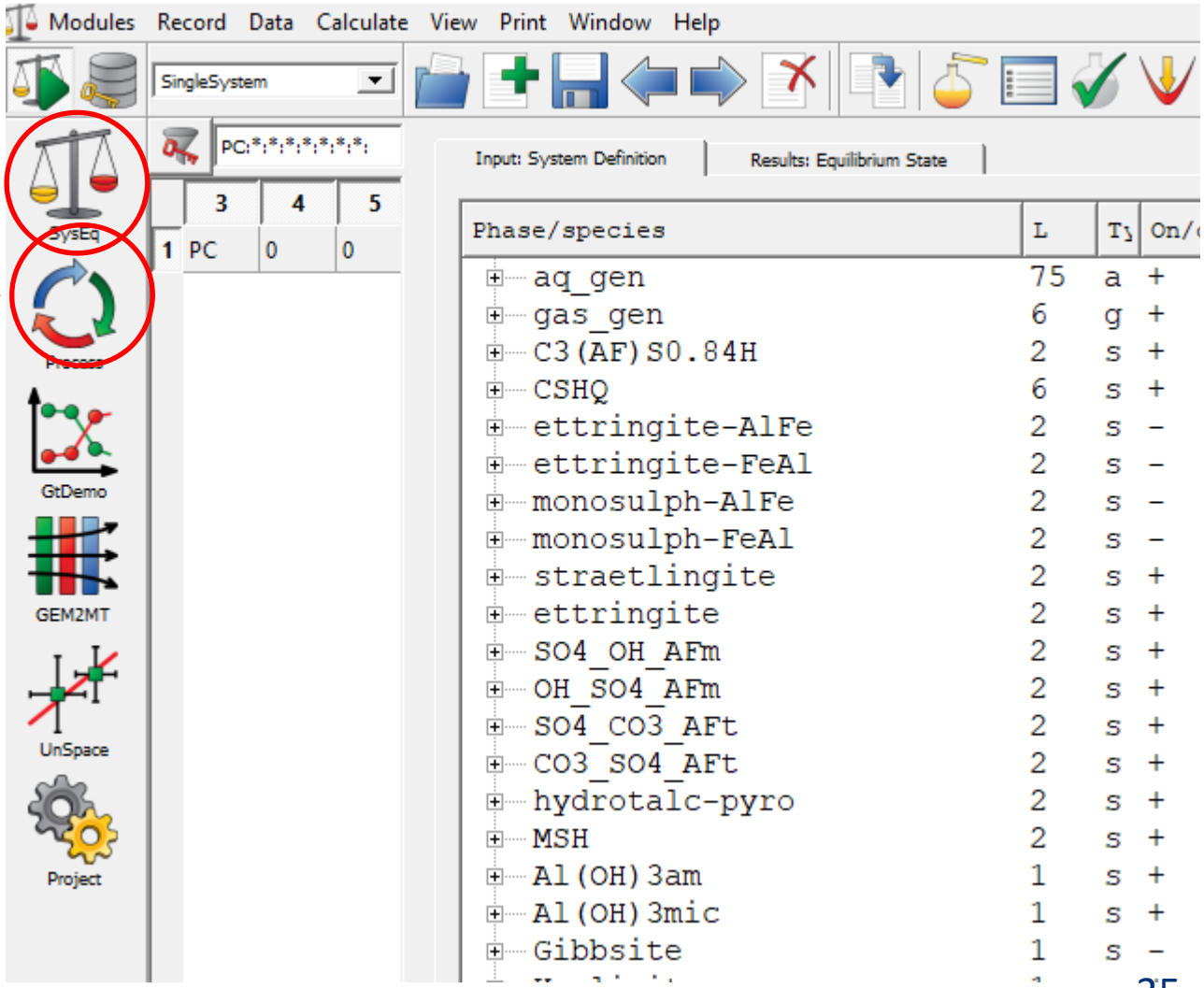
- initial amount of cement constant = 100 g
  "cement" = PC + limestone (= 100% $CaCO_3$)
- w/b ratio = 0.50 (50 g water), constant
- addition of 0.1 g O_2, constant
- 100% hydration

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 →

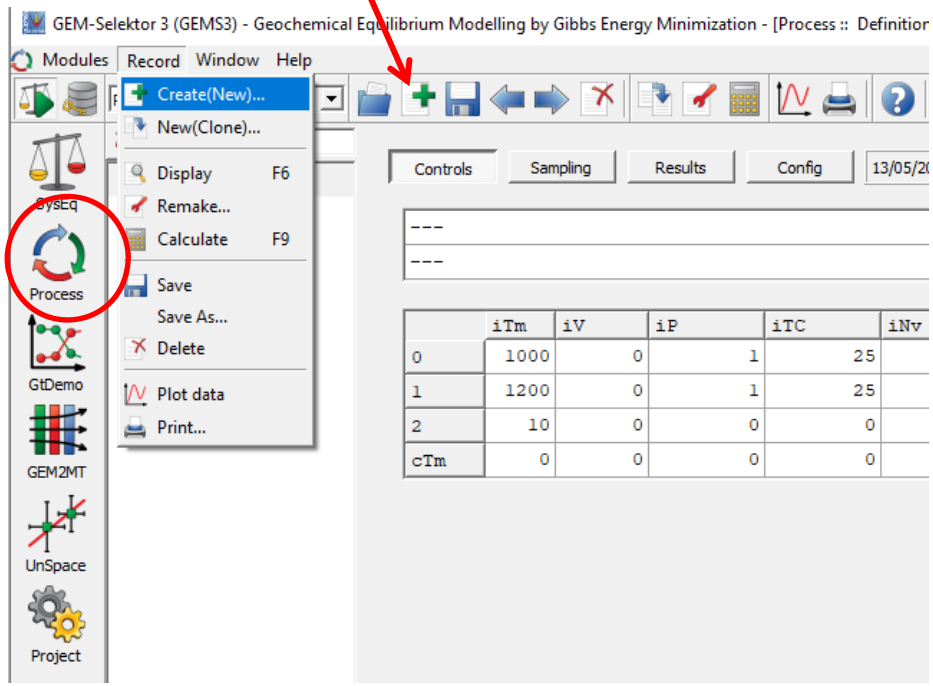


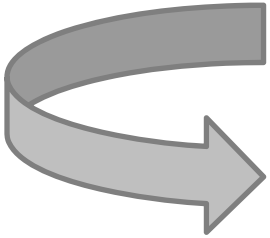
Process file - hydration of PC + limestone

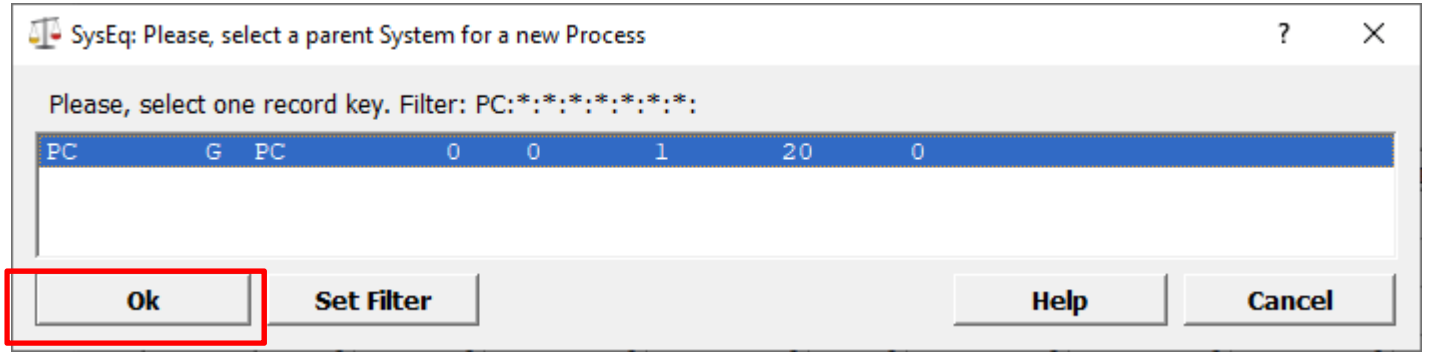
Create new process file

or click here

1.

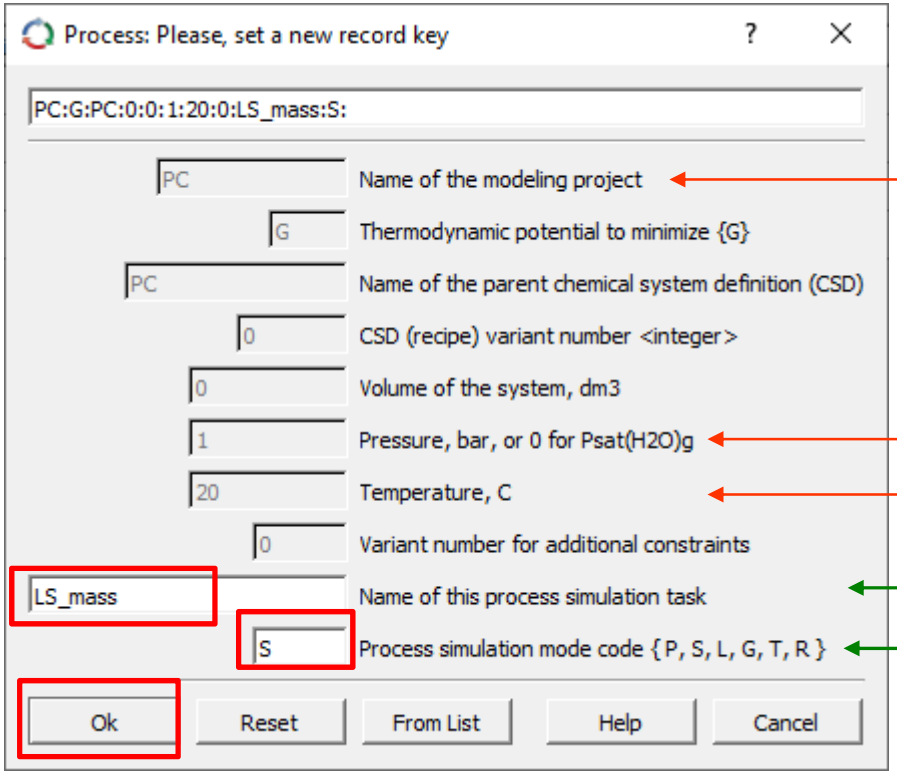






Select parent file

Process file - hydration of PC + limestone



project name

pressure

temperature

file name of process simulation

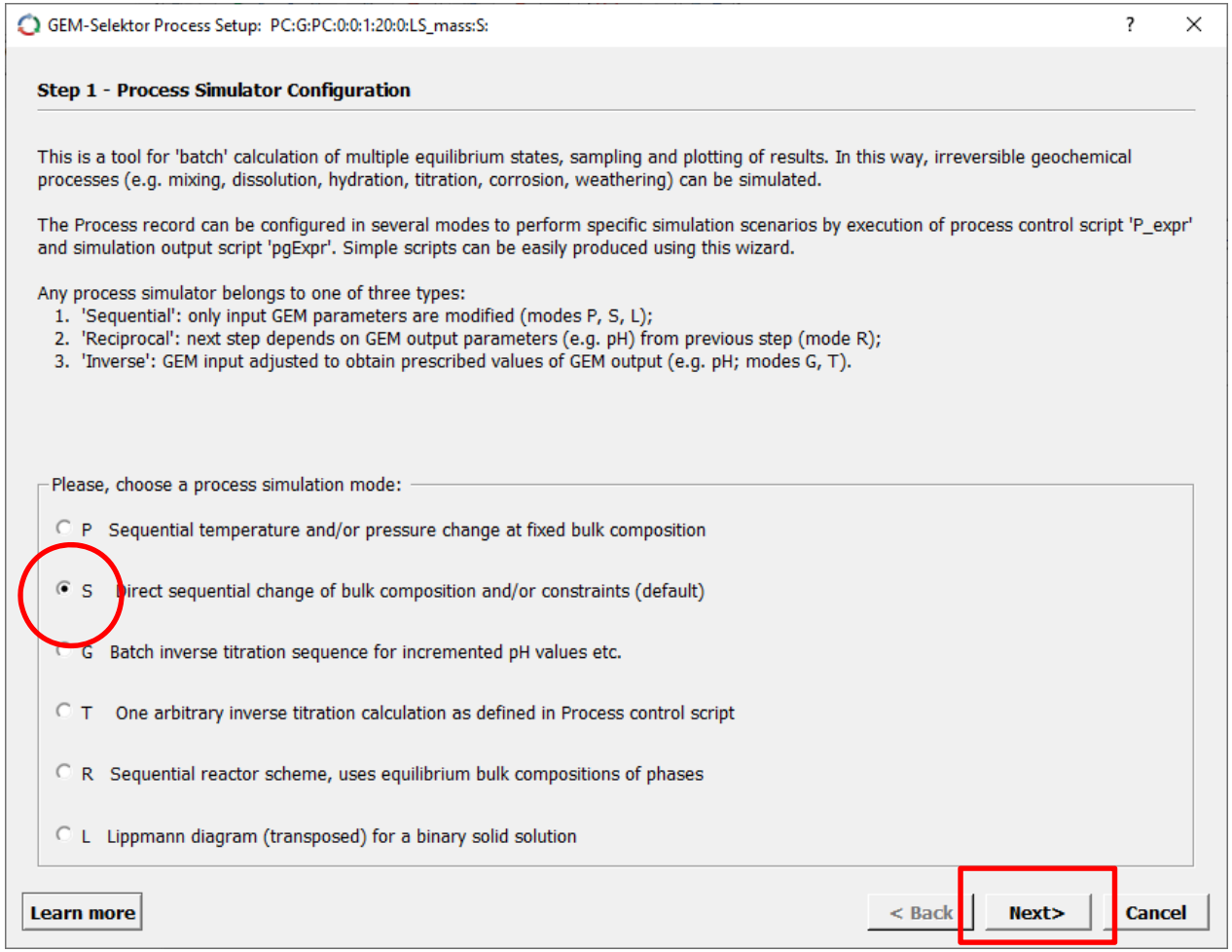
simulation type

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



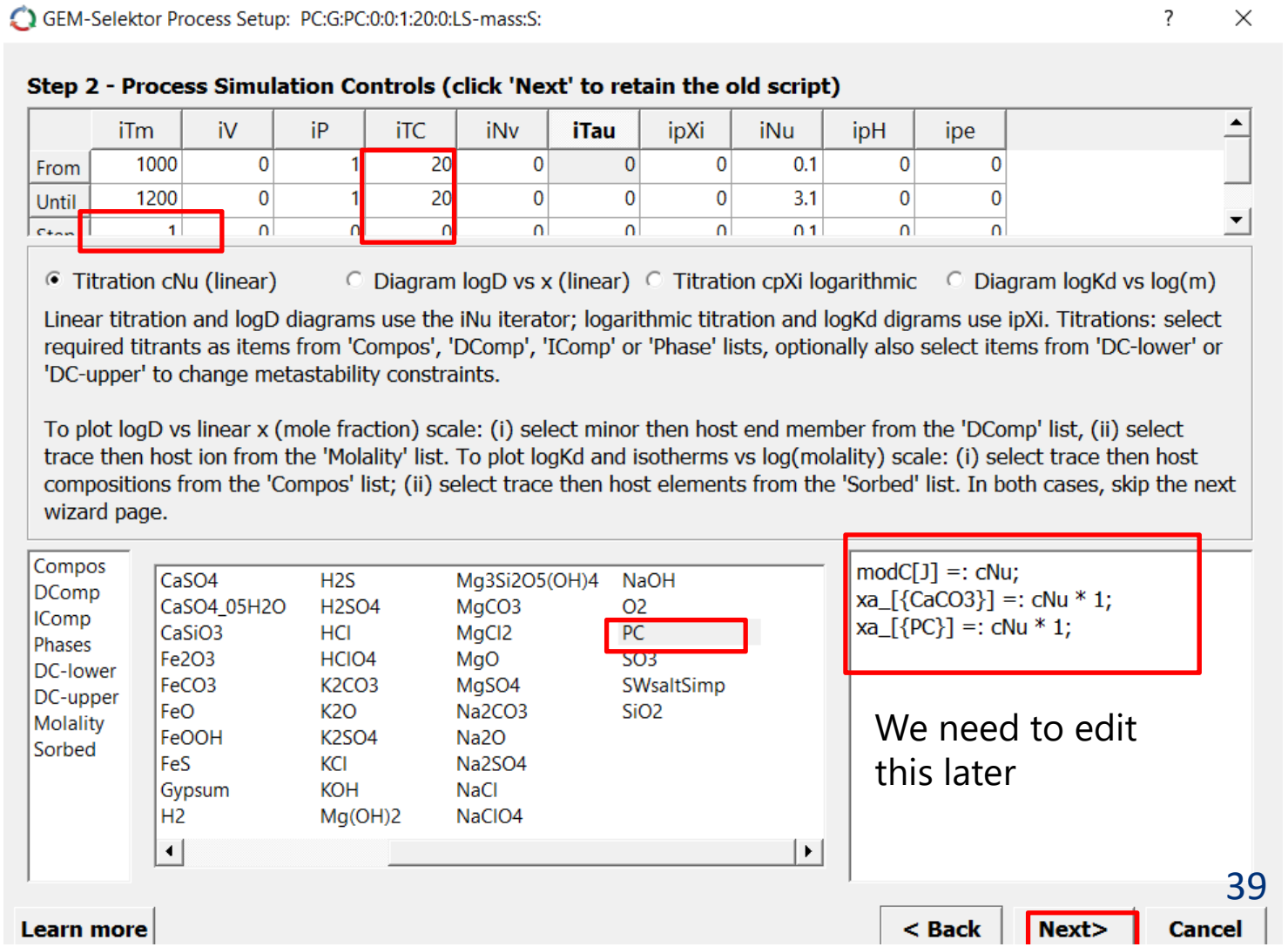
Process file - hydration of PC + limestone

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)

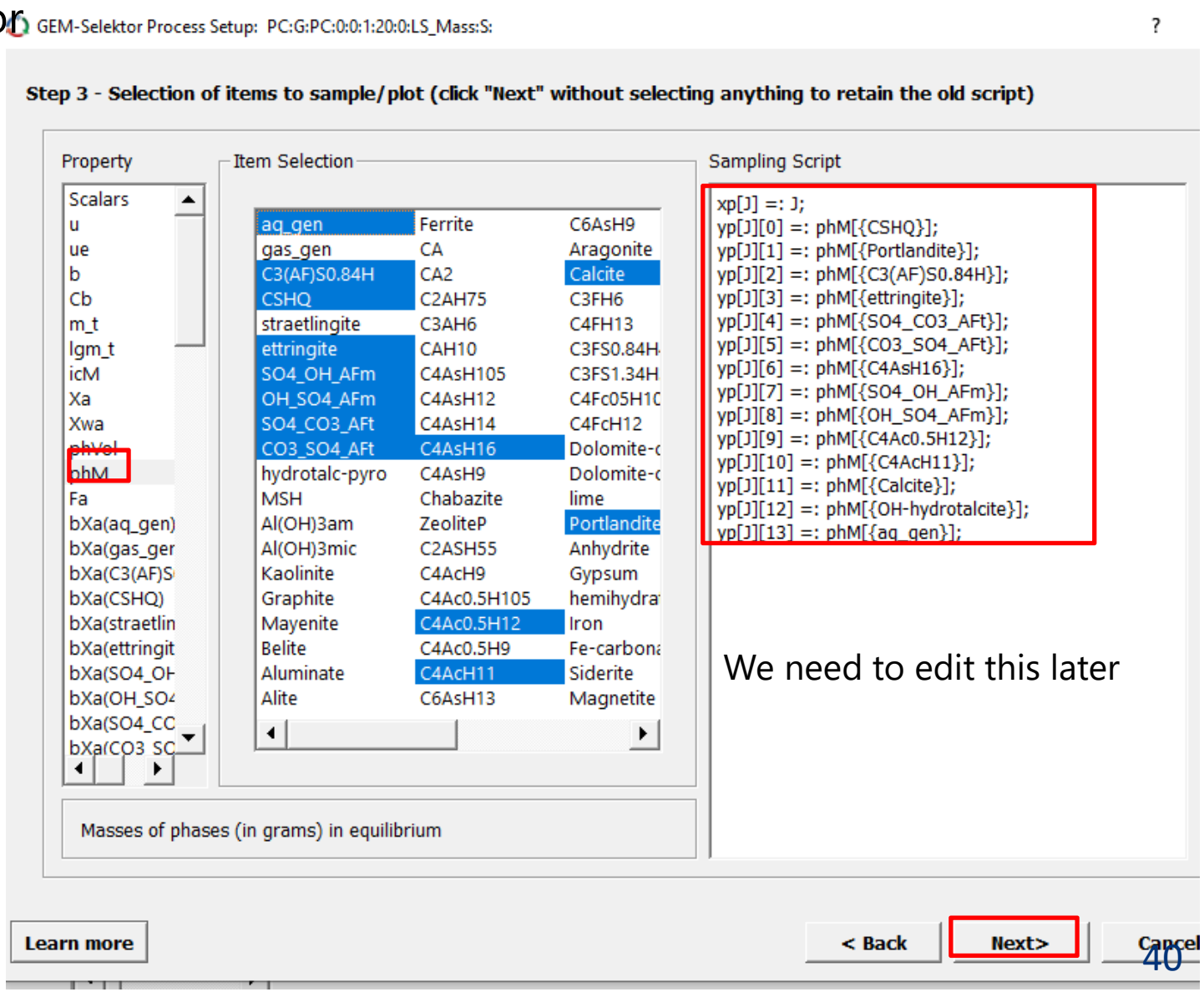
3. Select Aqua and O_2



Process file - hydration of PC + limestone

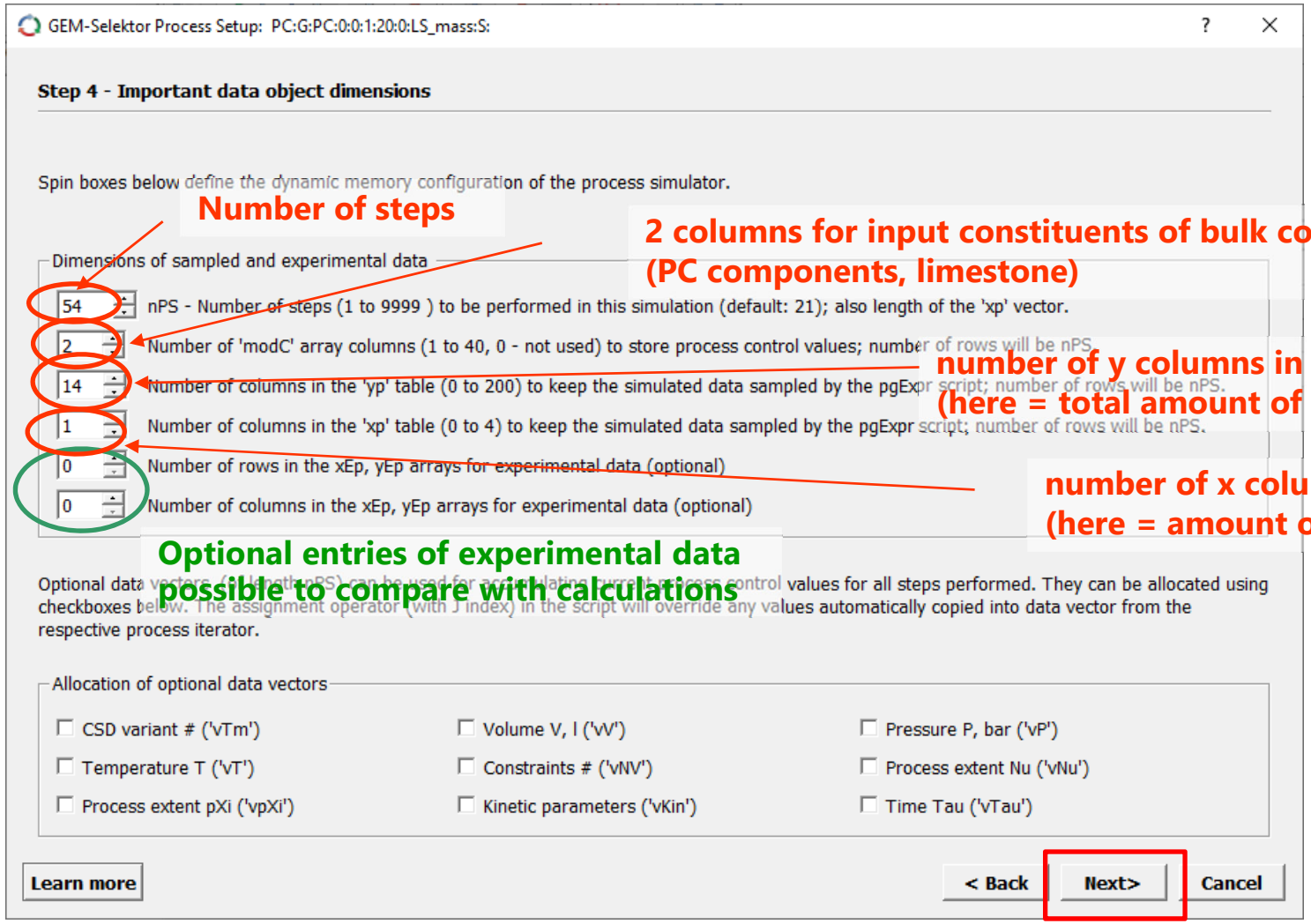
Wizard available for process files

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



Process file - hydration of PC + limestone

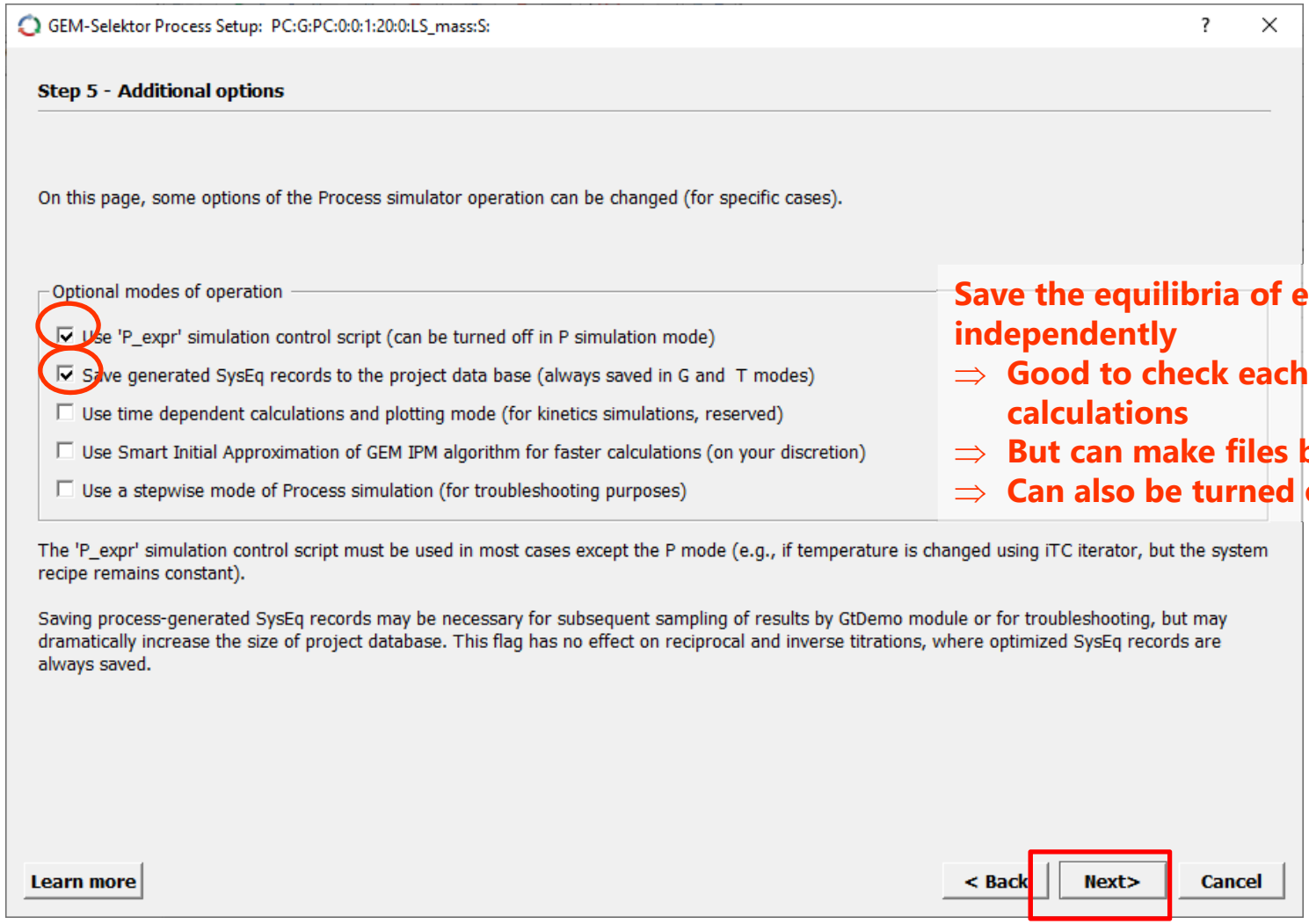
Numerical settings of process simulation



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

Process file - hydration of PC + limestone

Additional settings



Save the equilibria of each step independently

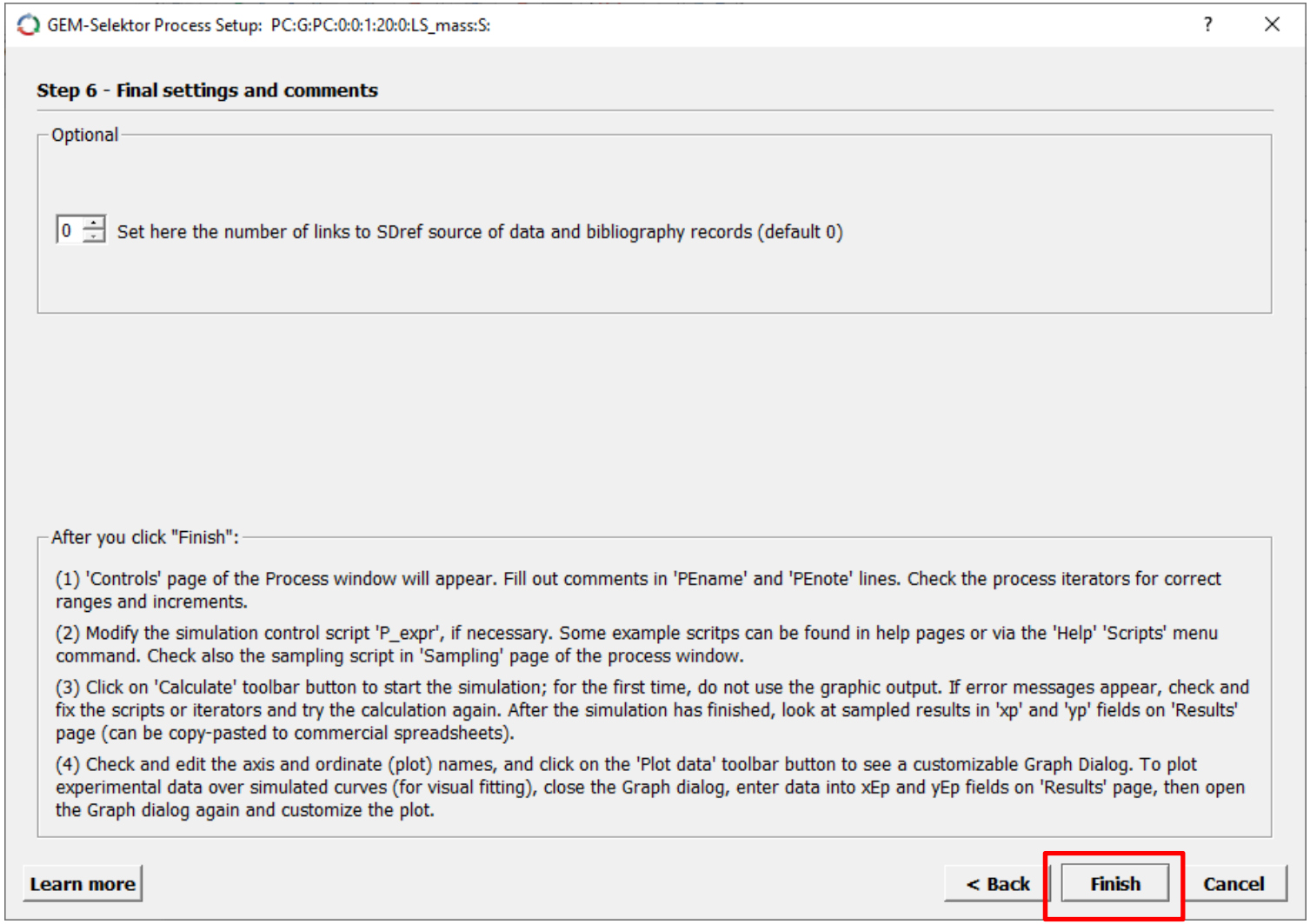
⇒ **Good to check each calculations**

⇒ **But can make files big**

⇒ **Can also be turned off**

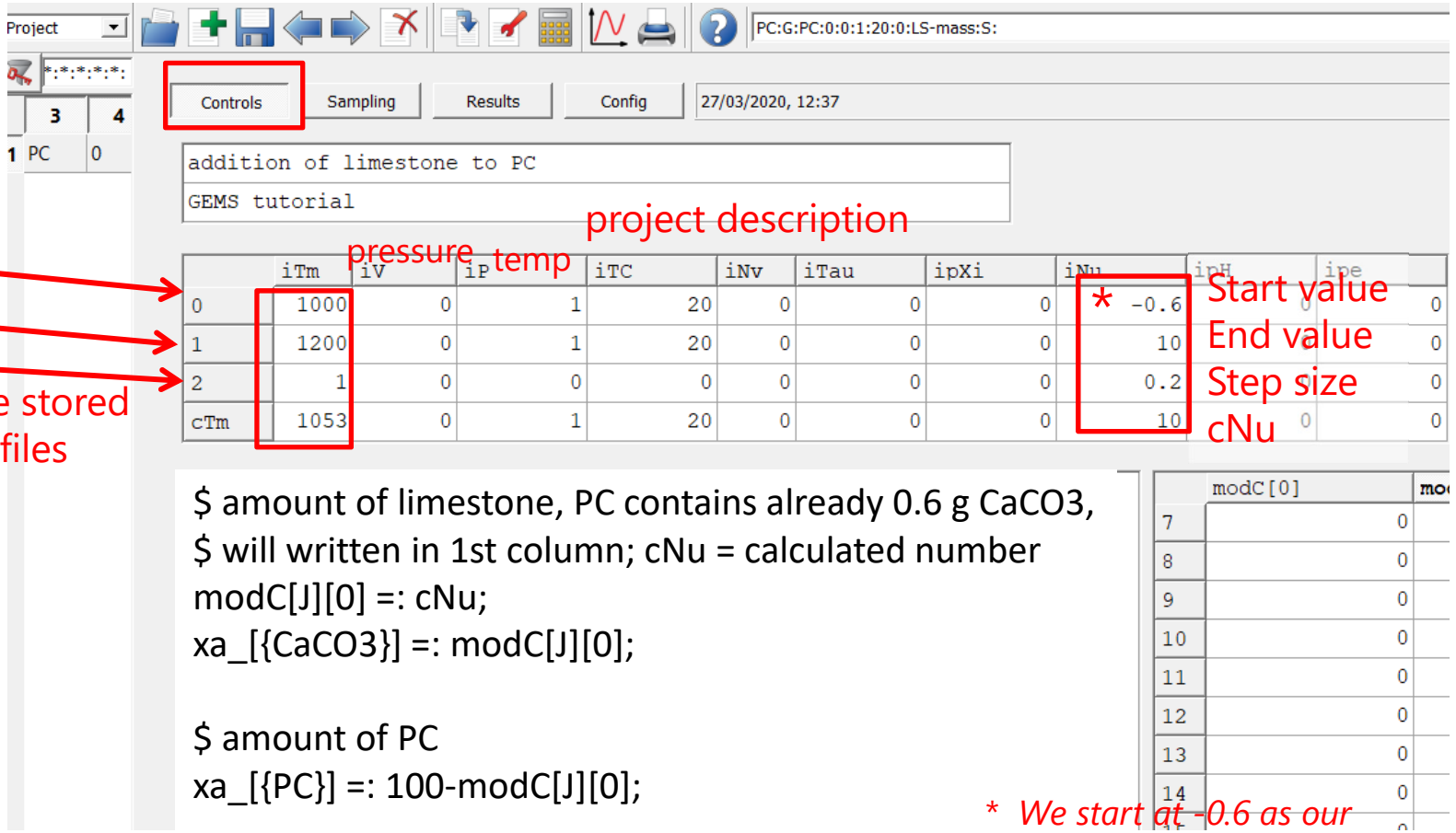
Process file - hydration of PC + limestone

Additional settings



Process file - hydration of PC + limes

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



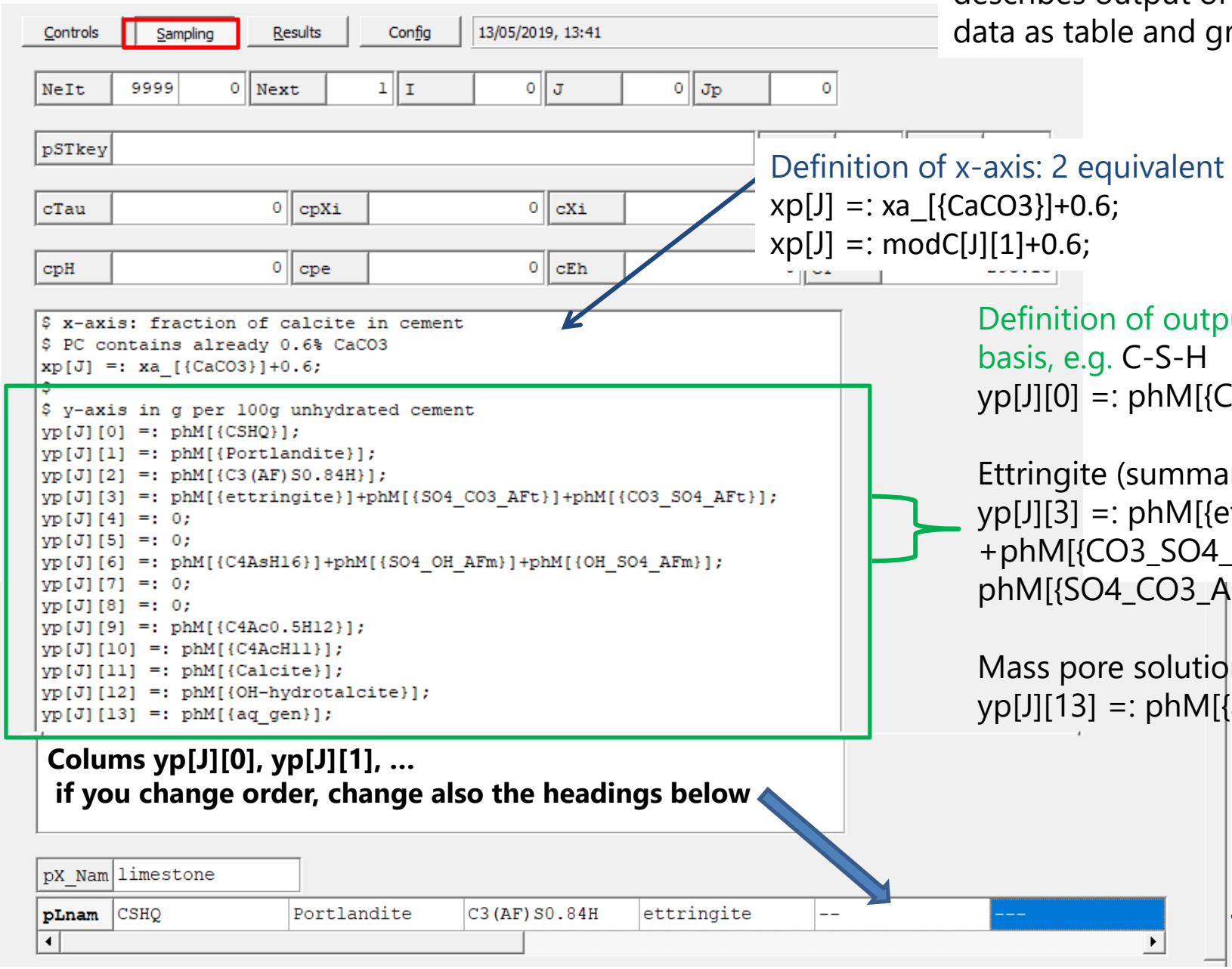
Modify text to
($ = comment)

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

* *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



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}];

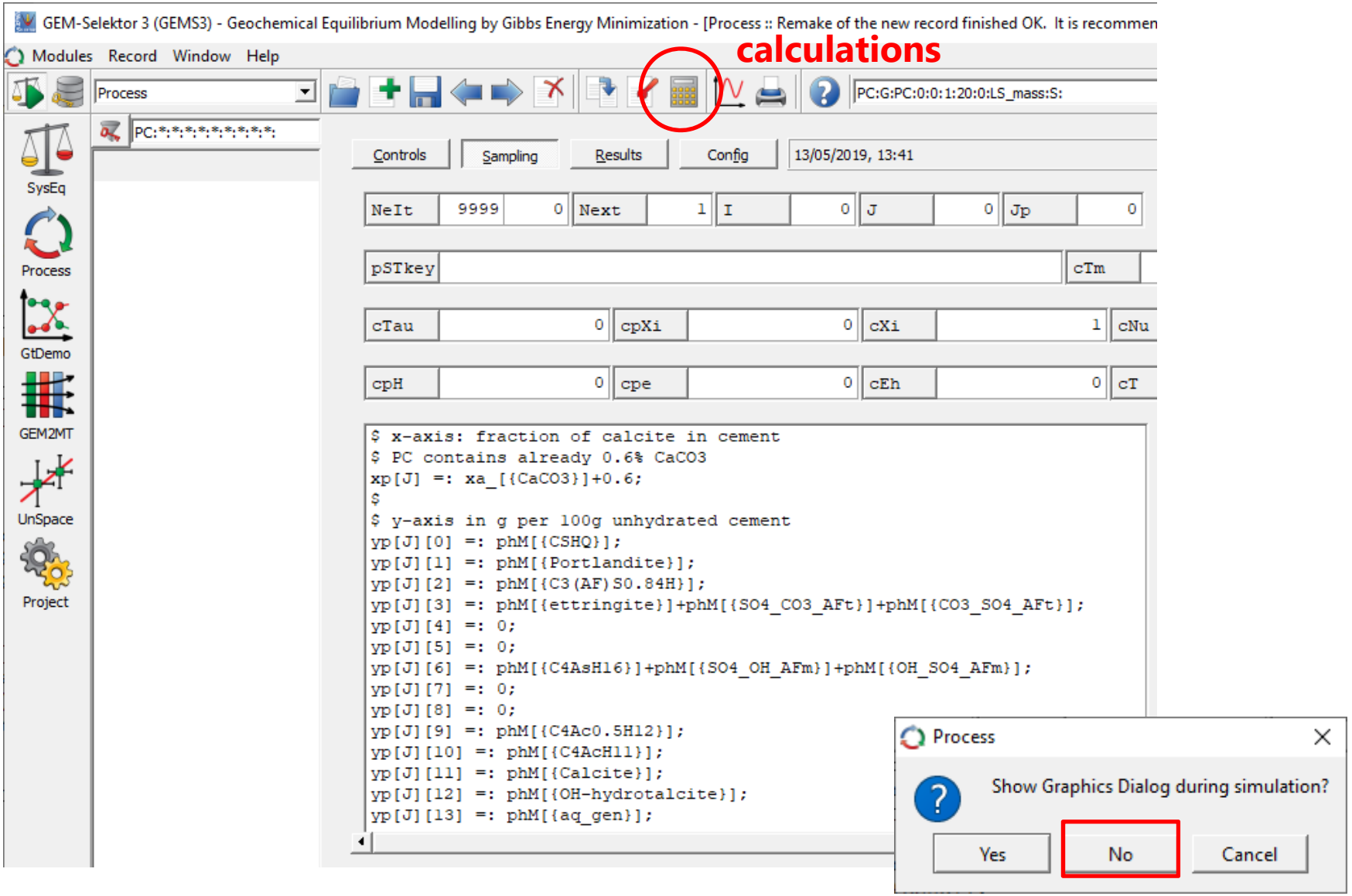
Ettringite (summarized):

yp[J][3] =: phM[{ettringite}] +phM[{CO3_SO4_AFt}]+ phM[{SO4_CO3_AFt}] ;

Mass pore solution:

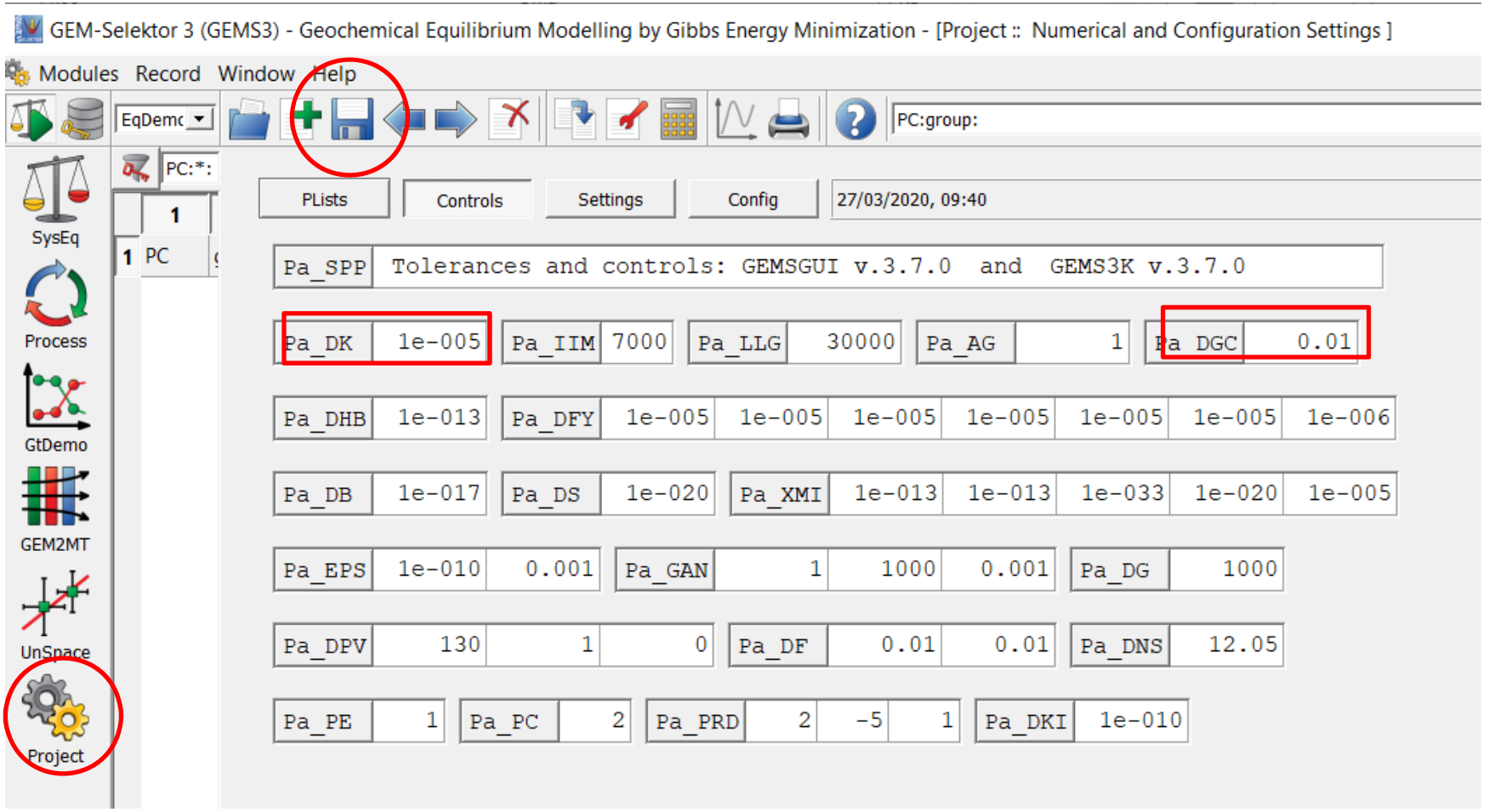
yp[J][13] =: phM[{aq_gen}];

Process file - hydration of PC + limestone



Process file - hydration of PC + limestone

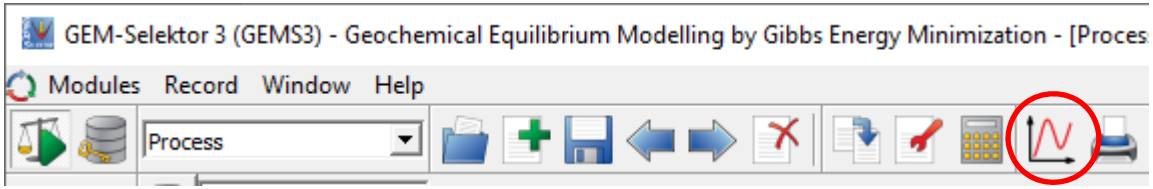
In case the convergence error occurs ...

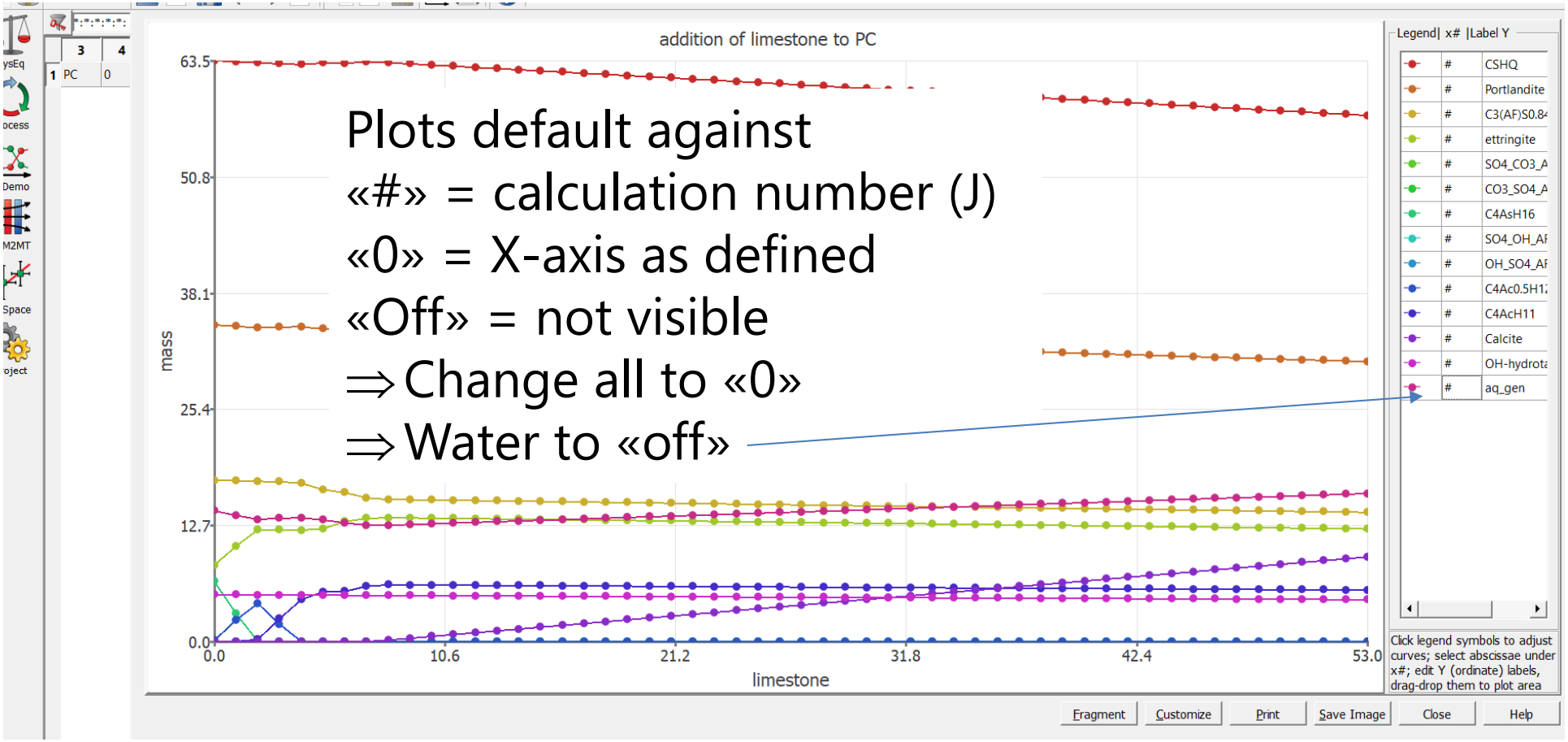


Process file - hydration of PC + limestone

1. open graph

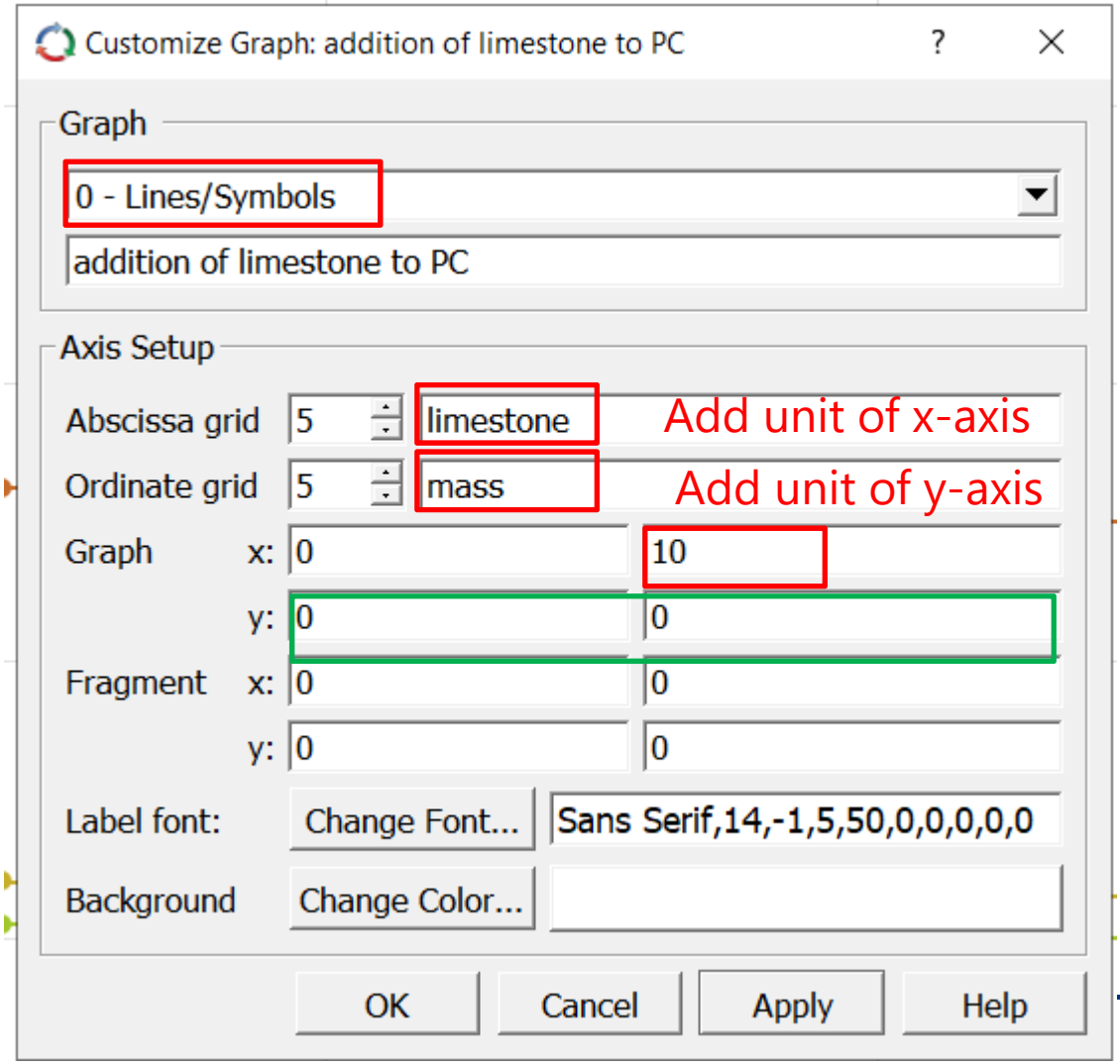
2. label graph





Process file - hydration of PC + limestone

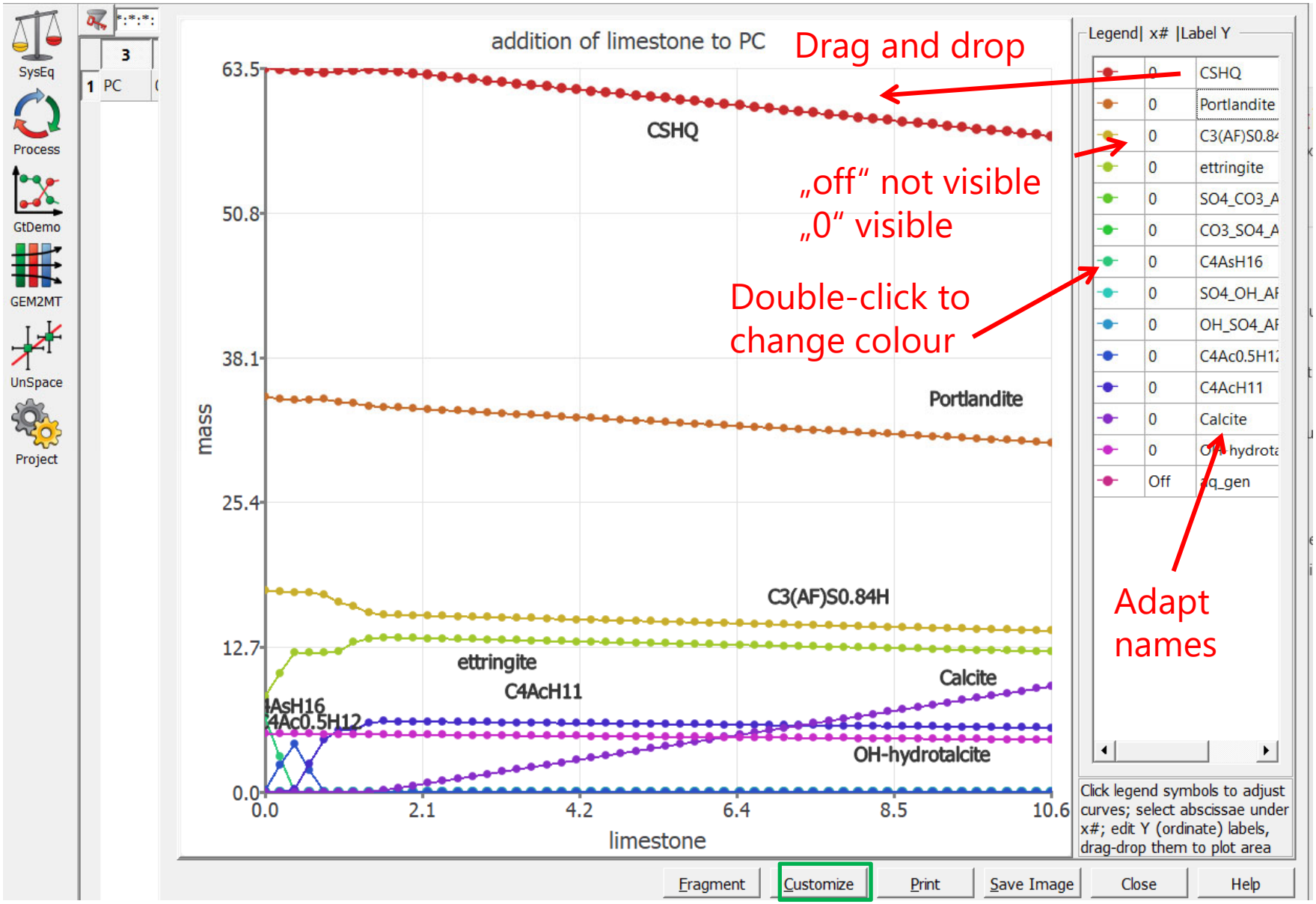
Modify the graph as you prefer: example



Min - max

0 – 0: autoscale

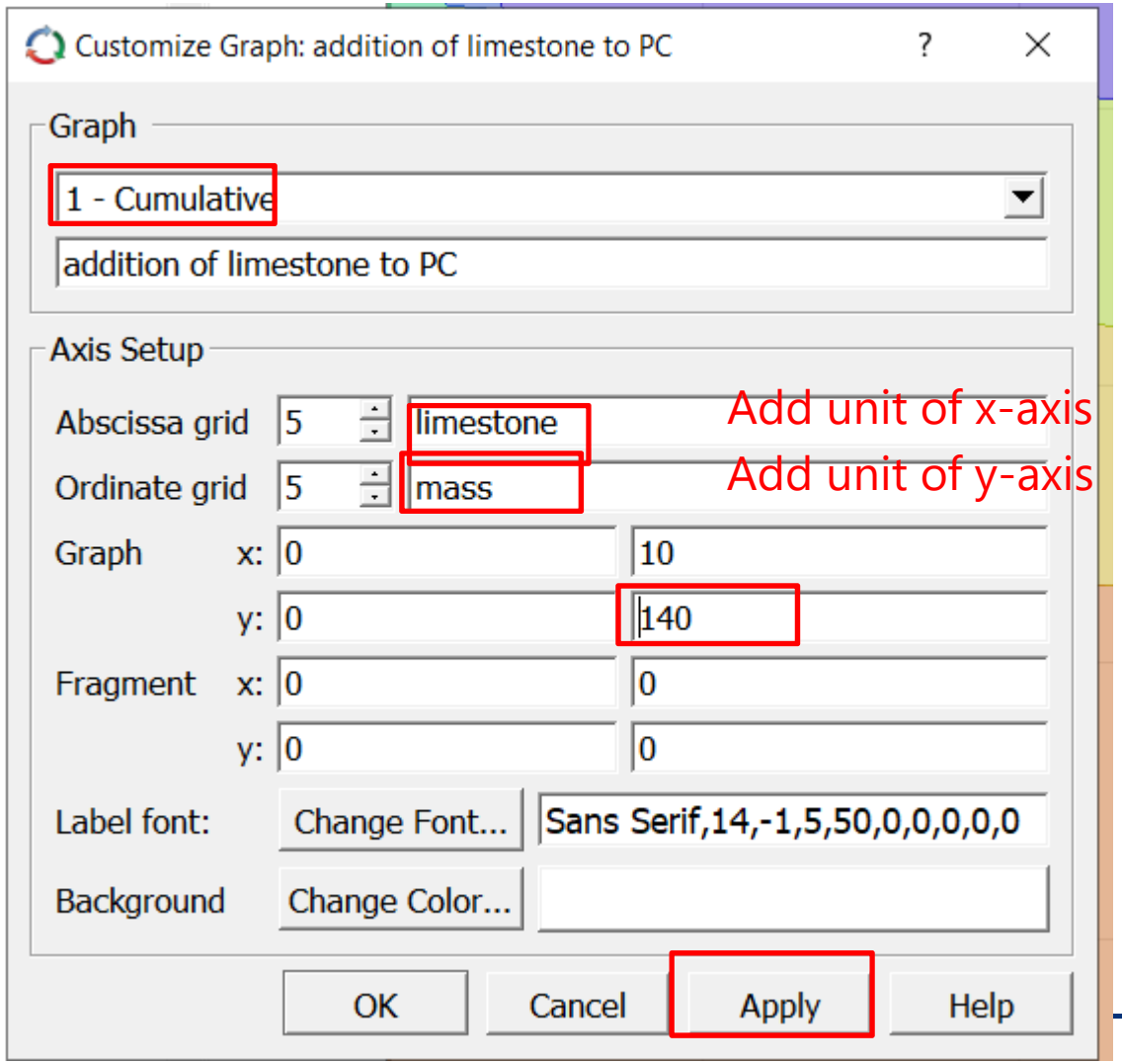
Process file - hydration of PC + limestone



To adapt scale / axis-labelling

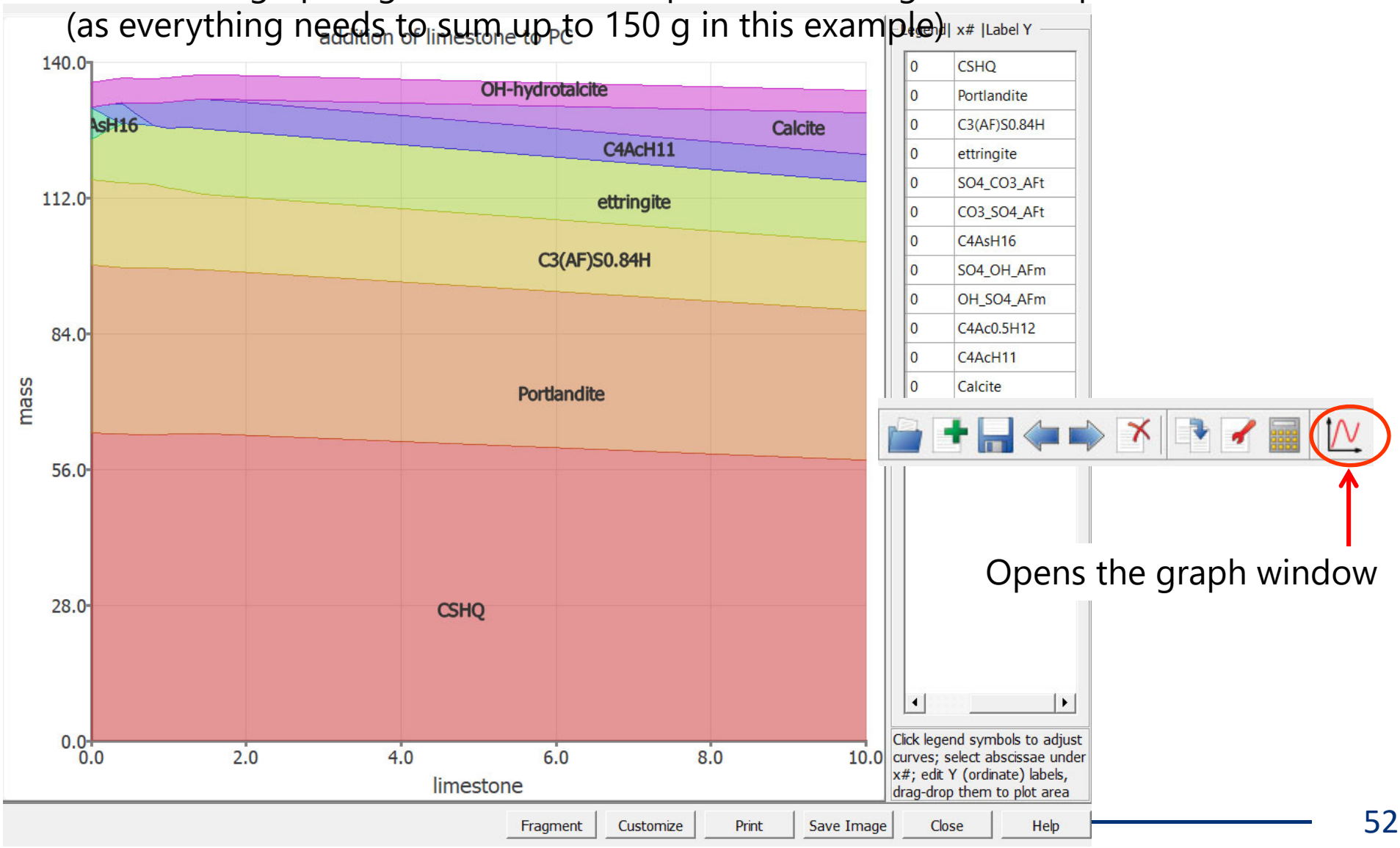
Process file - hydration of PC + limestone

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)



Opens the graph window

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

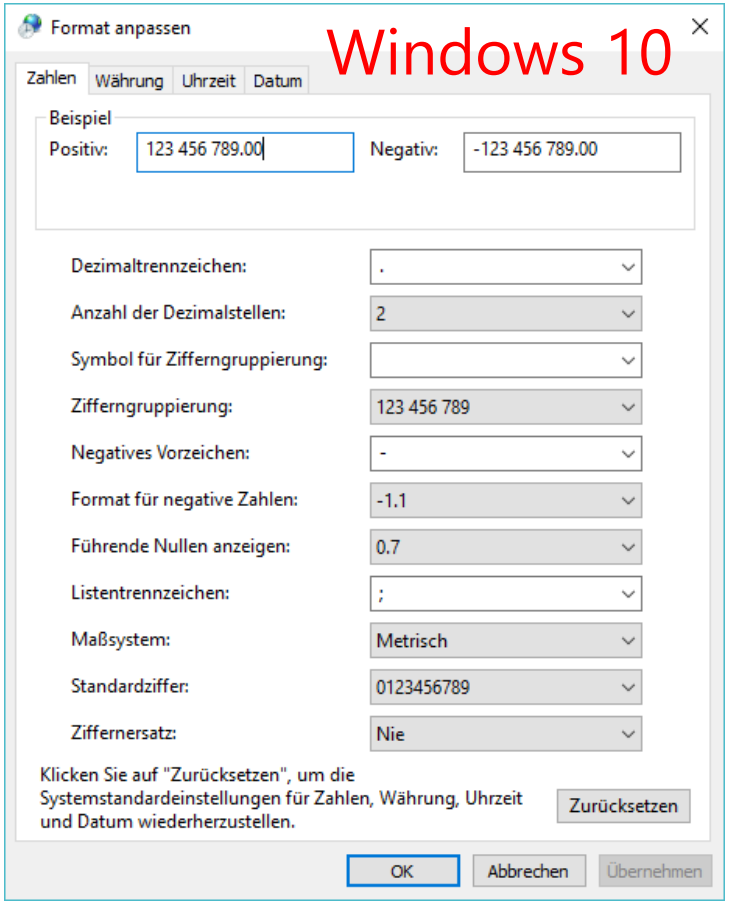
pX_Nam	limestone	CSHQ	Portlandite	C3(AF)S0.84H	ettringite	S
0	0	63.479529	34.639764	17.577815	8.3255595	
1	0.2	63.354146	34.477327	17.542837	10.388585	
2	0.4	63.247179	34.325451	17.464707	12.194956	
3	0.6	63.120692	34.402836	17.429852	12.170592	
4	0.8	63.049524	34.424192	17.266221	12.144797	
5	1	63.2112	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	

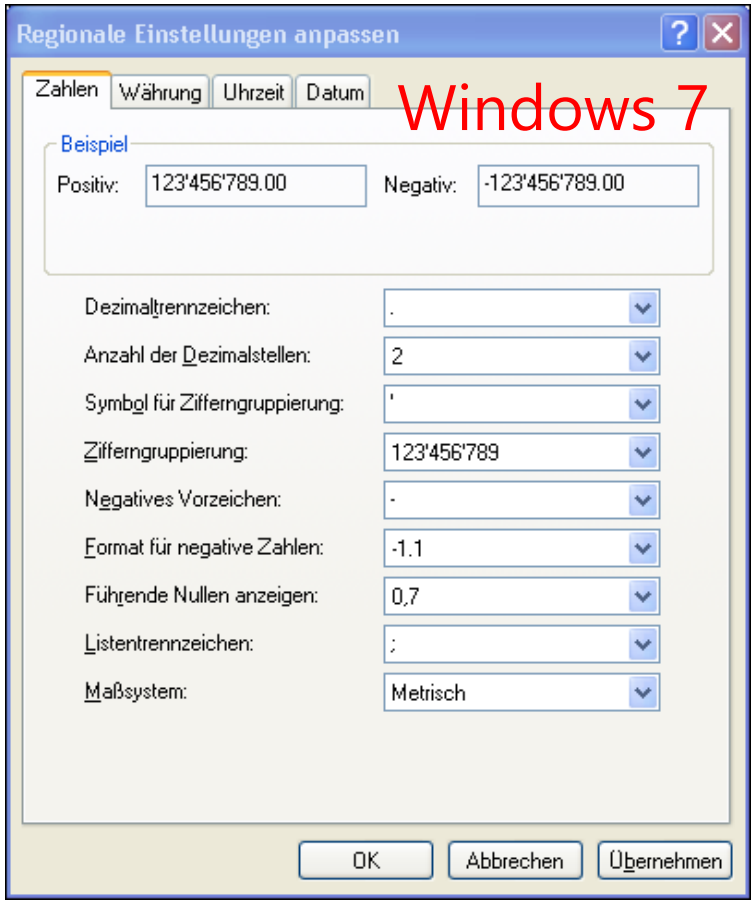
Process file - hydration of PC + limestone

Copying data to or from Excel files

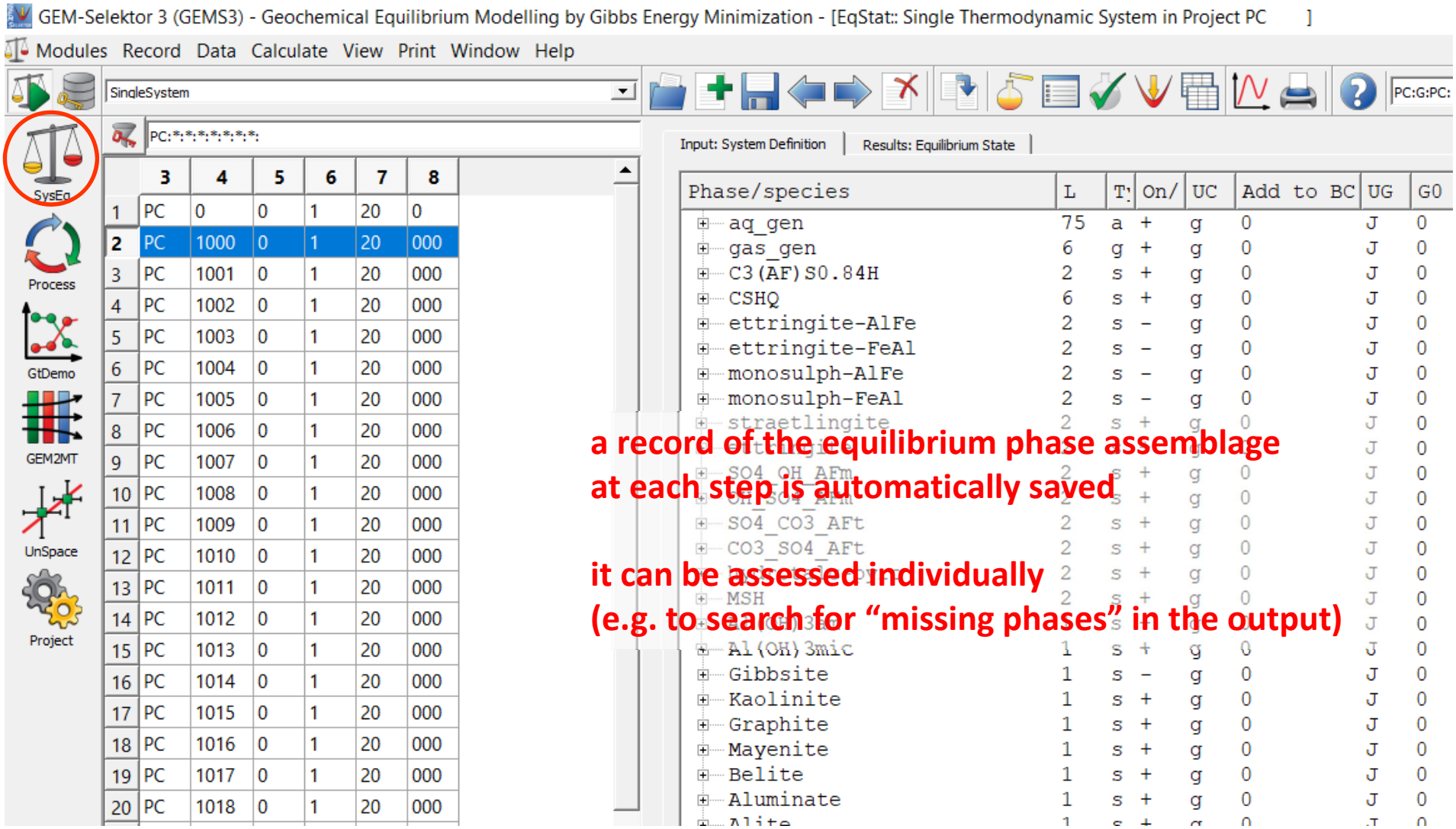
We need **decimal points**, **not commas** !

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





Process file - hydration of PC + limestone



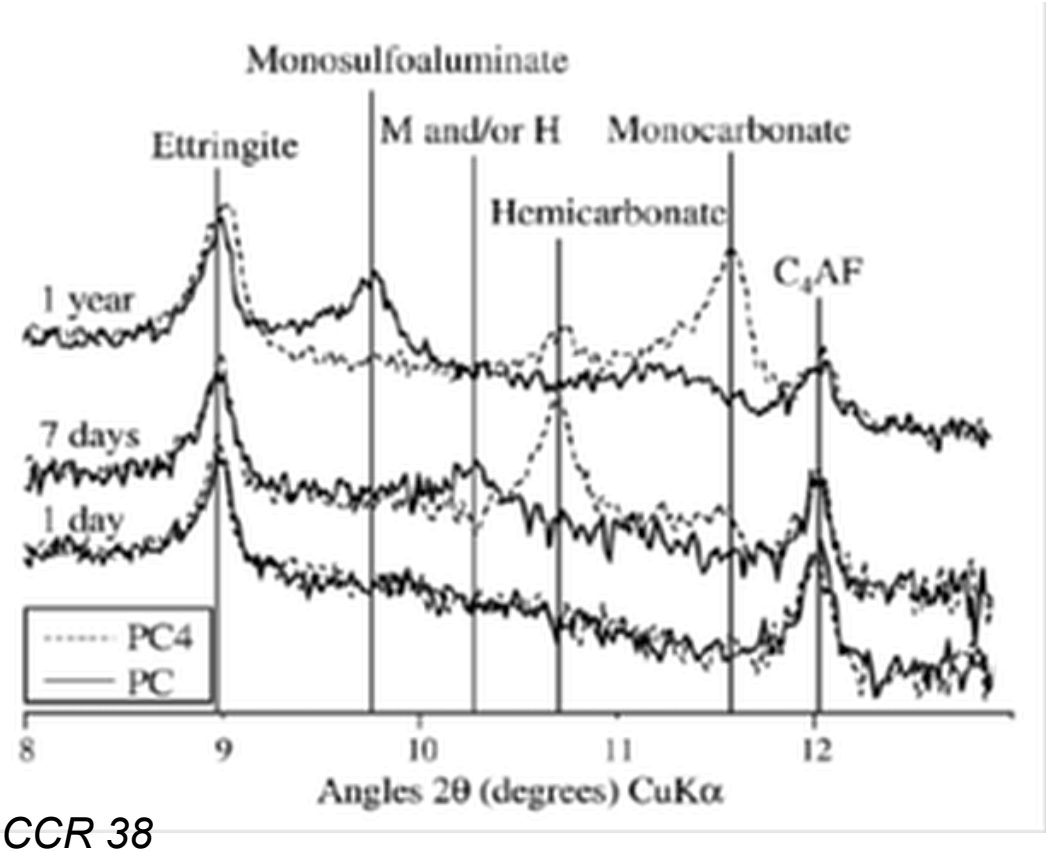
	3	4	5	6	7	8
1	PC	0	0	1	20	0
2	PC	1000	0	1	20	000
3	PC	1001	0	1	20	000
4	PC	1002	0	1	20	000
5	PC	1003	0	1	20	000
6	PC	1004	0	1	20	000
7	PC	1005	0	1	20	000
8	PC	1006	0	1	20	000
9	PC	1007	0	1	20	000
10	PC	1008	0	1	20	000
11	PC	1009	0	1	20	000
12	PC	1010	0	1	20	000
13	PC	1011	0	1	20	000
14	PC	1012	0	1	20	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

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

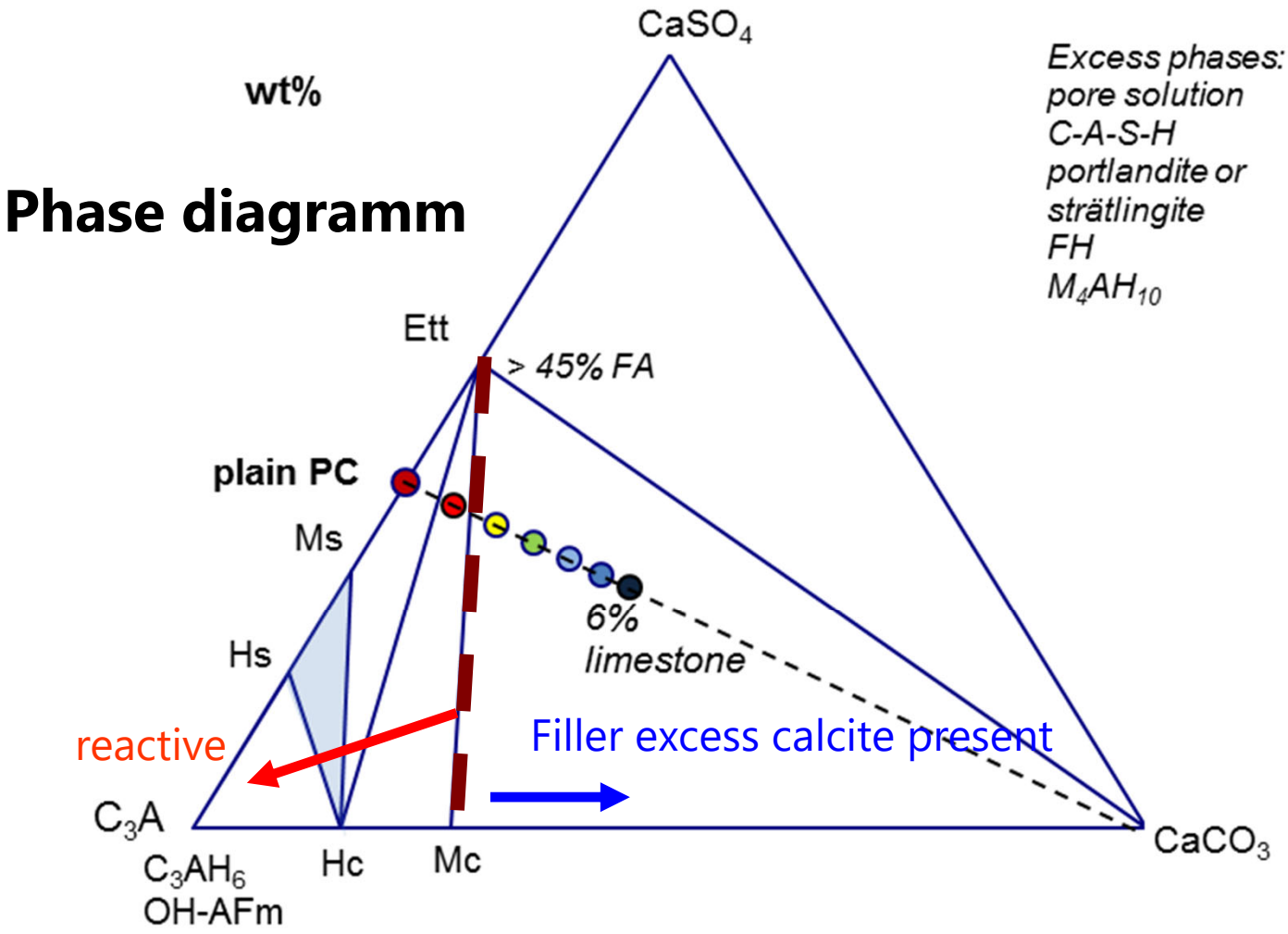
Formation of monosulfoaluminate in carbonate free paste, whereas monocarboaluminate+AFt are predominant in calcite blended paste



Lothenbach ea 2008, CCR 38

Good agreement between experiments and calculations

Background: Limestone addition to PC



Tutorial – process: hydration of Portland cement

Empa
Materials Science and Technology

Hydration of Portland cement

1) Hydration of PC - single system

2) Influence of limestone on hydration of PC – process file

Guided tutorial

3) Mass based -> volume based output

4) Influence of fly ash on hydration of PC – process file

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.

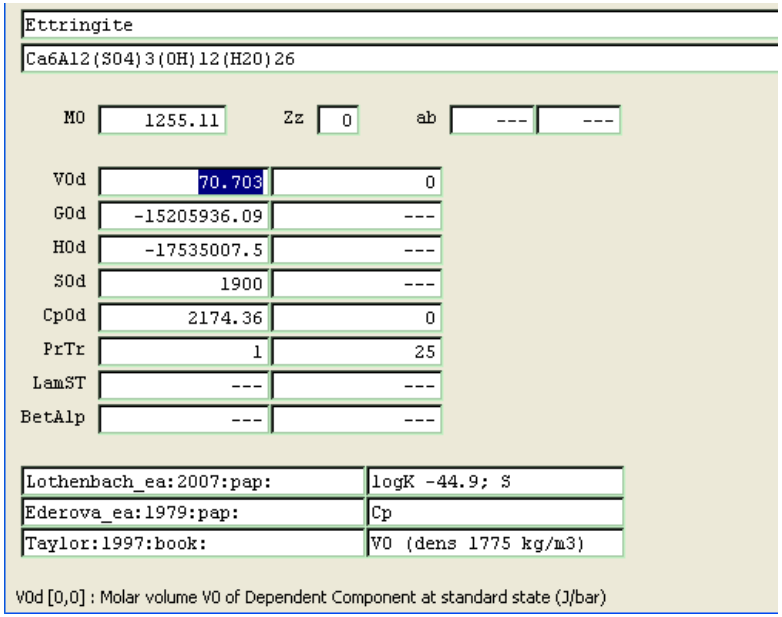
Modification of the existing process to plot specific volumes of the individual phases present in the chosen example

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



For example ettringite:

Theor. density: 1.775 g/cm^3 (derived from fitted unit cell size)

Molar volume

= 1255.11g/mol / 1.775g/cm^3 = 707cm^3/mol

1cm^3/mol = 10^{-1}J/bar → <u>70.7 J/bar</u>

Process file - hydration of PC + limestone

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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}];

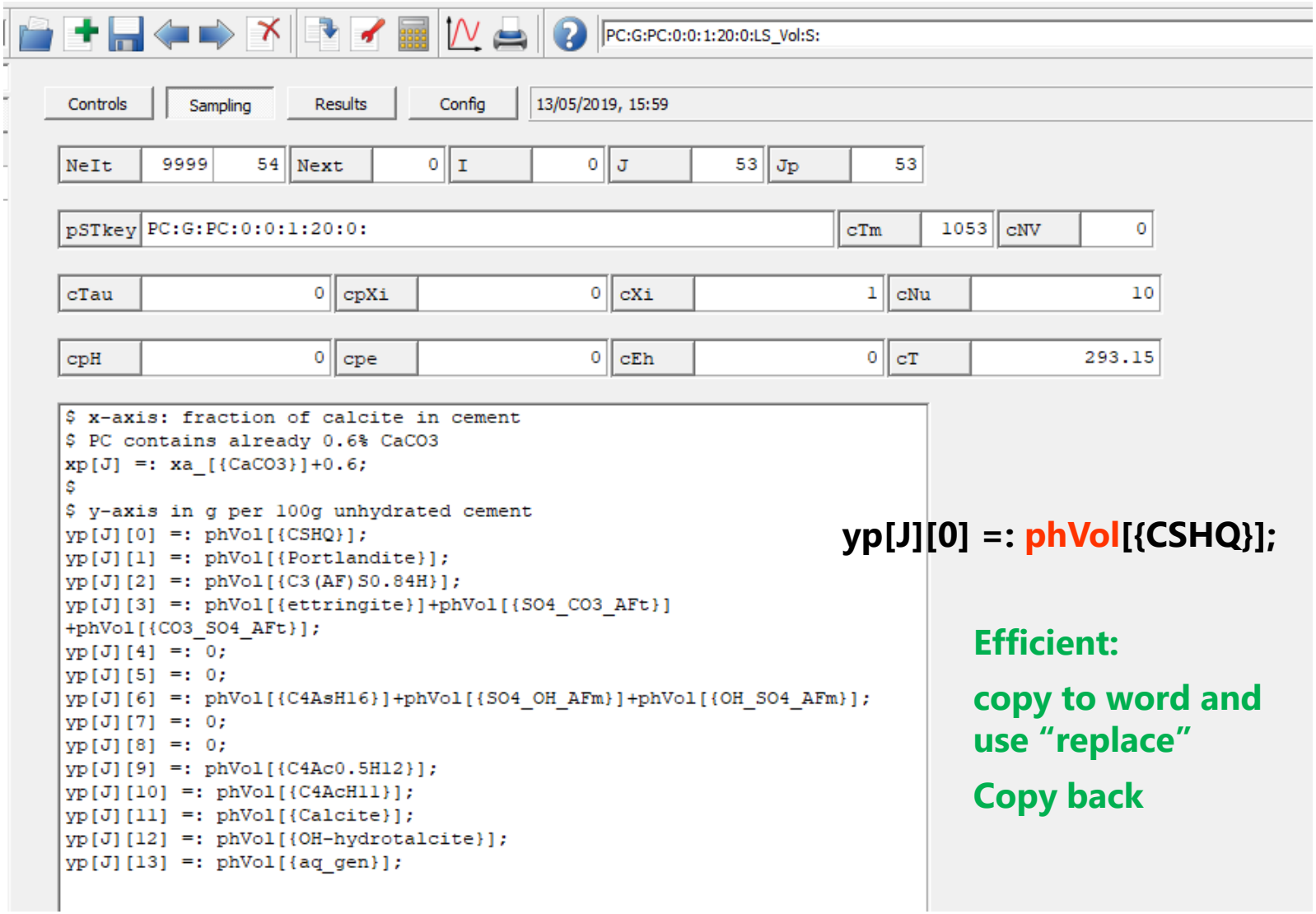
volume:
yp[J][0] =: phVol[{CSHQ}];

- **Efficient: copy to word and use "replace"**

yp[J][0] =: Xa[{CSHQ}]; **=> *Moles***

- **Change y-axis labelling to $cm^3/100g$ and make a cumulative plot.**

Process file - hydration of PC + limestone



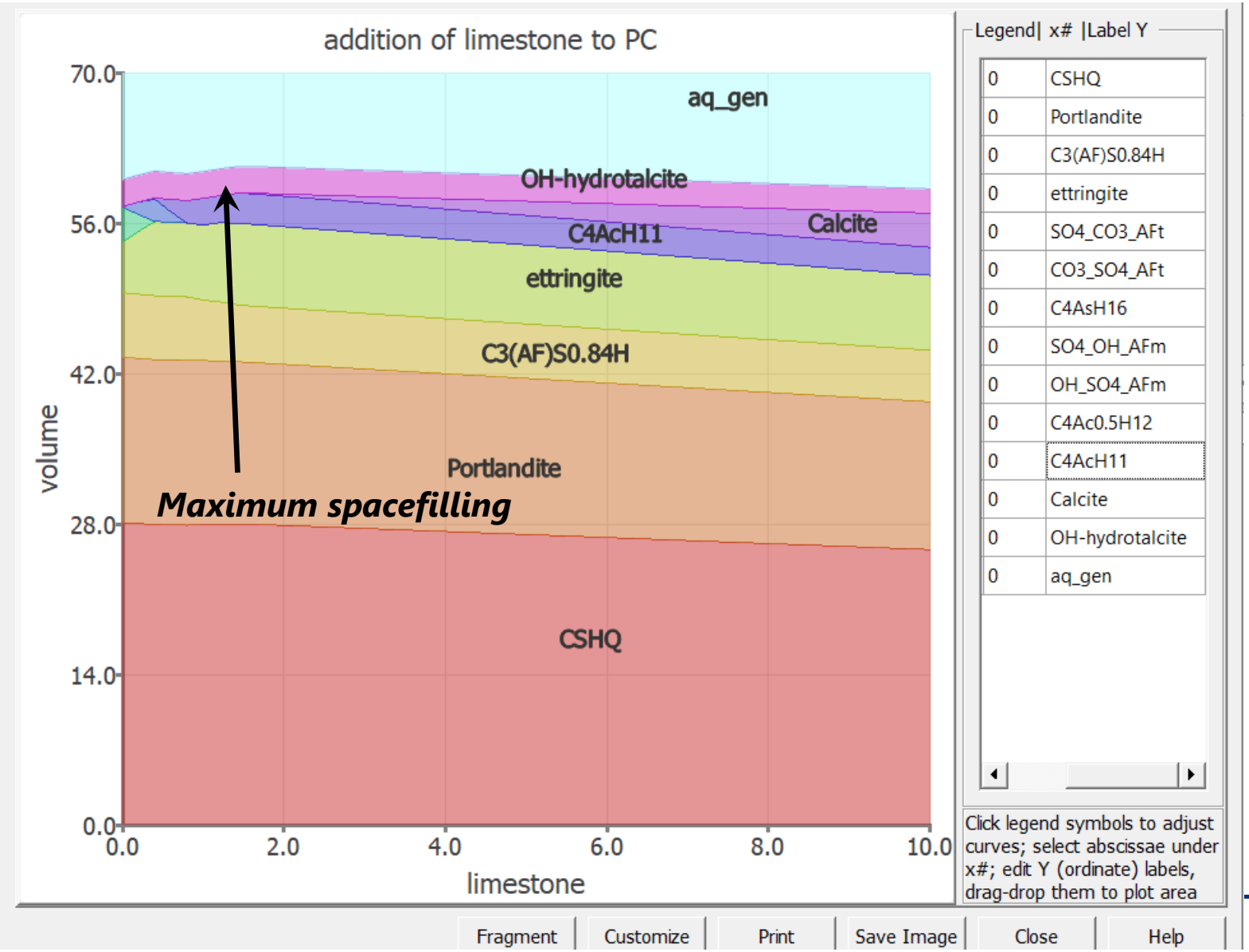
yp[J][0] =: phVol[{CSHQ}];

Efficient:

copy to word and use "replace"

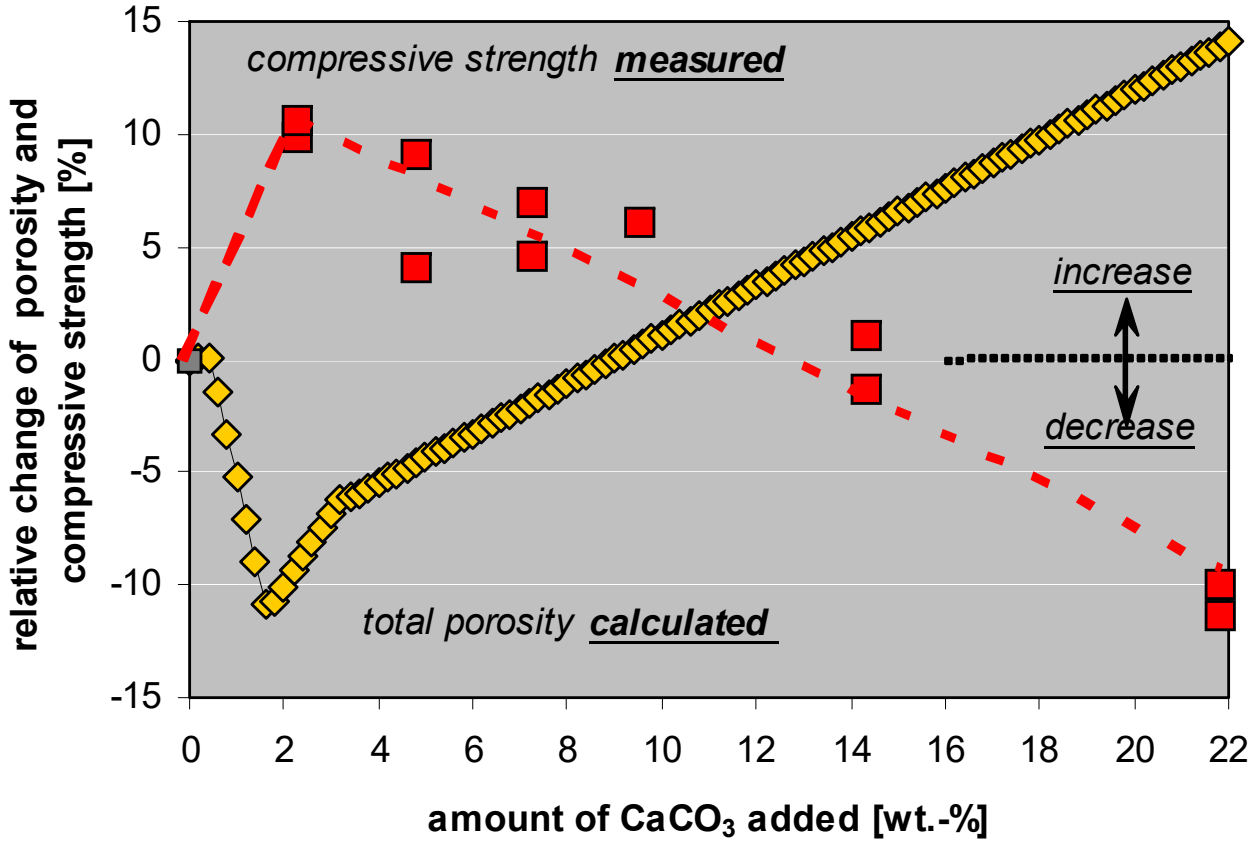
Copy back

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

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Materials Science and Technology

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	

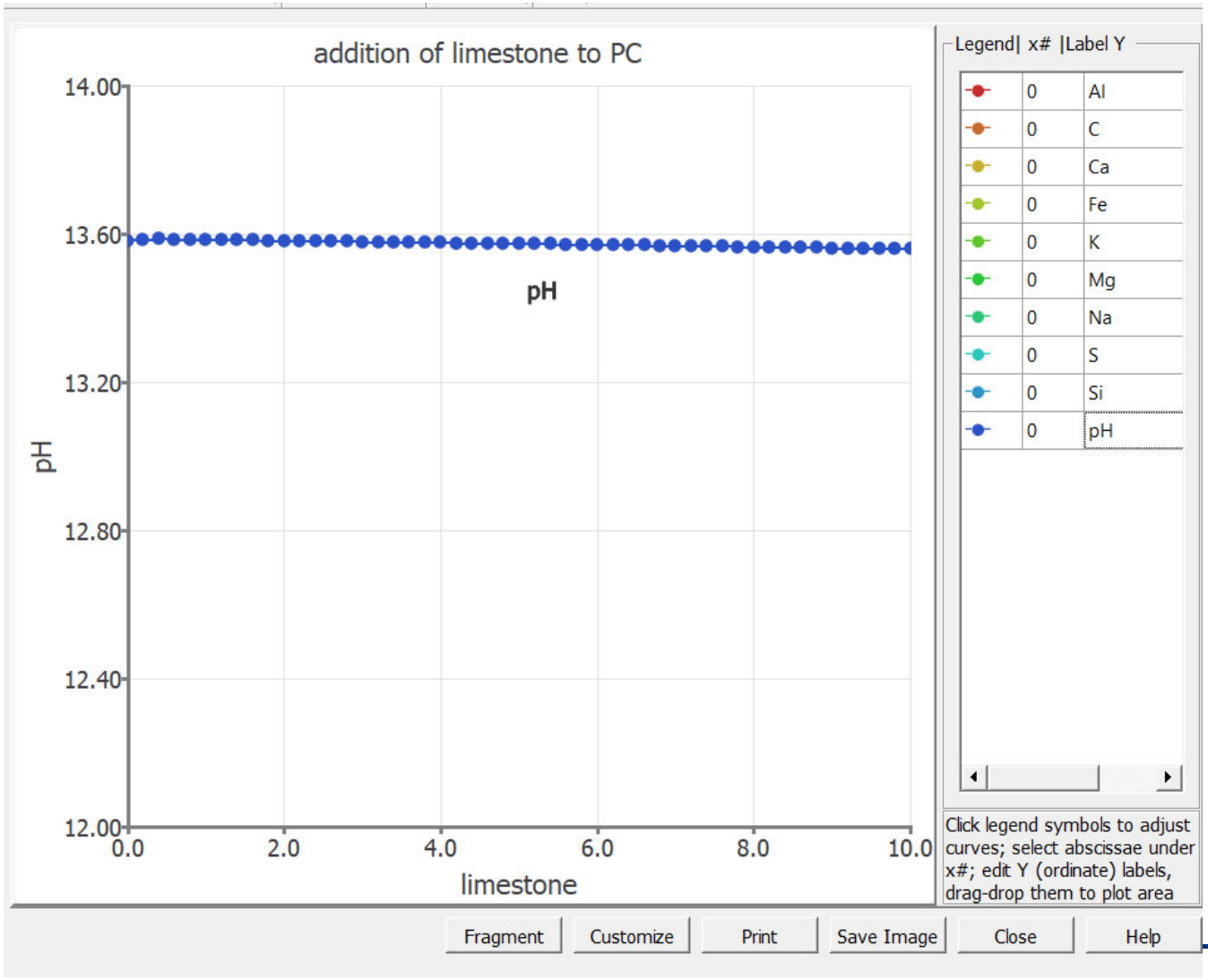
```
$$x axis: total fraction of CaCO3 in cement
$PC contains already 0.6 wt%
xp[J] =: xa_[{CaCO3}]+0.6;

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)

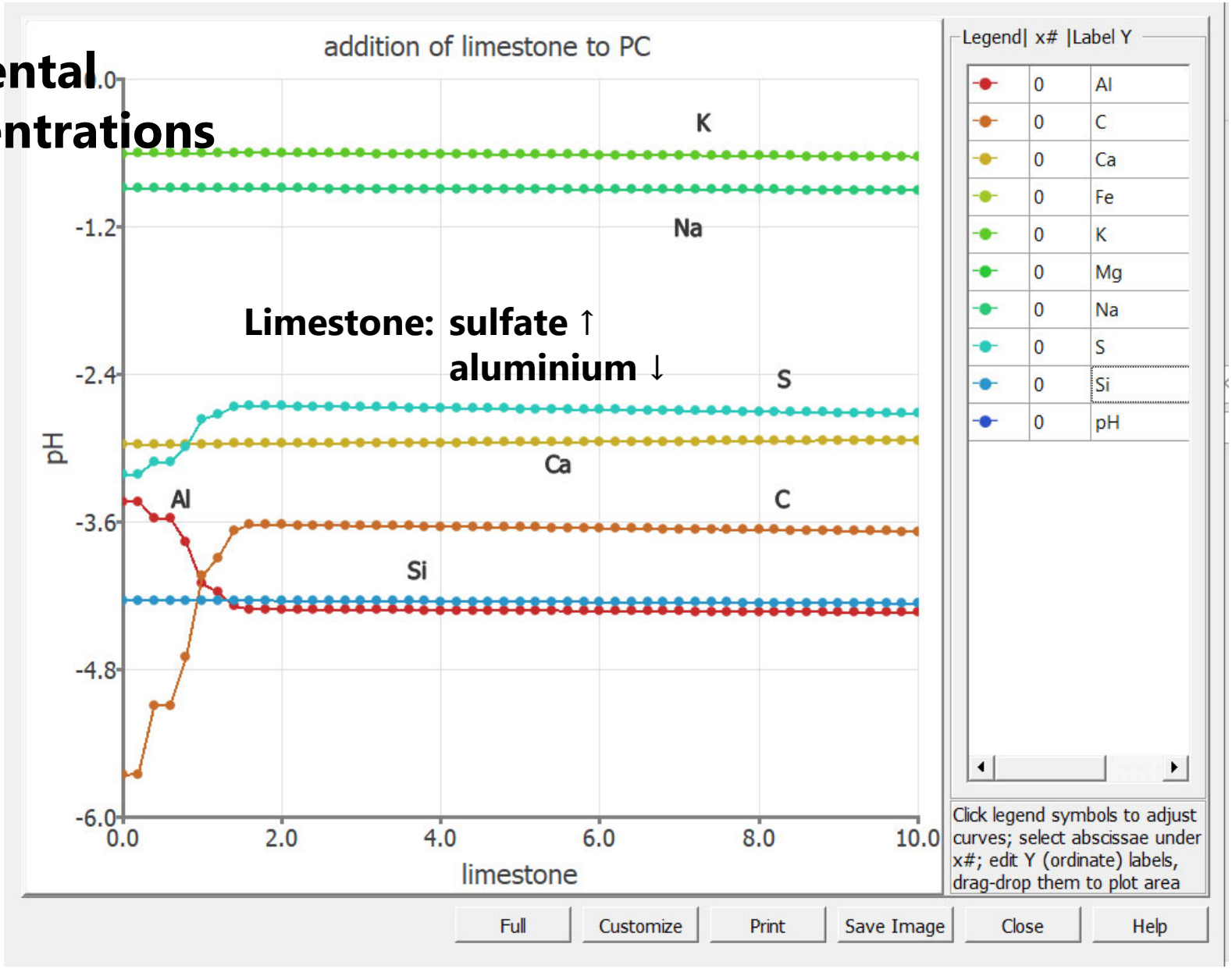
Process file - hydration of PC + limestone

pH - value

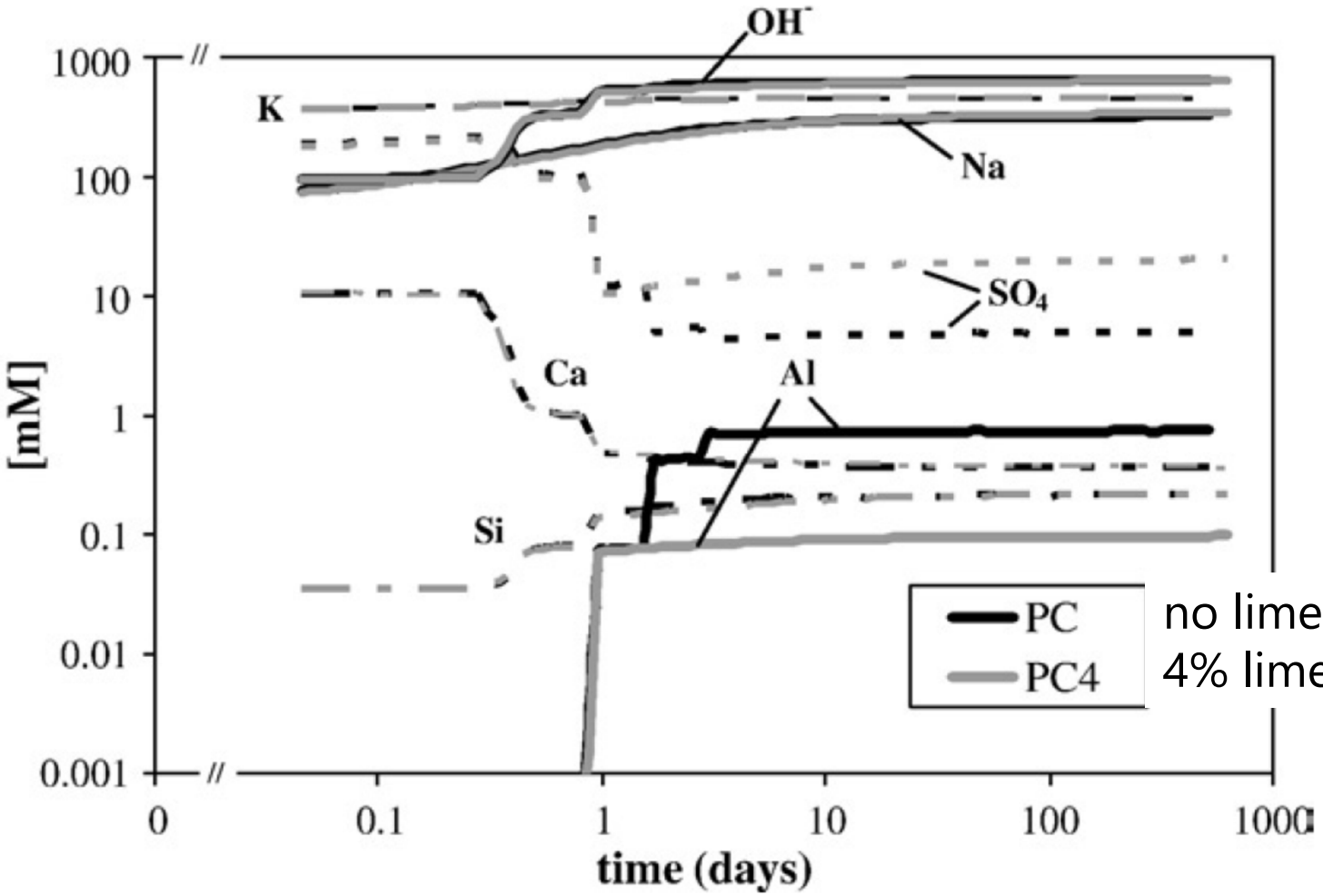


Process file - hydration of PC + limestone

Elemental concentrations



Process file - hydration of PC + limestone



no limestone added
4% limestone

Lothenbach ea 2008, CCR 38

Limestone: sulfate ↑
aluminium ↓

Process file - hydration of PC + limestone

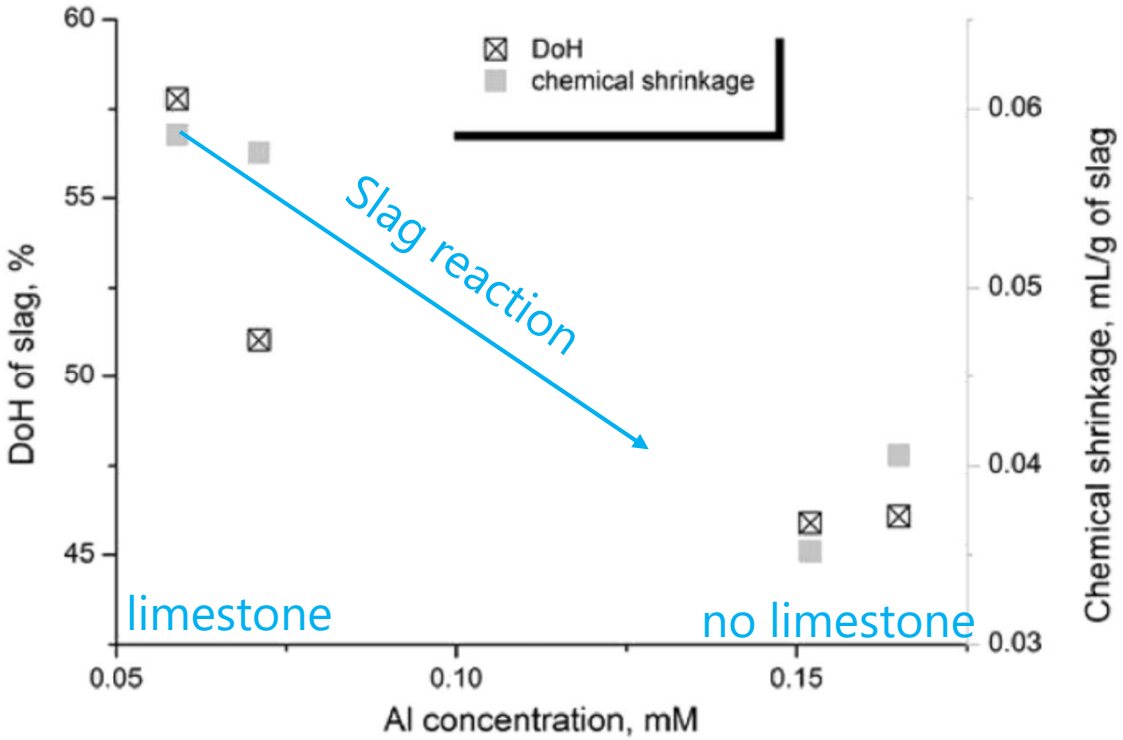


Fig. 21. The relationship between Al concentration in the pore solution and chemical shrinkage and degree of hydration of slag at 28 days. Note, there is ± 2% error associated with the method for measuring the DoH of slag.

Adu-Amankwah ea 2017, CCR 100

Limestone: sulfate ↑
aluminium ↓

⇒ High Al suppresses slag and alite reaction
⇒ Limestone accelerates

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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

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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: modC[J][0] =: cNu*0.4;
  - Fly ash quantity as xa_[{FA}] =: ...
  - 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

average glass composition

XRF-analysis[a] [wt%]	F1
SiO_2	50.9
Al_2O_3	24.7
Fe_2O_3	7.3
CaO	3.7
MgO	1.8
K_2O	3.9
Na_2O	0.9
TiO_2	1.1
Mn_2O_3	0.1
P_2O_5	0.8
SO_3	0.4[c]
SrO	
LOI	3.5
C	2.7[d]
Sum	99.1

Mineralogical phase composition[b] [wt%]	F1
Mullite	8.2
Quartz	7.0
Hematite	0.7
Magnetite	0.8
Anhydrite	
Periclase	
Lime	
Amorphous	83.3
	100.0

Glass composition [wt%]	F1
SiO_2	54.4
Al_2O_3	24.8
Fe_2O_3	5.7
CaO	4.6
MgO	2.1
K_2O	4.9
Na_2O	1.1
TiO_2	1.4
Mn_2O_3	0.1
P_2O_5	0.9
SO_3	0.0
	100.0

We only consider the «big four»

Deschner et al., Cem Concr. Res. 42 (2012), 1389-1400.

Process file - hydrated PC + fly ash

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Two options for input:

Glass composition [wt%]	F1
SiO_2	54.4
Al_2O_3	24.8
Fe_2O_3	5.7
CaO	4.6
MgO	2.1
K_2O	4.9
Na_2O	1.1
TiO_2	1.4
Mn_2O_3	0.1
P_2O_5	0.9
SO_3	0.0

Option 1: Input in g oxide

recalculation in mol-%

	in glass	normalised	molar mass	normalised
	g/100g	g/100g	g/mol	mol/100g
SiO2	54.4	60.6	60.08	1.00943076
Al2O3	24.8	27.6	101.96	0.27116236
Fe2O3	5.7	6.4	159.69	0.03979282
CaO	4.8	5.4	56.08	0.0954203
total	89.7	100		

recalculation in atom-%

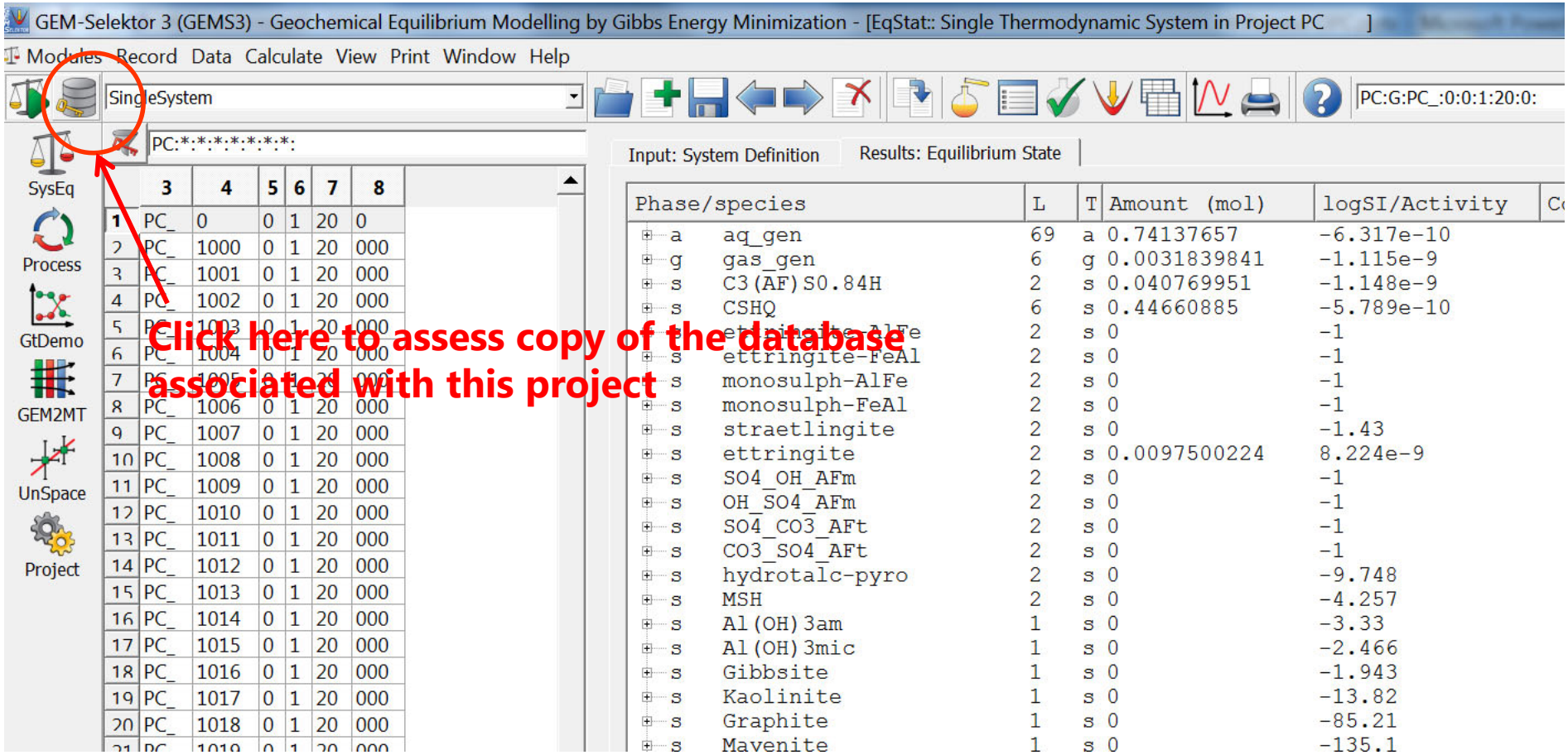
	normalised
	mol/100g
Si	1.00943
Al	0.54232
Fe	0.07959
Ca	0.09542
O	3.04715

=> Different options for input in predefined composition

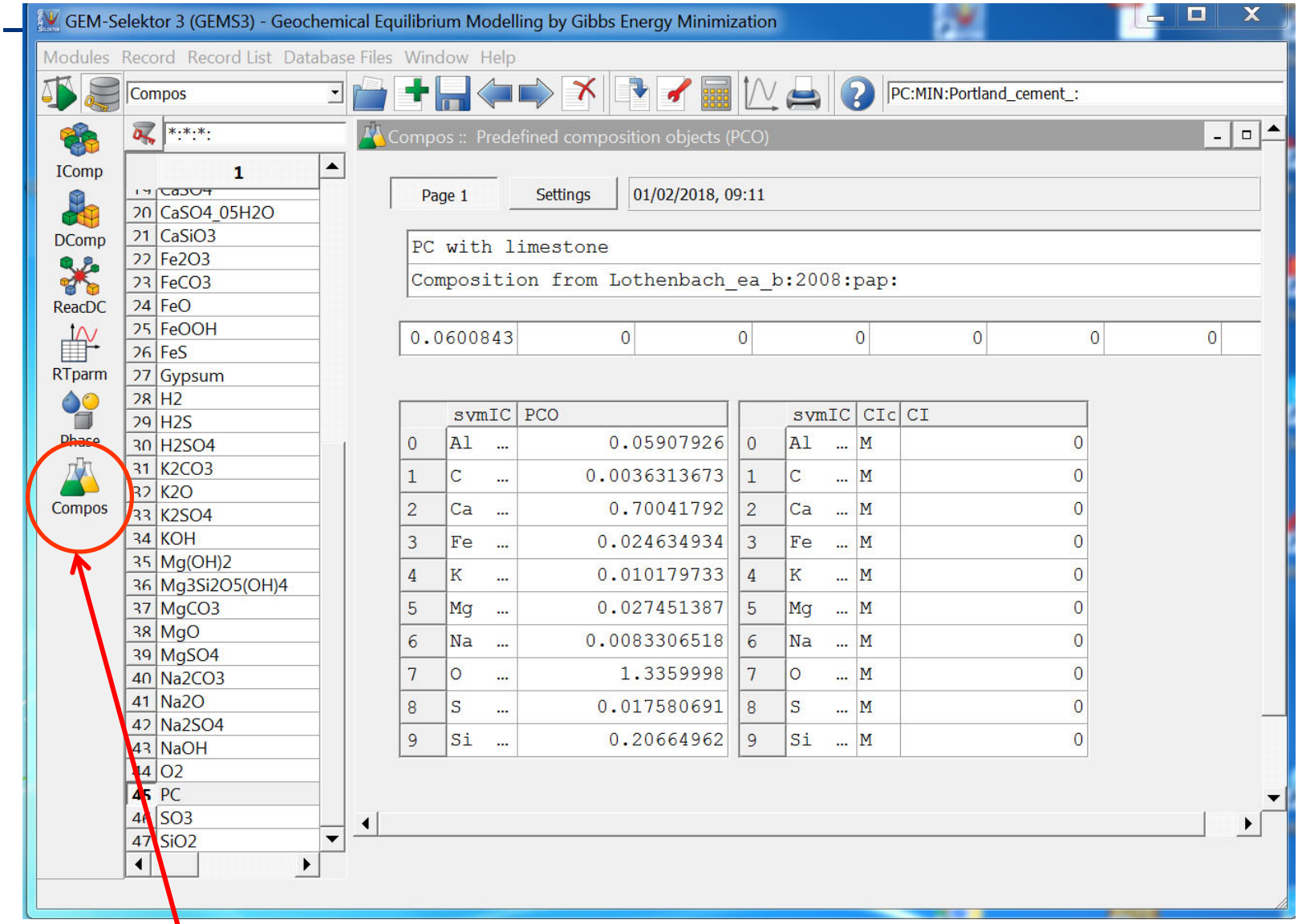
Option 2: Input in mol elements

Process file - hydrated PC + fly ash

Make a predefined composition for fly ash

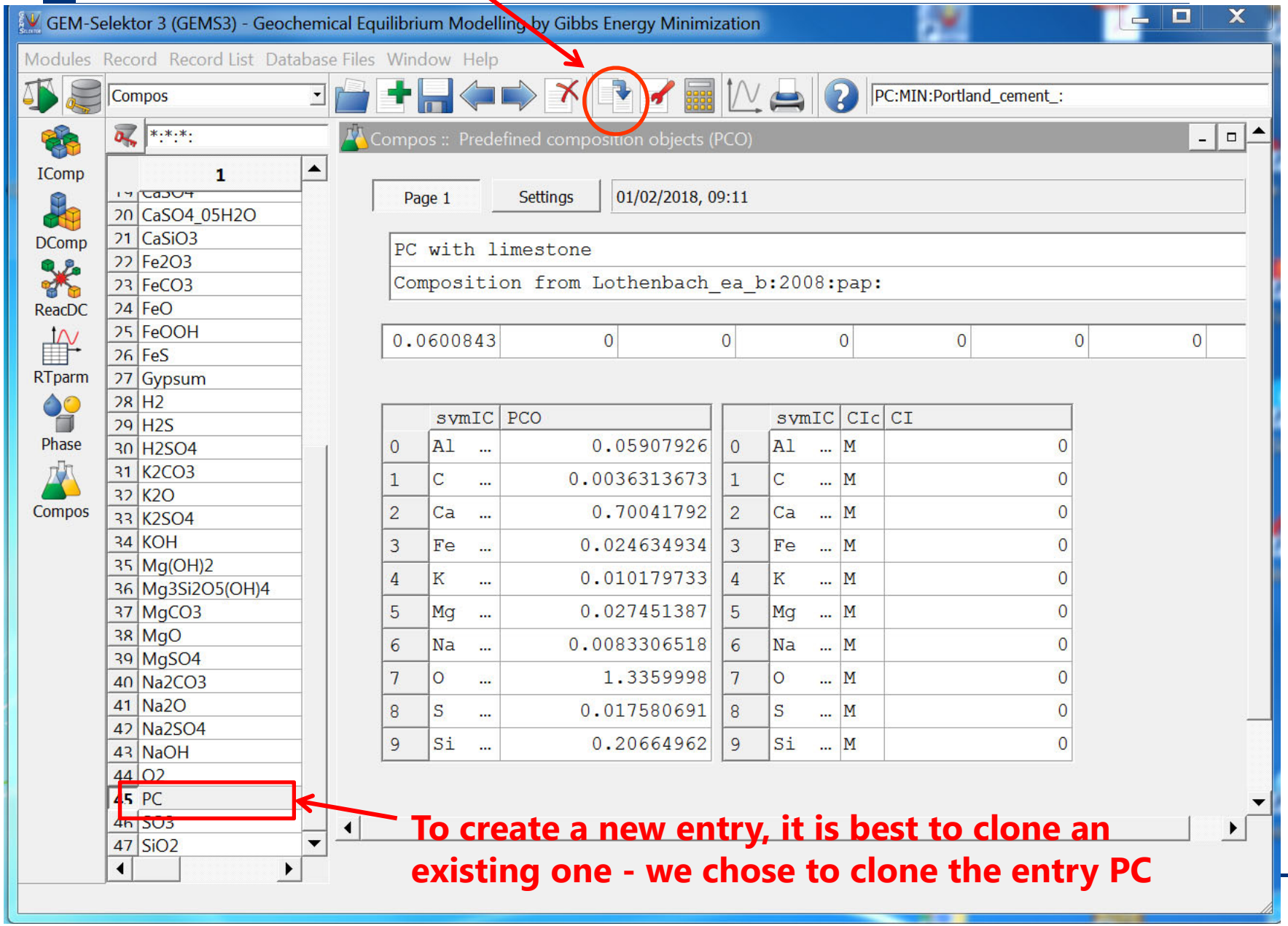


Make a predefined composition for fly ash



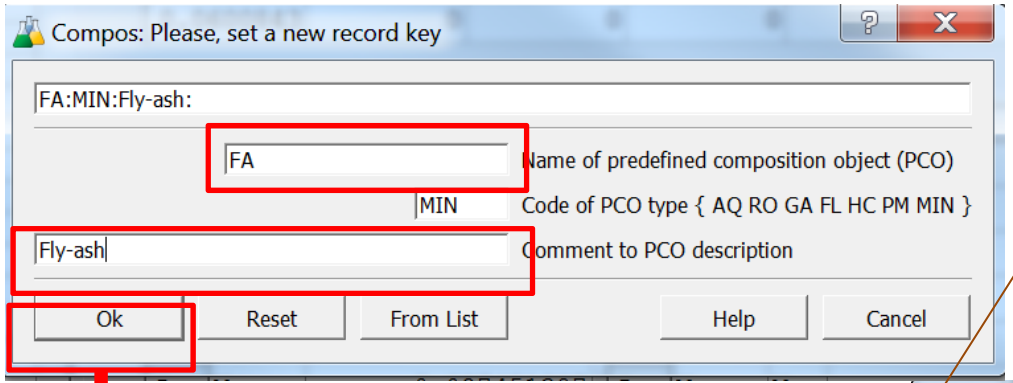
Click here to assess the list of predefined compositions and to create a new one

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



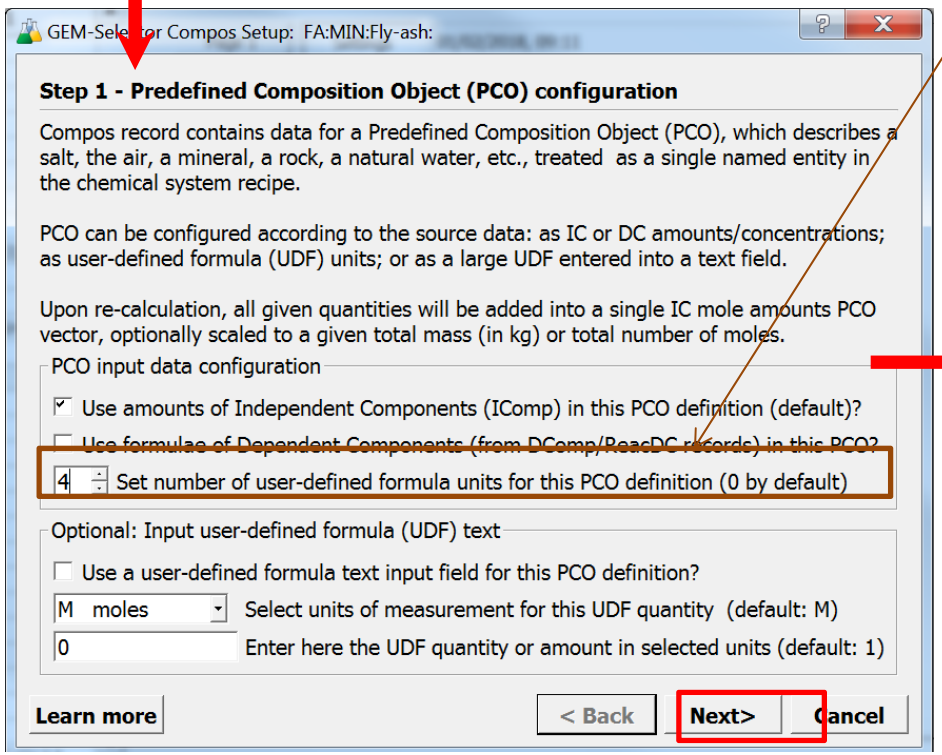
To create a new entry, it is best to clone an existing one - we chose to clone the entry PC

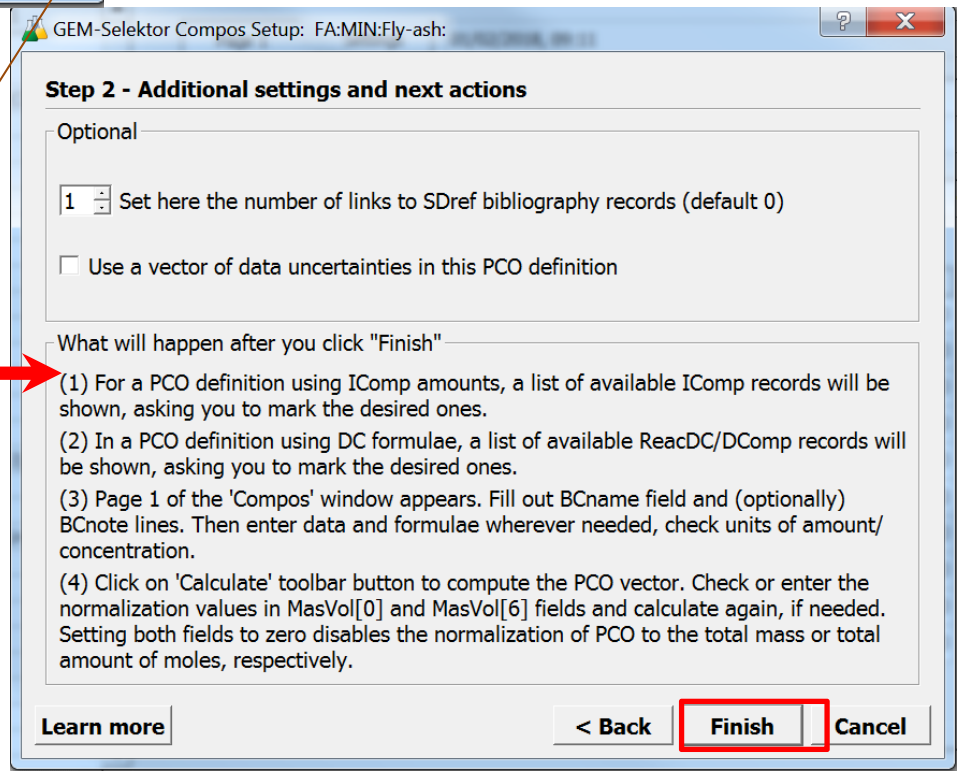
Make a predefined composition for fly ash: option 1, add g oxides



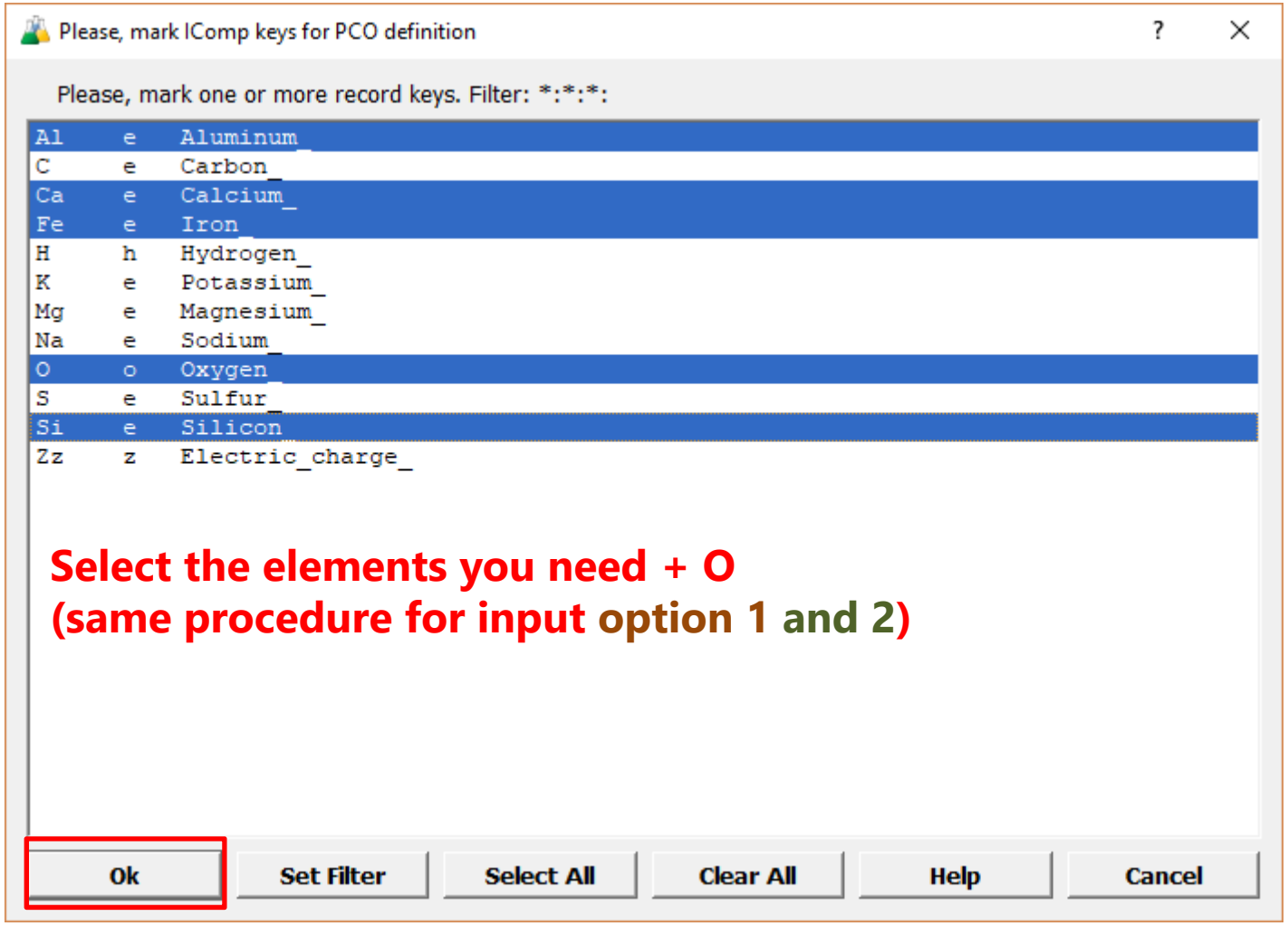
Can be used to add g oxides 4 as CaO, Al2O3, SiO2, Fe2O3

Will have to written manually

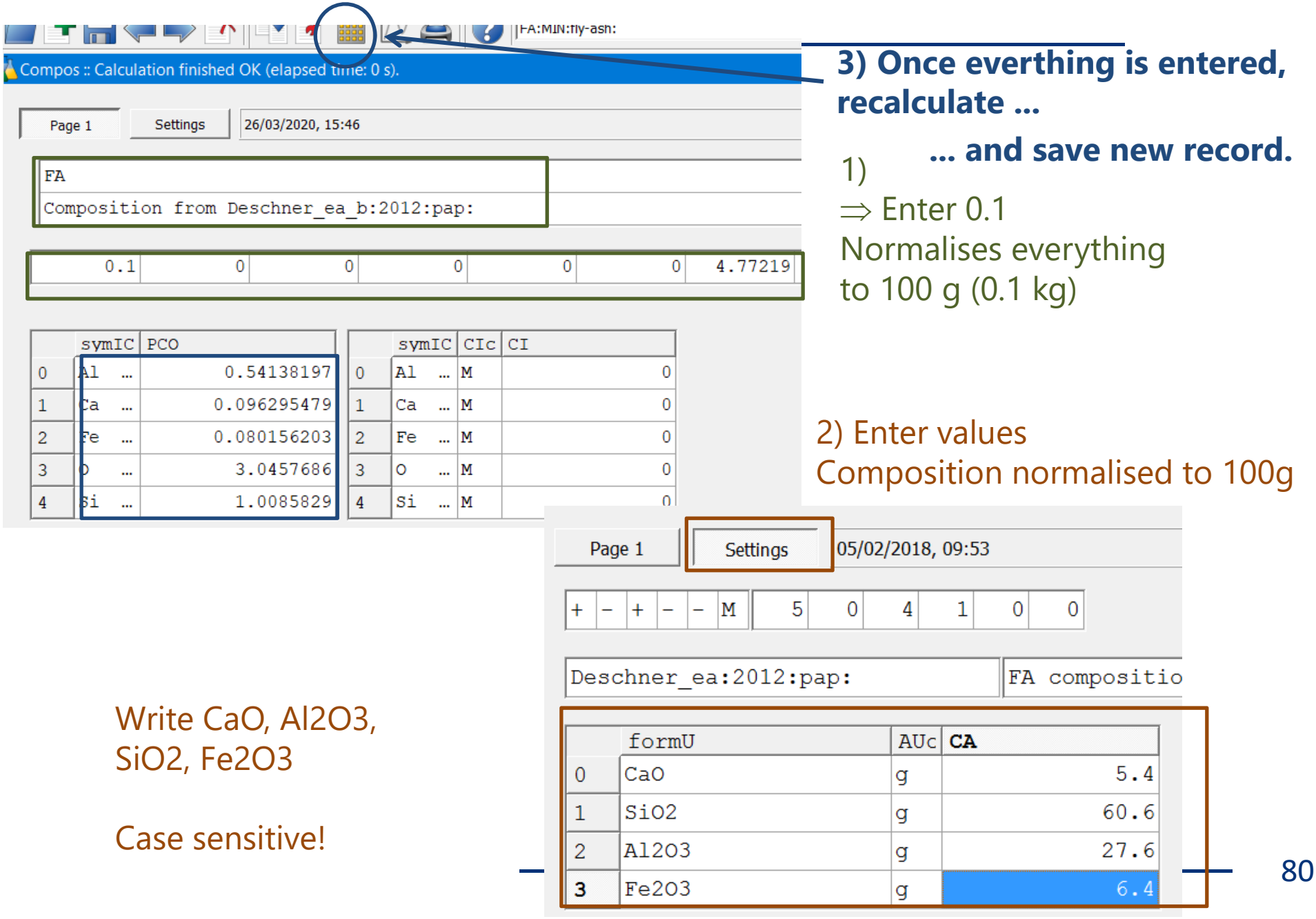




Make a predefined composition for fly ash: option 1 and 2



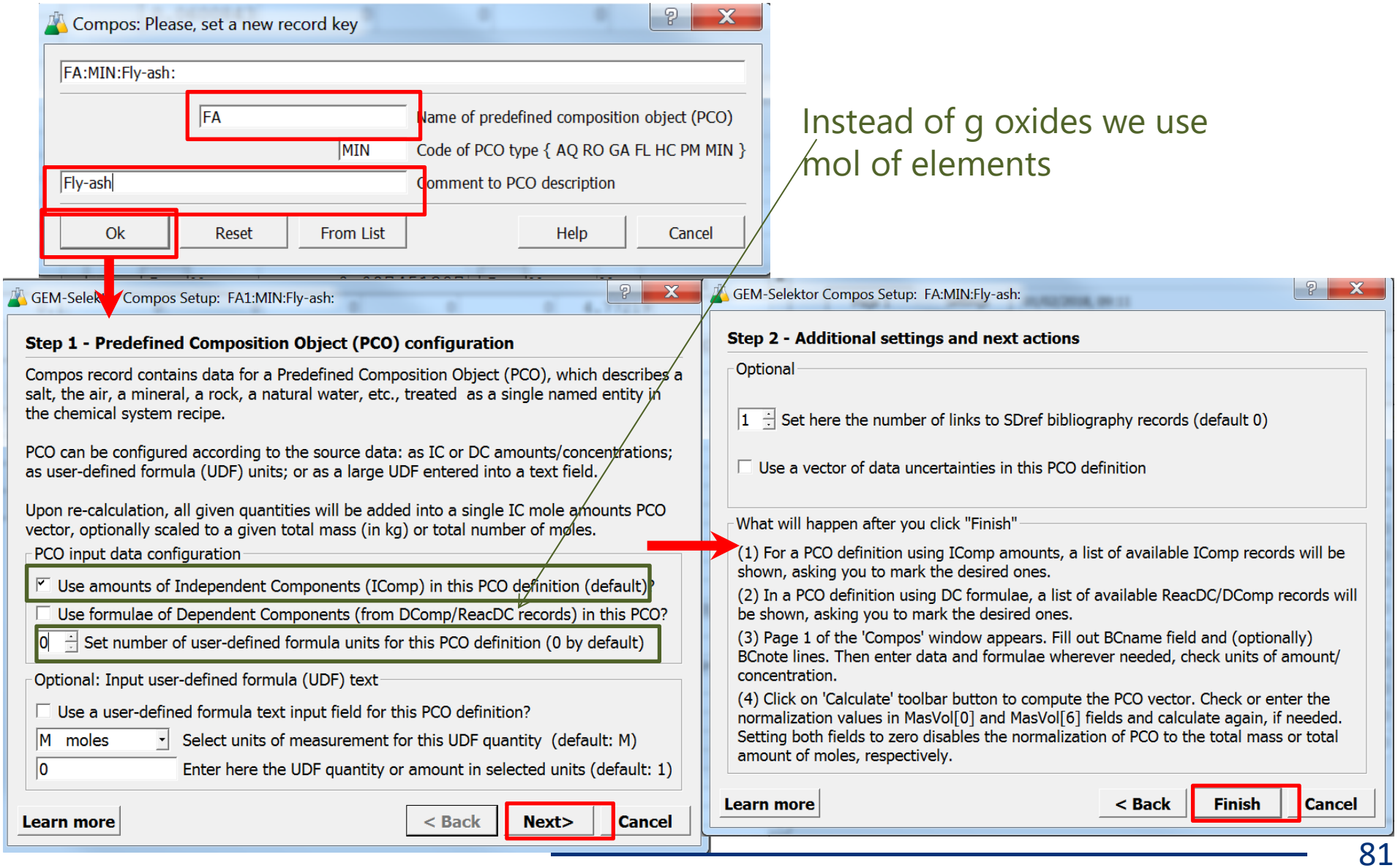
Make a predefined composition for fly ash: option 1, add g oxides



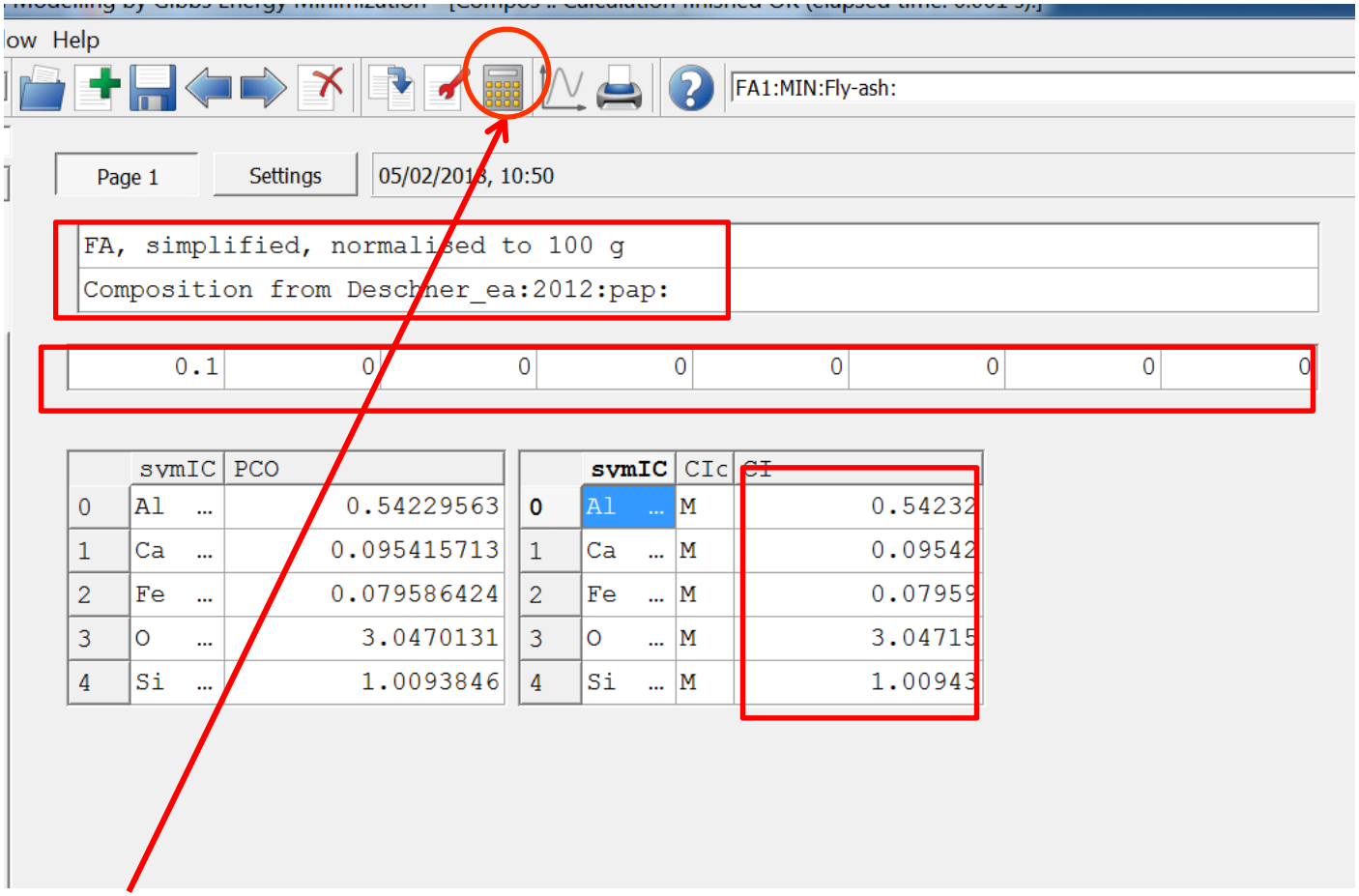
Write CaO, Al2O3, SiO2, Fe2O3

Case sensitive!

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



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



recalculation in atom-%

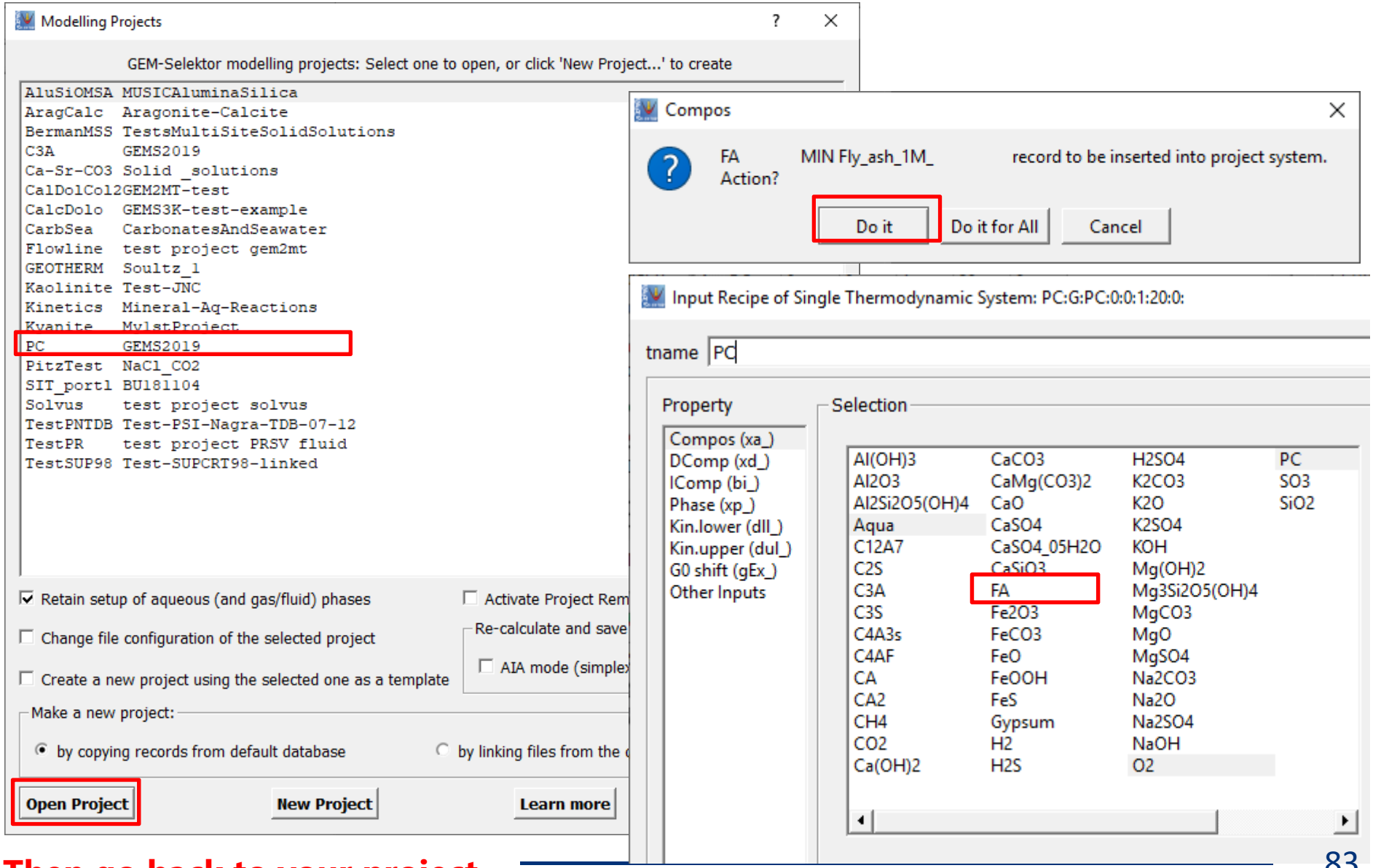
	normalised
	mol/100g
Si	1.00943
Al	0.54232
Fe	0.07959
Ca	0.09542
O	3.04715

=> Enter values

When everthing is entered, recalculate … **… and save new record.**

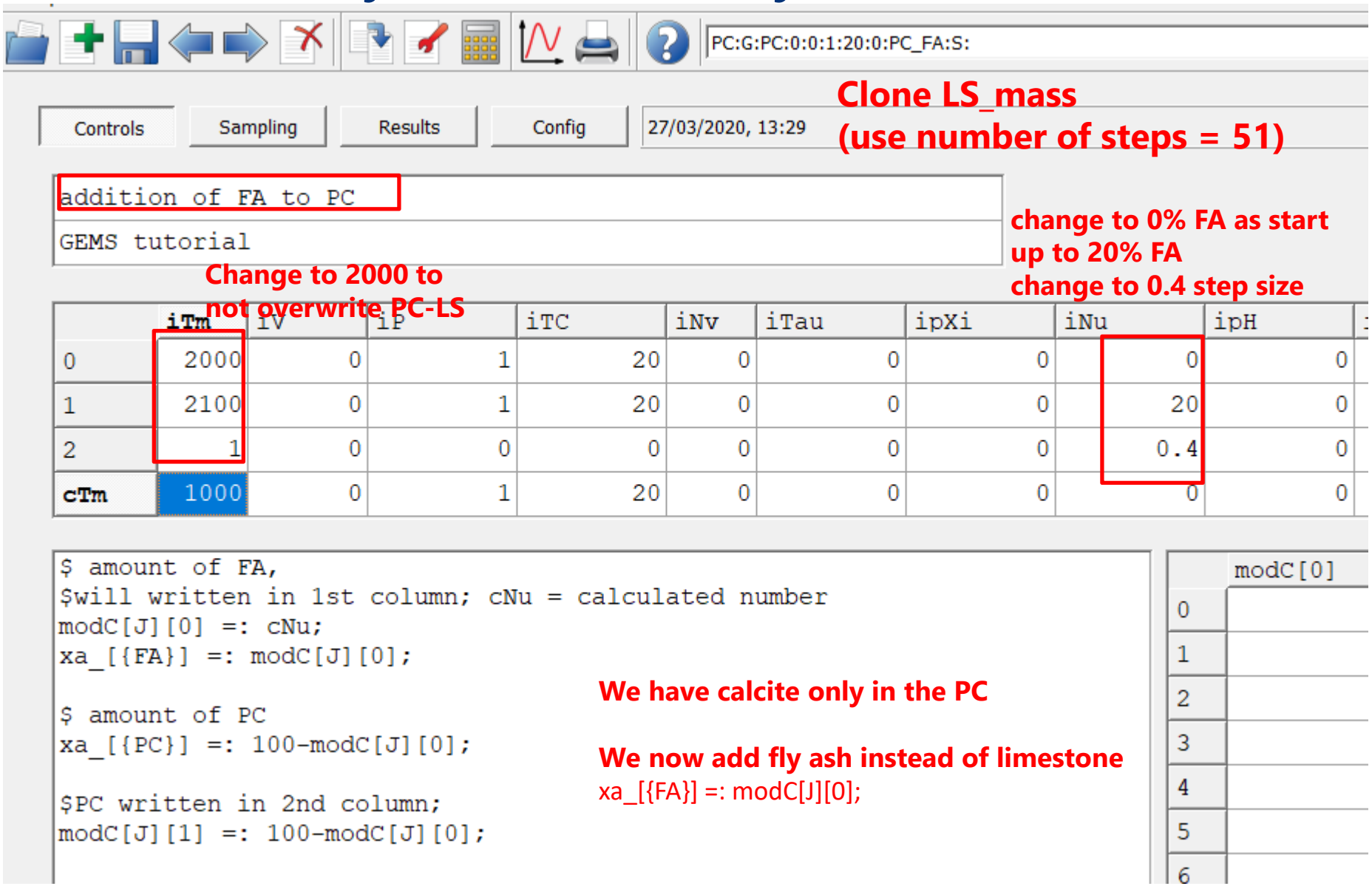
equivalent options, minor difference due rounding off (number of digits …

Process file - hydration of PC + fly ash



Then go back to your project

Process file - hydration of PC + fly ash



Process file - hydration of PC + fly ash

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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	cl

cTau	0	cpXi	0	cXi	1	cNu	

cpH	0	cpe	0	cEh	0	cT	

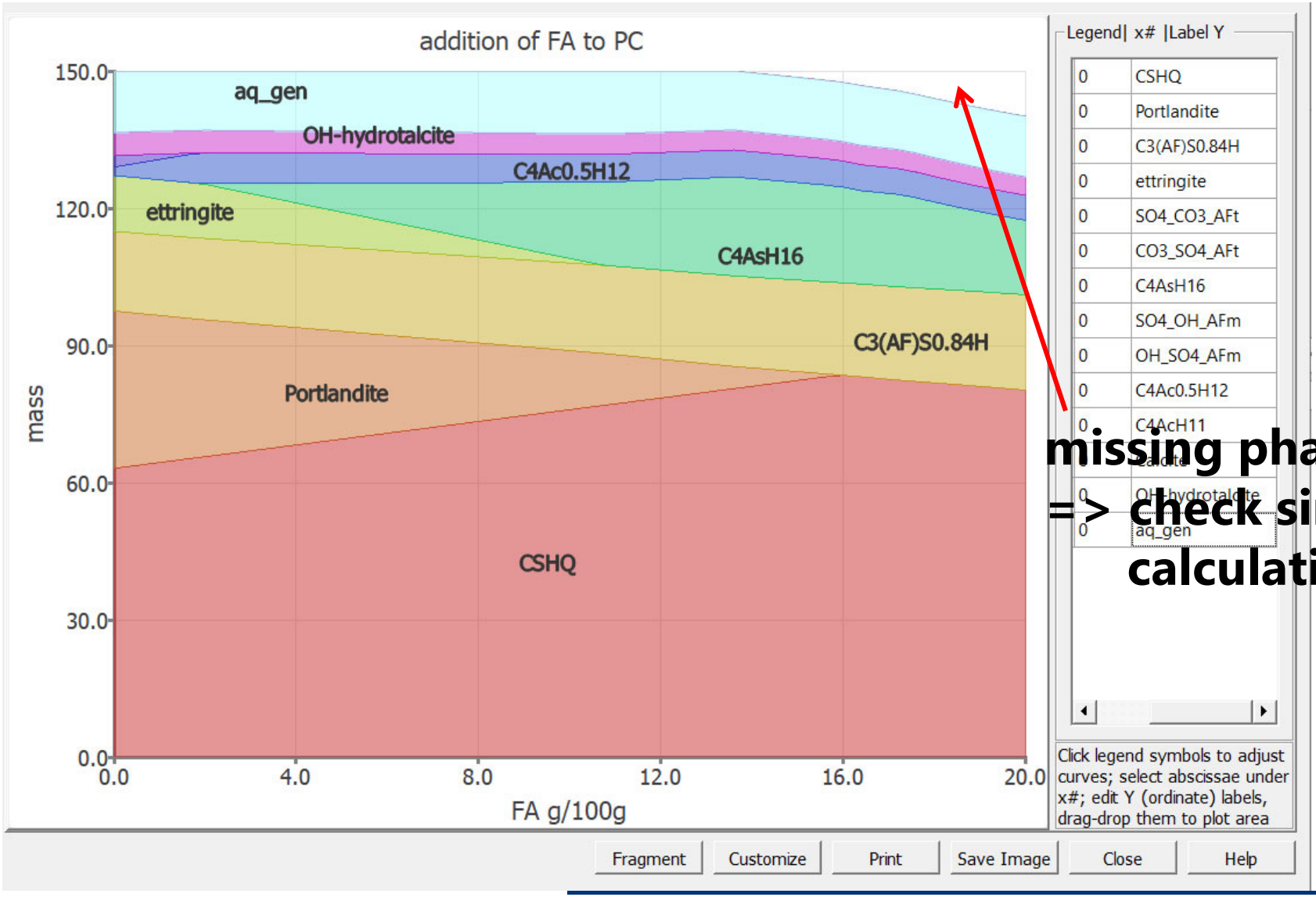
```
$x axis: total fraction of FA in cement
xp[J] =: xa_[{FA}];

$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}];
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}];
```

Change comment, change x-axis

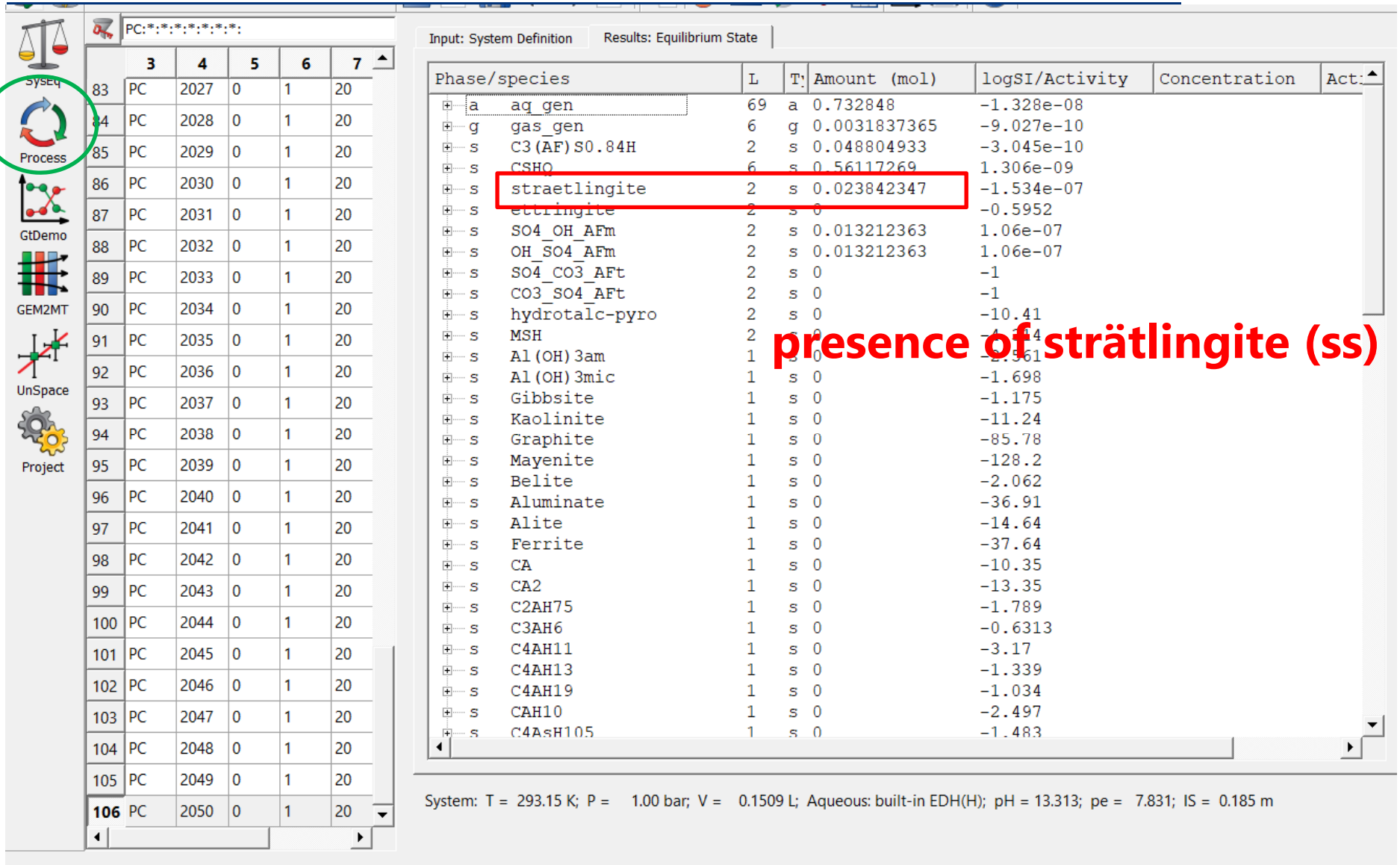
New phase: (CaO)2Al2O3SiO2(H2O)7-8

Process file - hydration of PC + fly ash



missing phase(s) => check single calculations

Process file - hydration of PC + fly ash



	3	4	5	6	7
83	PC	2027	0	1	20
84	PC	2028	0	1	20
85	PC	2029	0	1	20
86	PC	2030	0	1	20
87	PC	2031	0	1	20
88	PC	2032	0	1	20
89	PC	2033	0	1	20
90	PC	2034	0	1	20
91	PC	2035	0	1	20
92	PC	2036	0	1	20
93	PC	2037	0	1	20
94	PC	2038	0	1	20
95	PC	2039	0	1	20
96	PC	2040	0	1	20
97	PC	2041	0	1	20
98	PC	2042	0	1	20
99	PC	2043	0	1	20
100	PC	2044	0	1	20
101	PC	2045	0	1	20
102	PC	2046	0	1	20
103	PC	2047	0	1	20
104	PC	2048	0	1	20
105	PC	2049	0	1	20
106	PC	2050	0	1	20

Check solids in single calculations

Process file - hydration of PC + fly ash

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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	

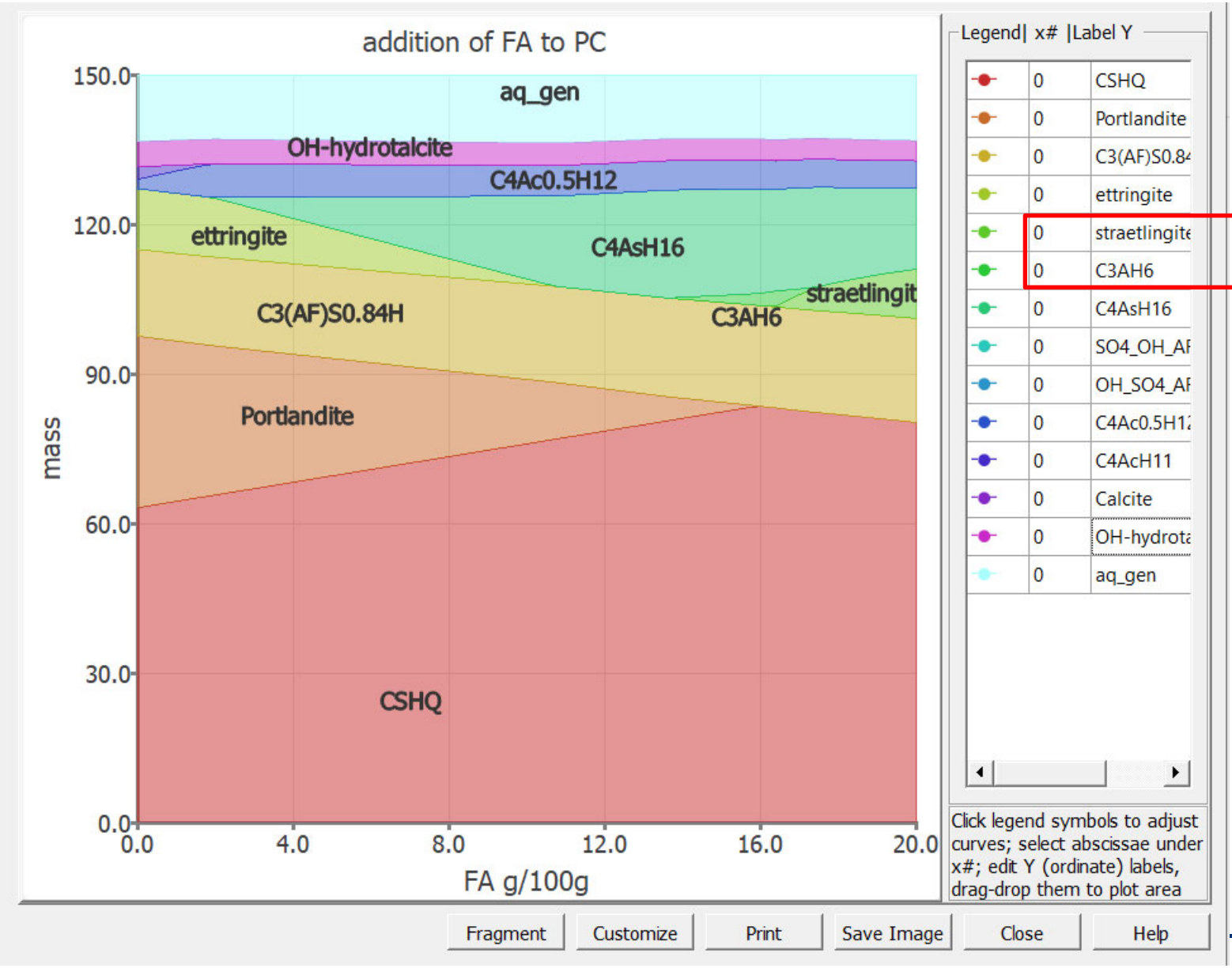
```
$x axis: total fraction of FA in cement
xp[J] =: xa_[{FA}];

$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}];
yp[J][5] =: phM[{C3AH6}];
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

katoite: (CaO)3Al2O3(H2O)6

=> Adapt also y-axis labels

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	

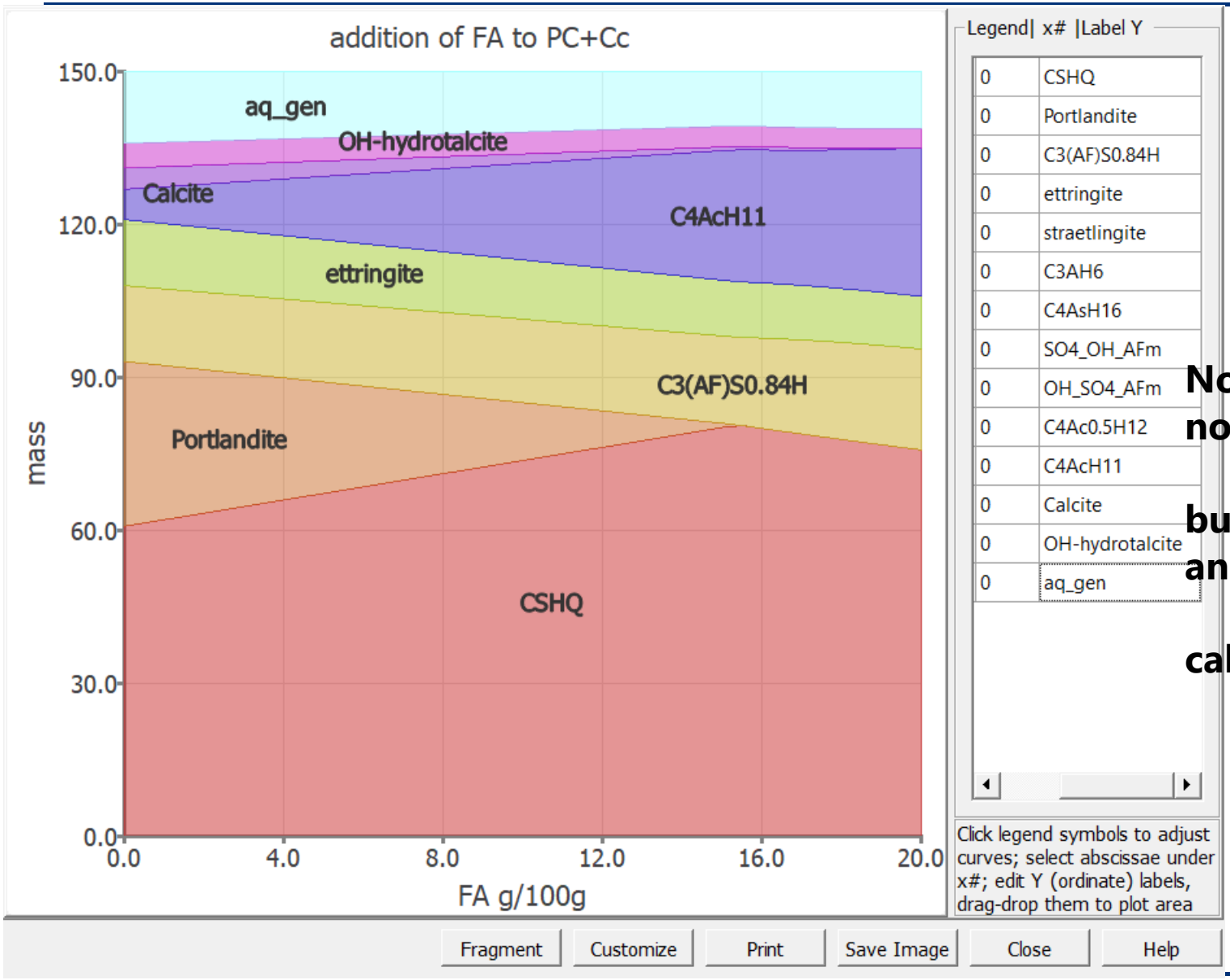
```
$ amount of FA,
$will written in 1st column; cNu = calculated number
modC[J][0] =: cNu;
xa_[{FA}] =: modC[J][0];

$ 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;
```

We substract the 5% LS from the PC …

… and add 5% $CaCO_3$.

	mo
0	
1	
2	
3	
4	
5	
6	

Process file - hydration of PC + fly ash



No monosulfate, no hemicarbonate

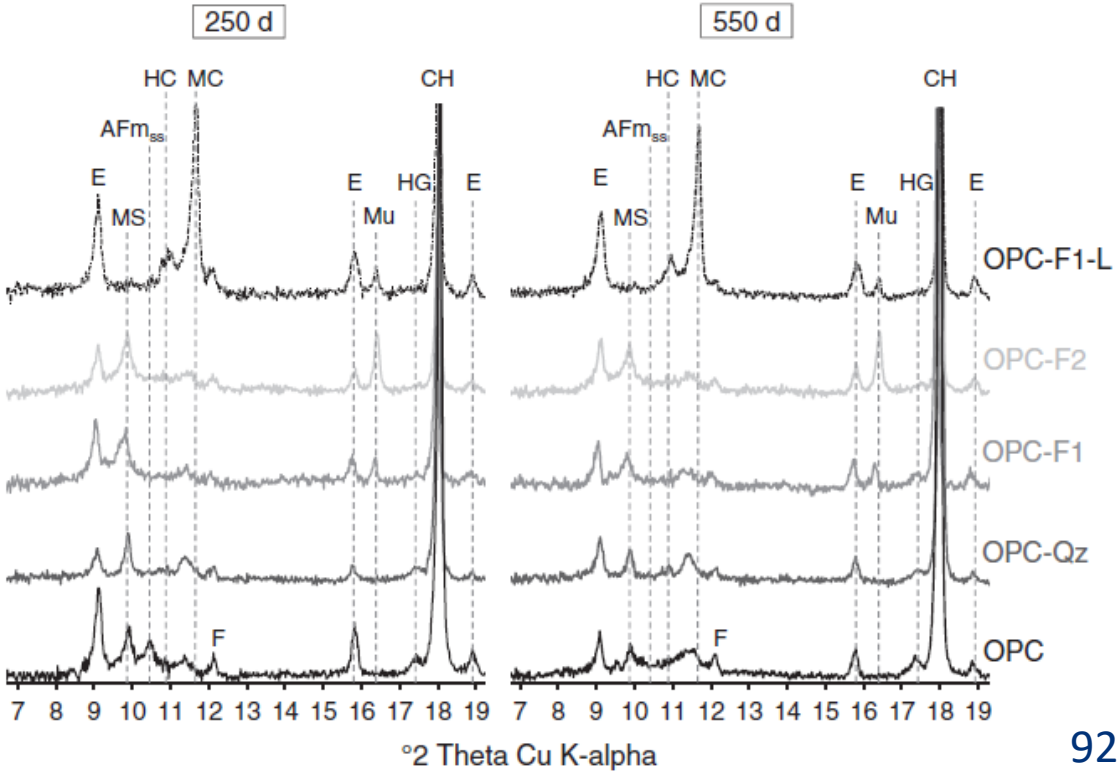
but monocarbonate and ettringite

calcite is consumed

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 Weerdt 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.