4th GEMS Workshop, May 7-8 2014
EMPA Dübendorf

kerneos
ALUMINATE TECHNOLOGIES

Modelling of CaO, Al_2O_3, $CaSO_4$ and $CaCO_3$ systems

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ÉCOLE POLYTECHNIQUE
FÉDÉRALE DE LAUSANNE

LABORATORY OF
CONSTRUCTION
MATERIALS

The project

- Products with special properties like rapid setting, shrinkage compensation

CAC | $C\$H_x$ | OPC

  - OPC has the higher environmental footprint
  - OPC is the more variable component

- The novelty of this project is to have a comprehensive study of ternary systems where the OPC is replaced by limestone (reduction of the variability):

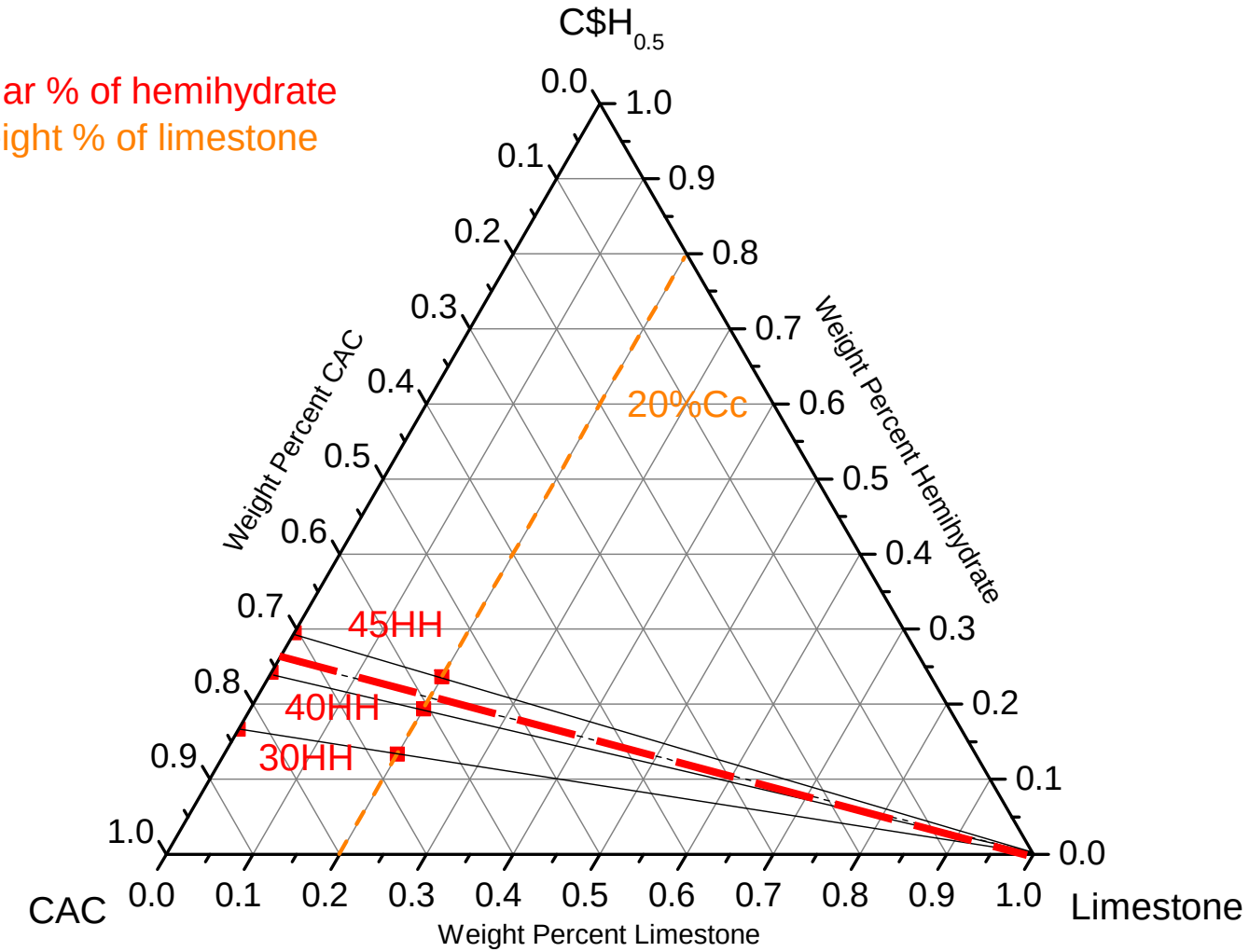
CAC | $C\$H_x$ | Limestone

  - Do the limestone act as filler or it participates in the hydration?

- Development of new binders
  - Reduction of the CO_2 emissions and energy consumption
  - Reduction of the price

Studied systems

Molar % of hemihydrate
Weight % of limestone



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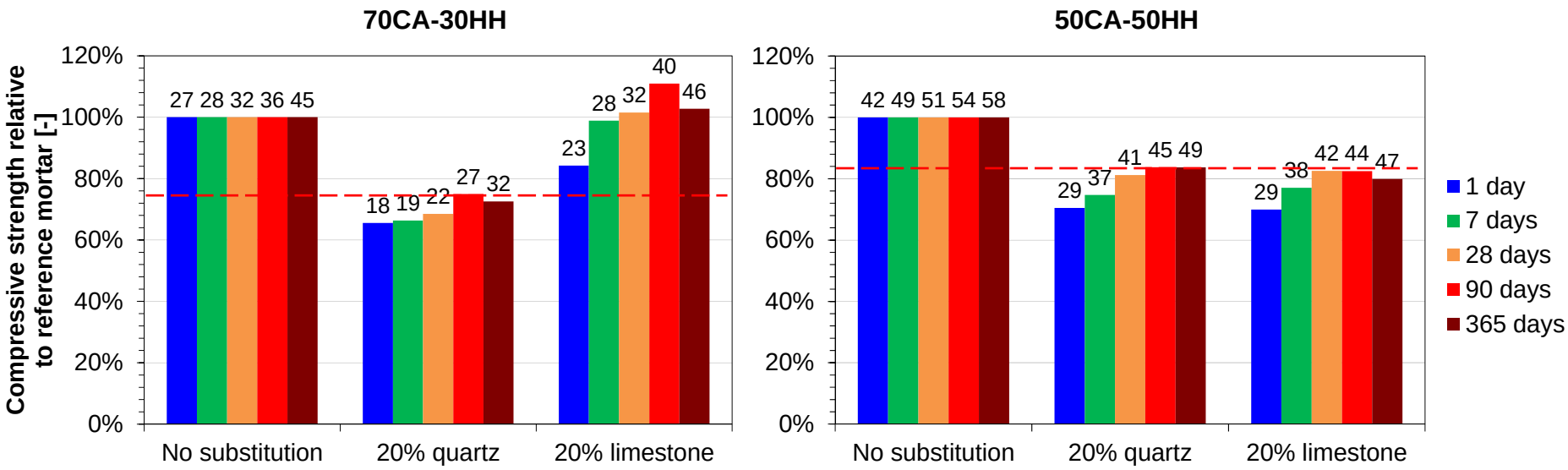
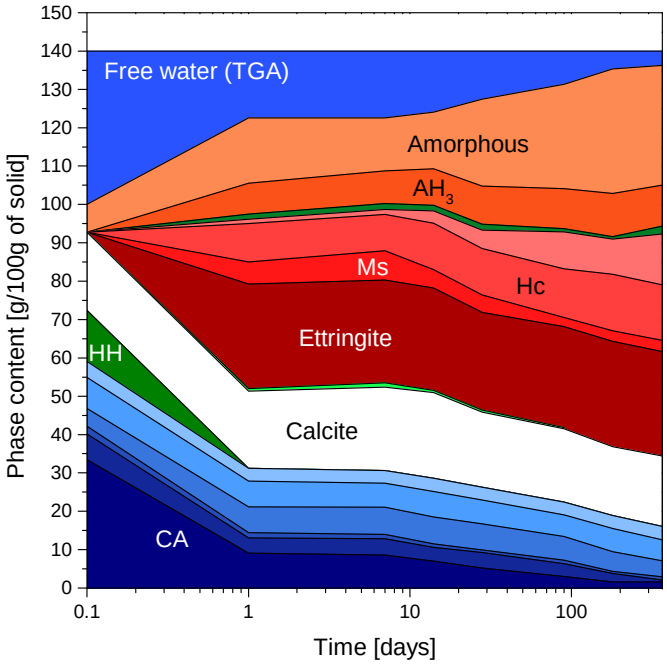
Mechanical properties on mortars



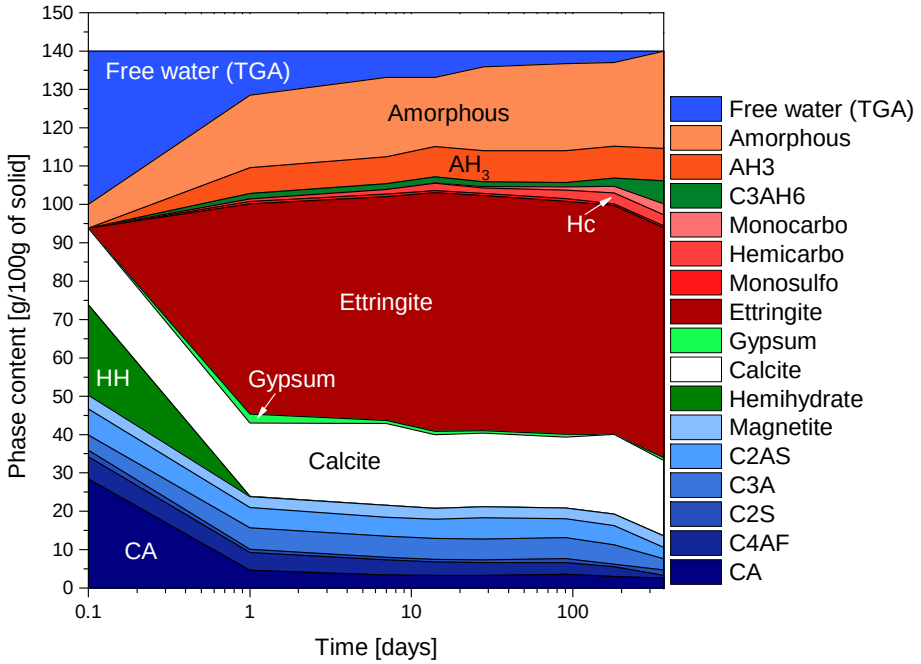
- Limestone enhances the mechanical properties already after 1 day of hydration
- Limestone seems to act as a filler in high sulfate systems

XRD Rietveld analysis

70CA-**30**HH-20Cc



55CA-**45**HH-20Cc



- Ettringite is stable (without Cc is consumed to form Ms)
- Other hydrates:
  - Monosulfoaluminate
  - Hemicarboaluminate
  - Monocarboaluminate

- Excess of gypsum (still 1%)
- Limestone acts as a filler, almost no sign of reaction

Main hydrates: Ettringite and AH_3 (mainly amorphous)

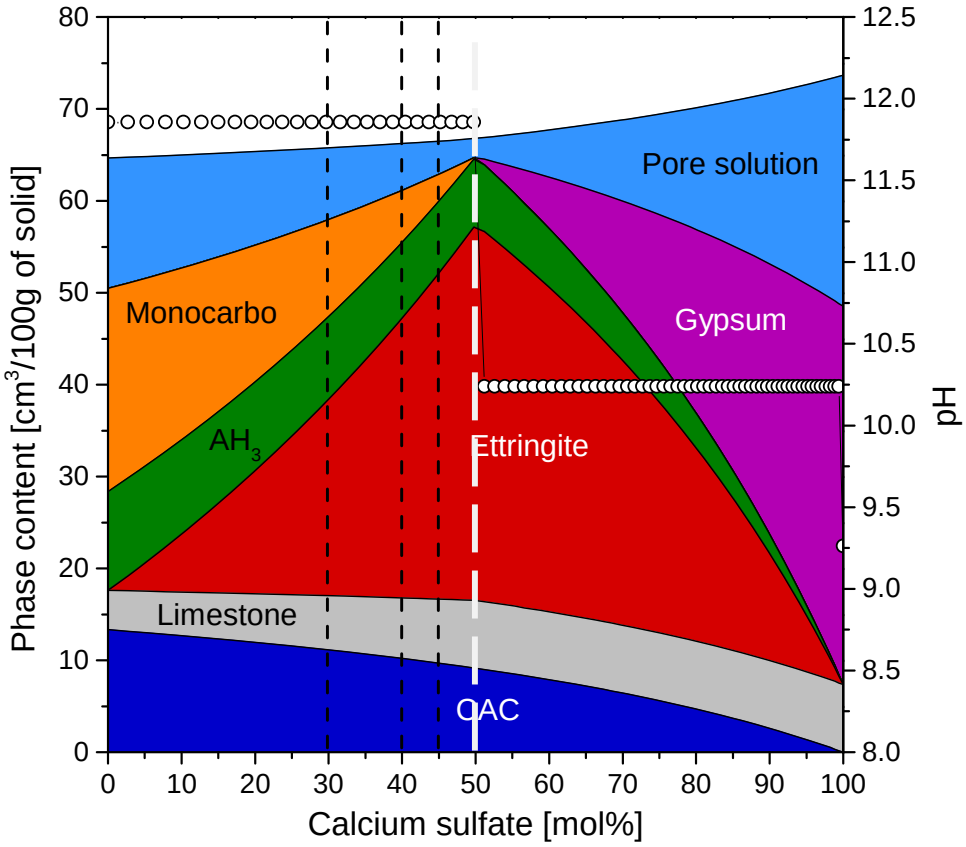
How to “quickly” understand the effect of HH on CA-HH-Cc systems?

Simply use

http://gems.web.psi.ch/

GEMS simulation

- Model system composed of CA, HH and Cc. w/b=0.4
- DH of CA=100%, DH of HH=100% and DH of Cc=100%



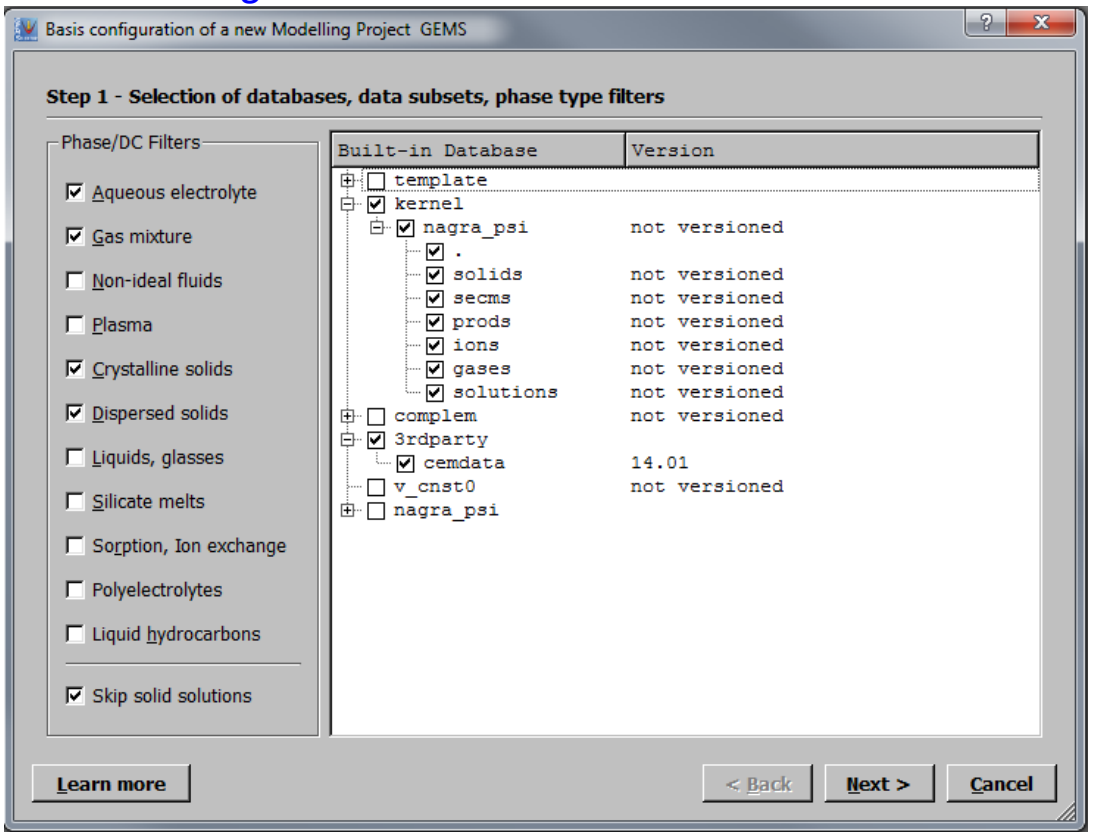
GEMS simulation, variable limestone DH

- Now we want to follow the hydrates evolution for variable amount of reacted limestone

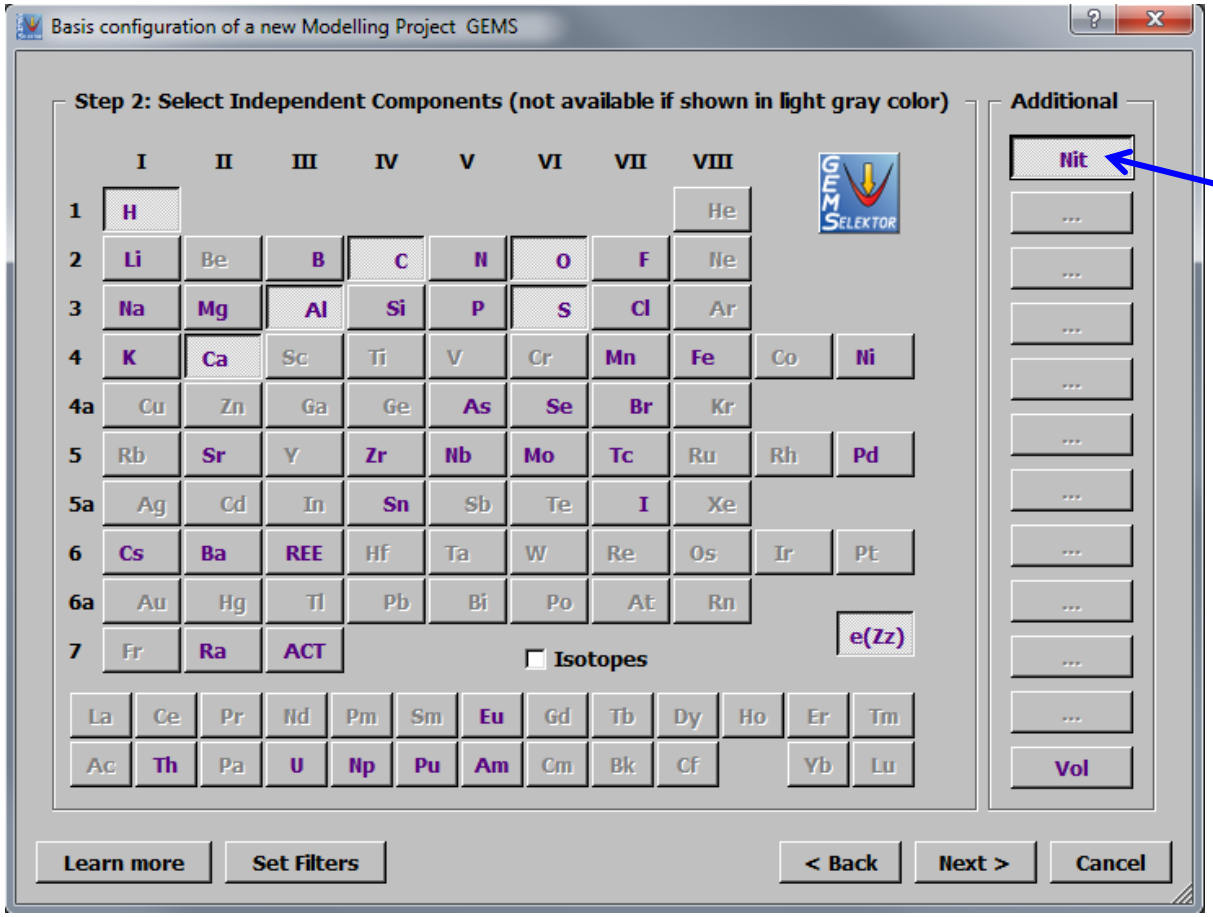
IT’s YOUR TURN!

Tutorial: CA-HH-Cc systems

- GEMS 3.2
- Cemdata'14 database
- Create a *New Project*
  - Name of the modelling project: *CA_HH_Cc*
  - Comment: *Training*



Select the elements



Need air for volume variations/ Or O2.

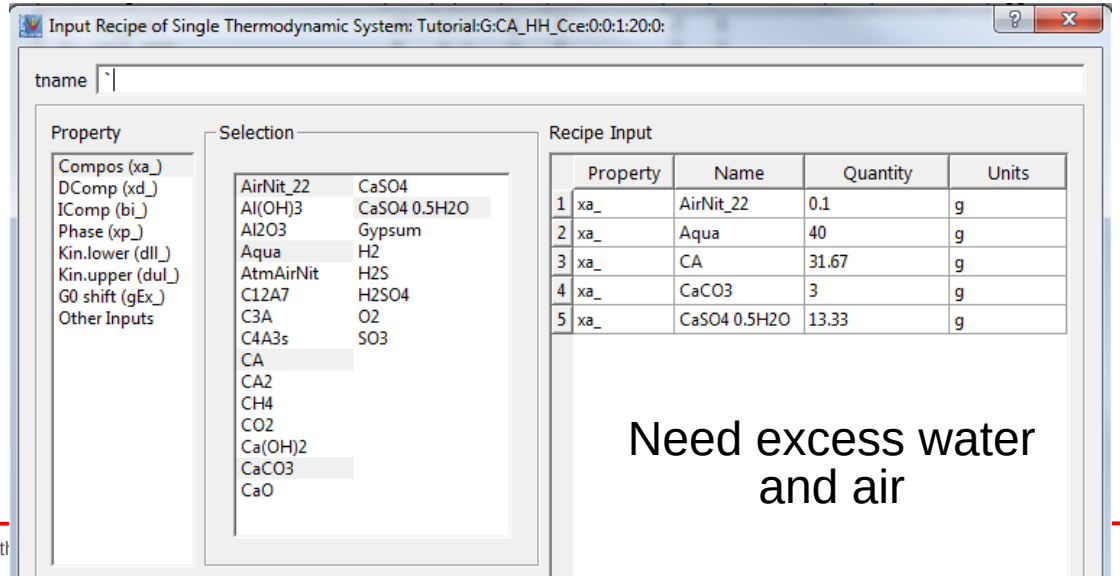
- Select: *Debye-Hueckel (Helgeson) option for aqueous electrolyte model*

SysEq: Enter a new record key

- Thermodynamic potential to minimize: *G*
- Name: *CA_HH_Cc*
- Temperature: *20°C*

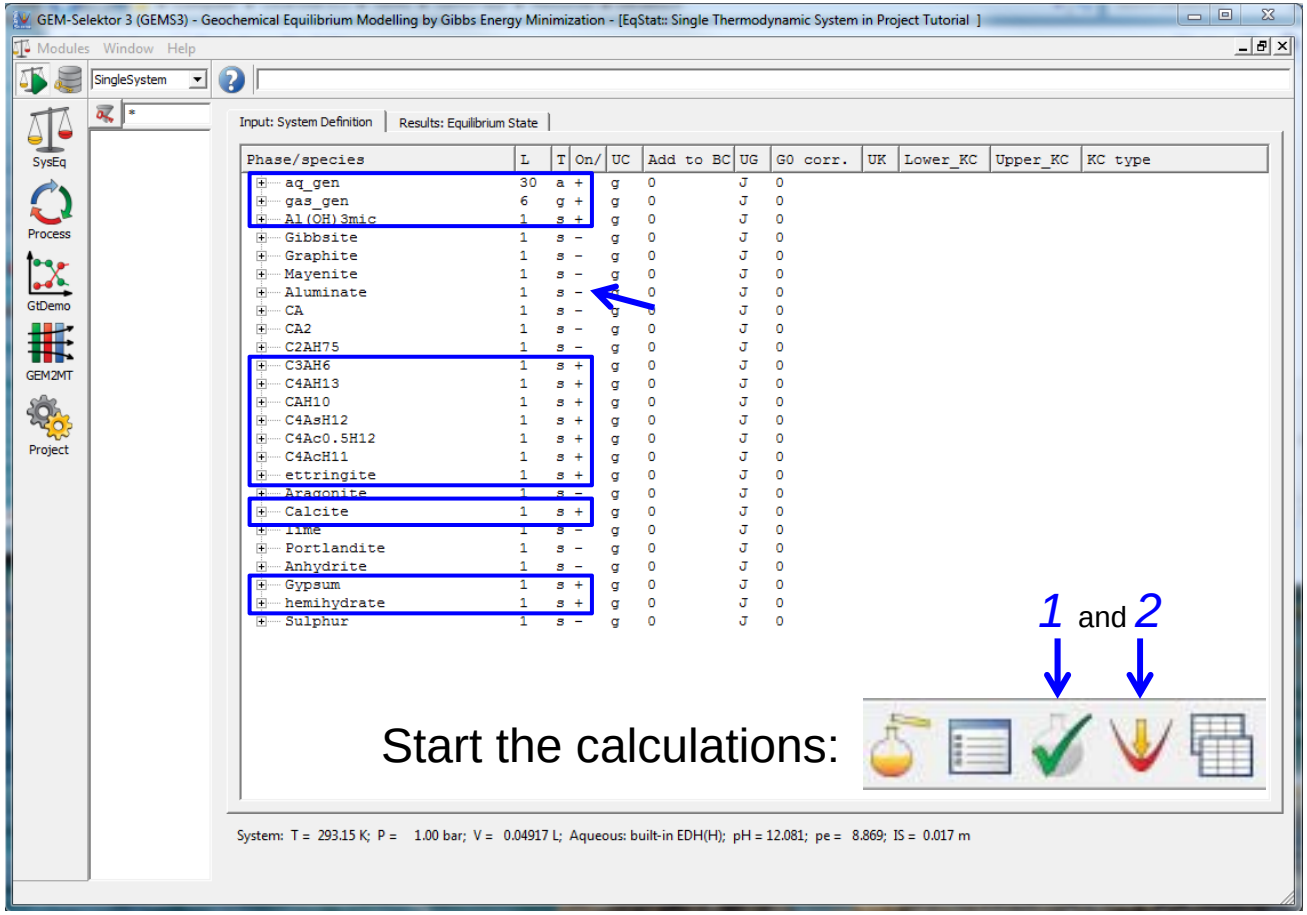
Input recipe:

- Name: *CA_HH_Cc*
- DH of CA: 95% — 66.67g *0.5*0.95 = *31.67g*
- DH of hemihydrate: 100% — *23.6g*
- DH of limestone: 15% — 20g *0.15 = *3g*

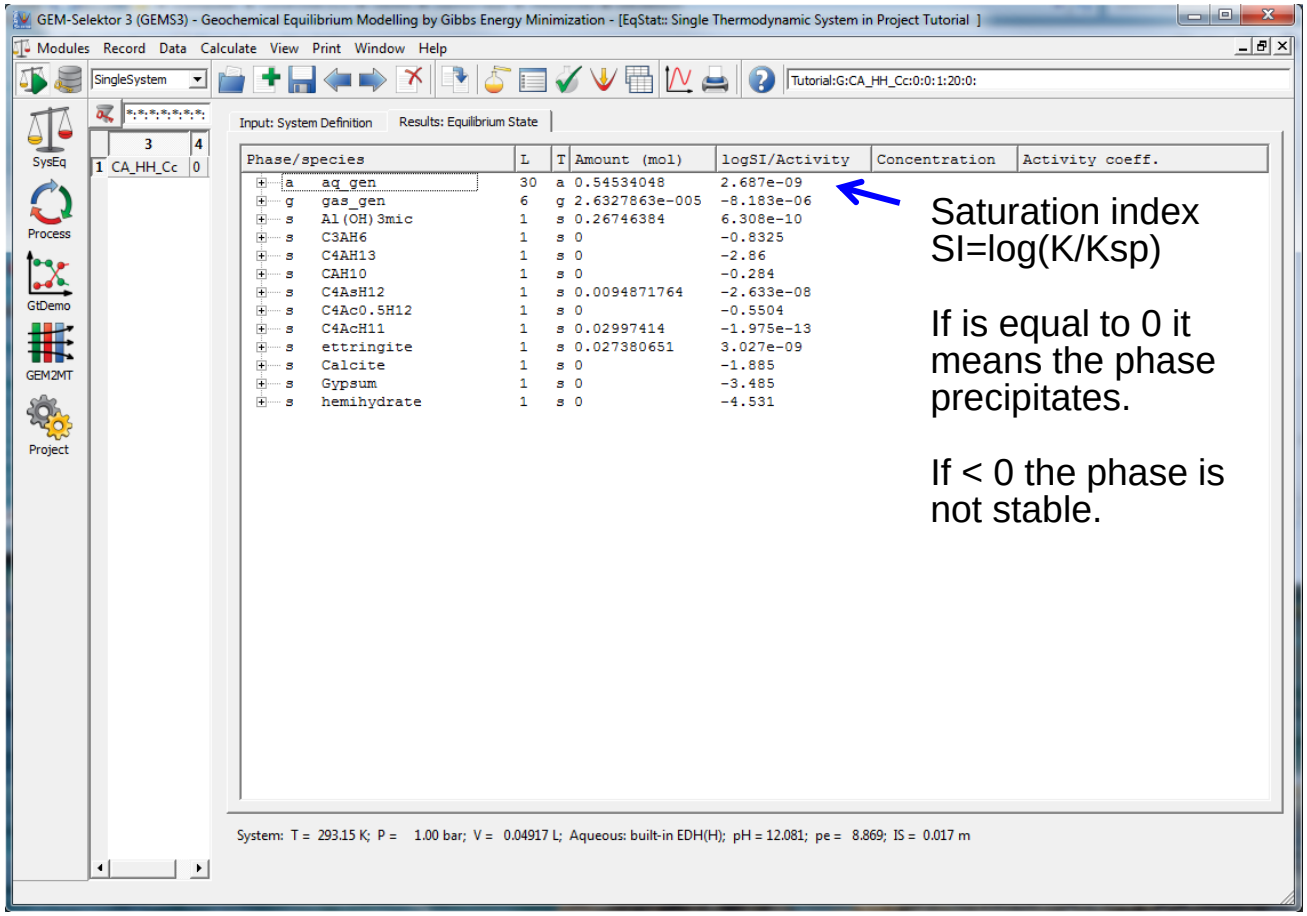


Input: System Definition

- Turn off the phases with –
- With the new database you don't need to create the CA phase!



Output: Equilibrium state



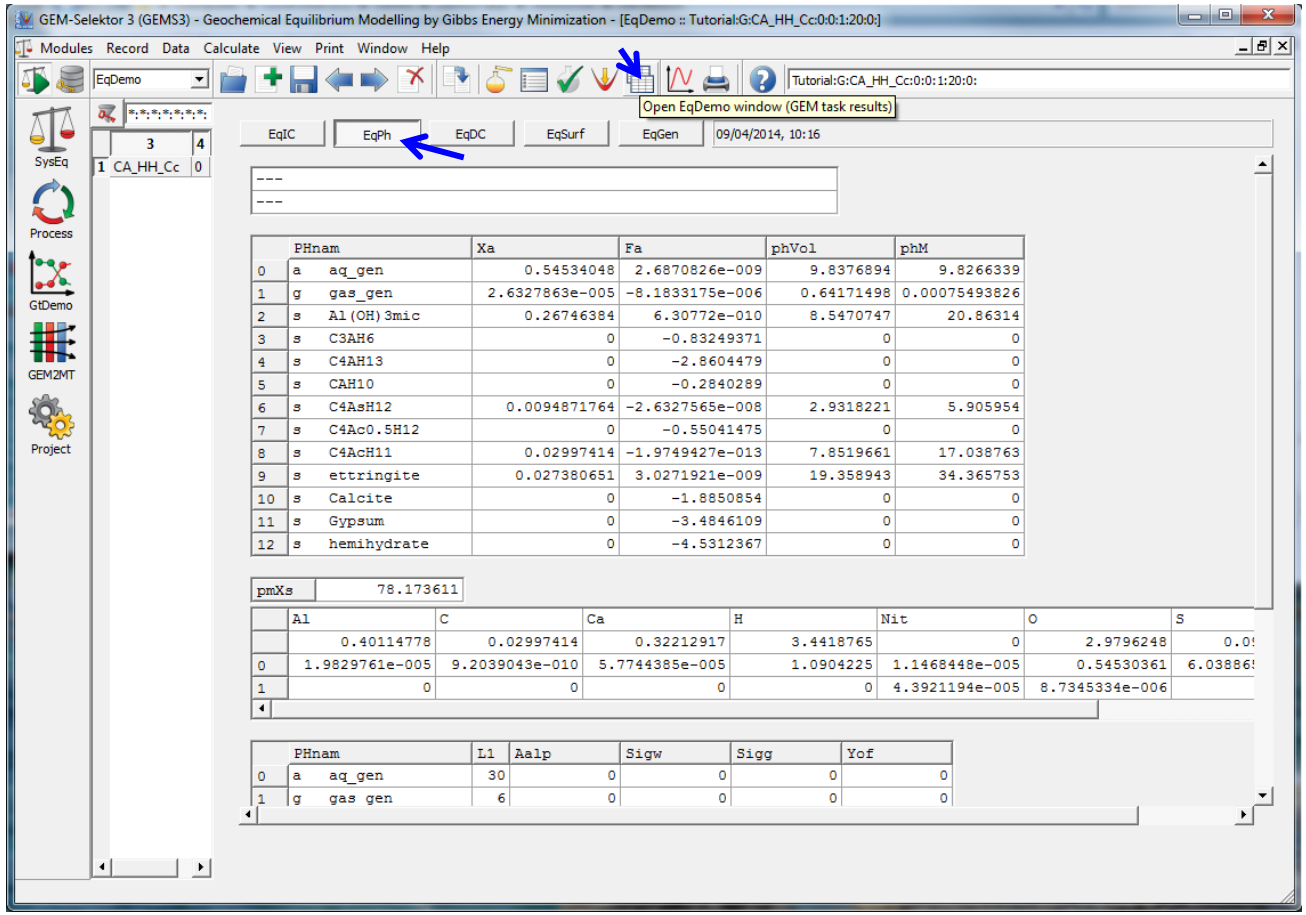
Saturation index SI=log(K/Ksp)

If is equal to 0 it means the phase precipitates.

If < 0 the phase is not stable.

EqDemo: EqPh

- Comparison between the mass amounts of the different phases measured with XRD Rietveld after 1 year and GEMS



	70CA-30HH-20Cc	
	XRD	GEMS
CA	1.7	1.7
HH	0.0	0.0
CaCO3	18.4	17.0
Gypsum	0.1	0.0
Ettringite	27.1	34.5
Monosulfo	3.0	5.8
Hc	14.4	0.0
Mc	13.3	17.0
C3AH6	2.0	0.0
Gibbsite	10.7	20.8
DH CA		95%
DH HH		100%

Process

- Select the single system you create (*CA_HH_Cc*)

GEM-Selektor Process Setup: Tutorial:G:CA_HH_Cc:0:0:1:20:0:CA_HH_Cc_process:S:

Step 1 - Process Simulator Configuration

This is a tool for 'batch' calculati
processes (e.g. mixing, dissolutic

The Process record can be confi
'P_expr' and simulation output sc

Any process simulator belongs tc
1. 'Sequential': only input GEM
2. 'Reciprocal': next step depe
3. 'Inverse': GEM input adjust

Please, choose a process simu
- P Sequential temperature
- S Direct sequential chang
- G Batch inverse titration s
- T One arbitrary inverse ti
- R Sequential reactor sche
- L Lippmann diagram (tran

Learn more

GEM-Selektor Process Setup: Tutorial:G:CA_HH_Cc:0:0:1:20:0:CA_HH_Cc:S:

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	25	0	0	0	0.1	0	0
Until	1031	0	1	25	0	0	0	3.1	0	0
Step	1	0	0	0	0	0	0	0.1	0	0

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

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

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

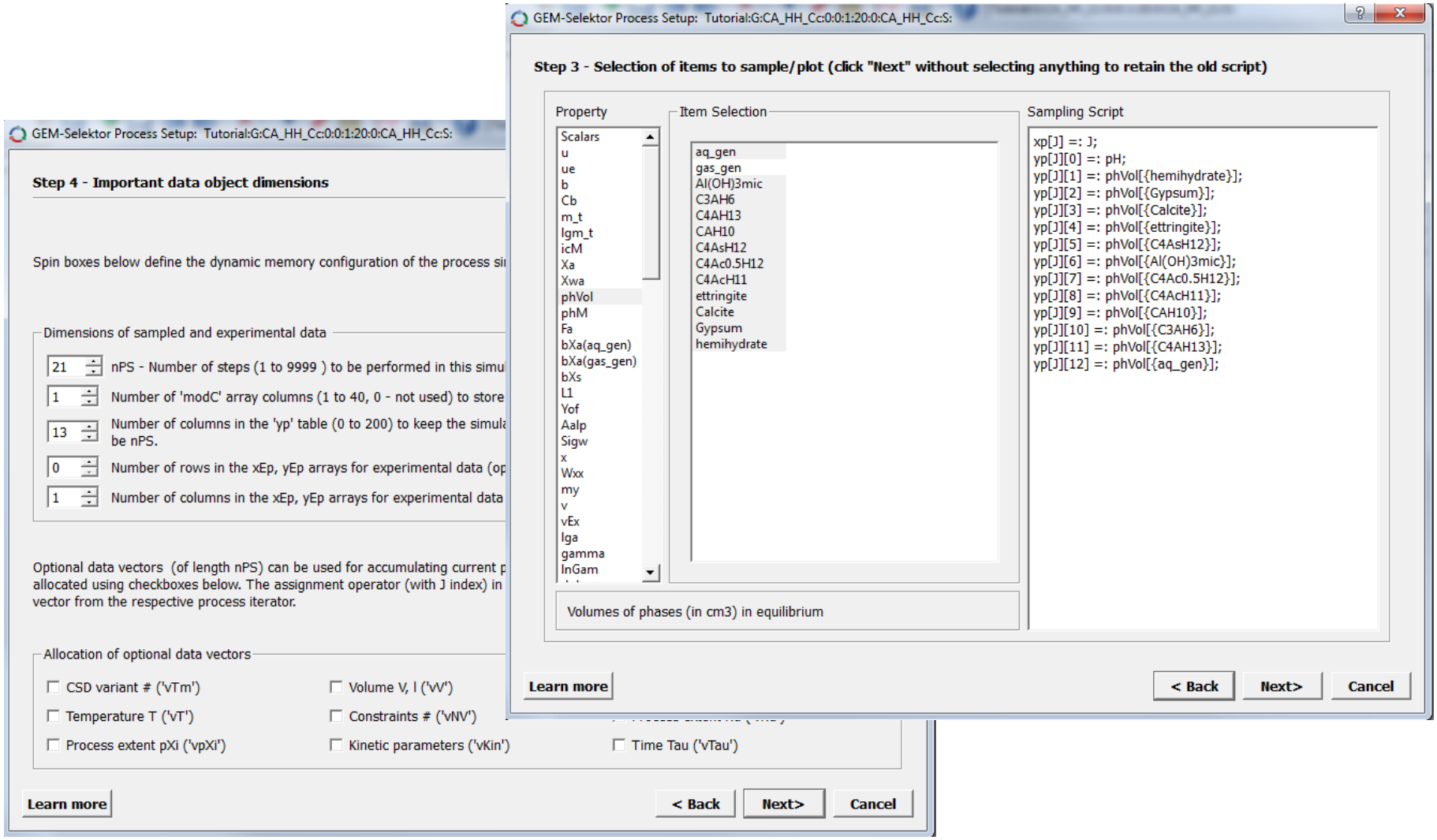
Compos
DComp
IComp
Phases
DC-lower
DC-upper
Molality
Sorbed

AirNit_22
Al(OH)3
Al2O3
Aqua
AtmAirNit
C12A7
C3A
C4A3s
CA
CA2
CH4
CO2
Ca(OH)2
CaCO3
CaO
CaSO4
CaSO4 0.5H2O
Gypsum
H2
H2S
H2SO4
O2
SO3

modC[J] =: cNu;
xa_[{CA}] =: cNu * 1;
xa_[{CaSO4 0.5H2O}] =: cNu * 1;
xa_[{CaCO3}] =: cNu * 1;
xa_[{Aqua}] =: cNu * 1;

Learn more < Back Next> Cancel

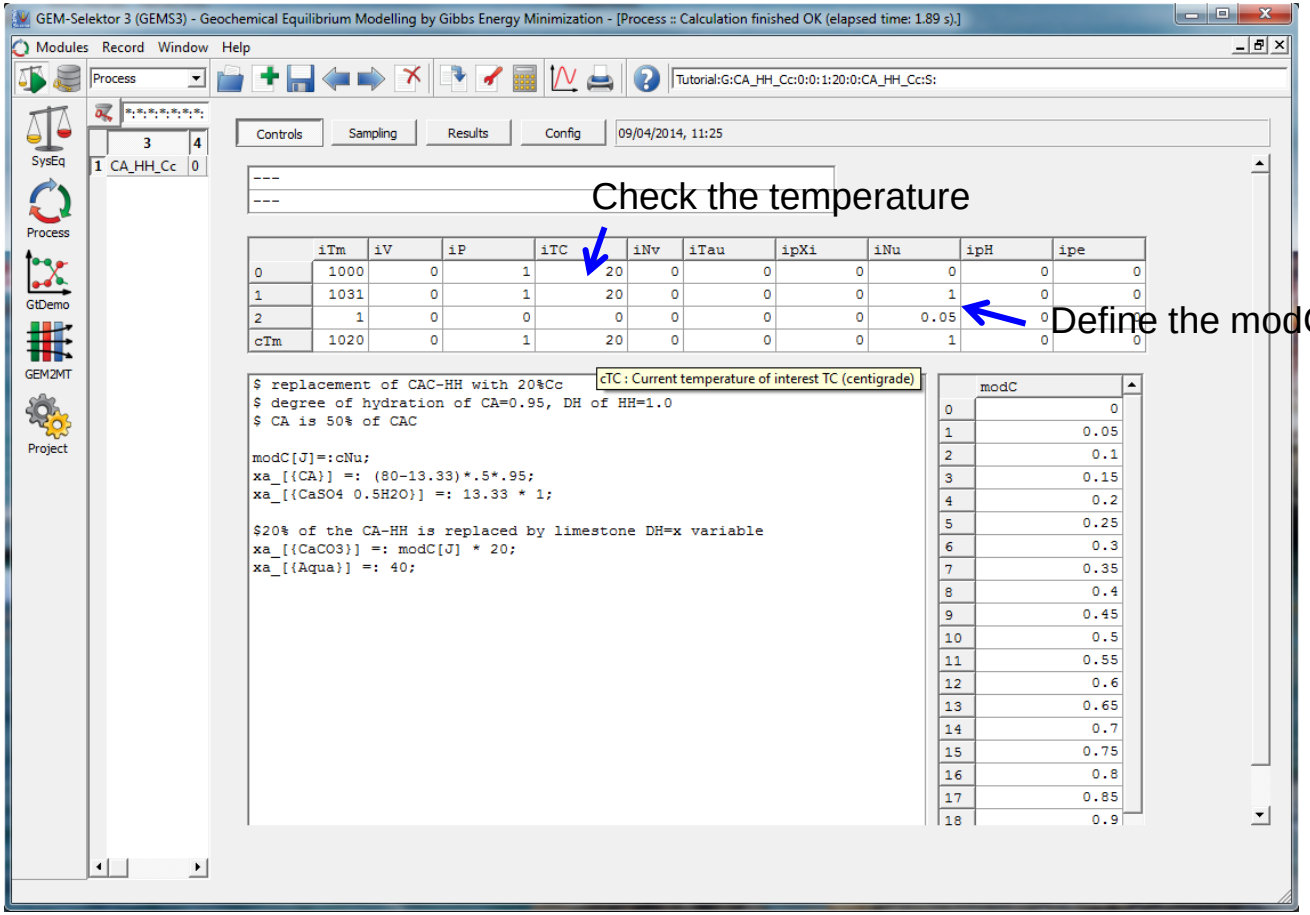
Process



- Step 5: select only the first option (*Use 'P_expr'*)

Controls

- Modify the script according to this tutorial

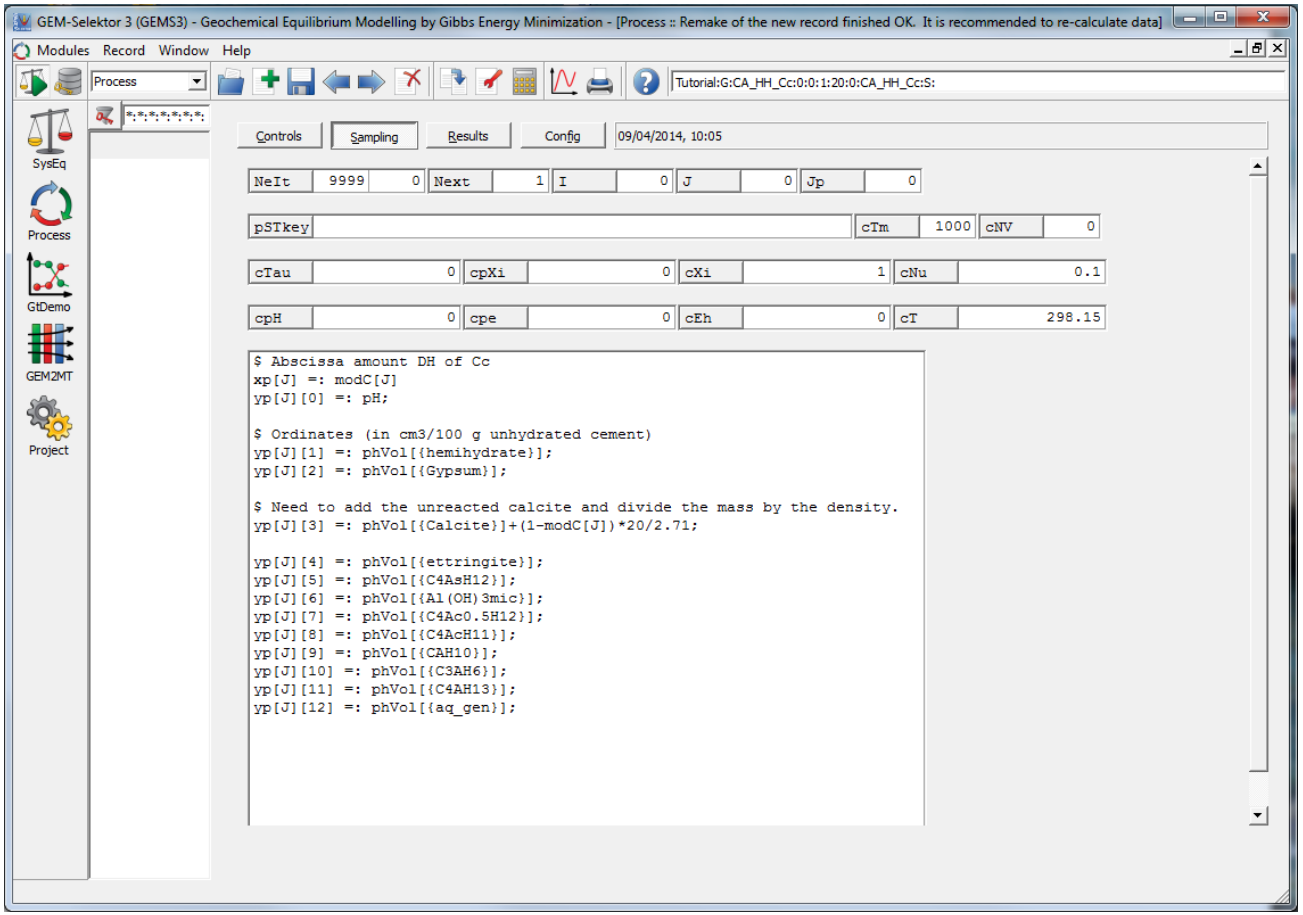


	iTm	iV	iP	iTC	iNv	iTau	ipXi	iNu	ipH	ipe
0	1000	0	1	20	0	0	0	0	0	0
1	1031	0	1	20	0	0	0	1	0	0
2	1	0	0	0	0	0	0	0.05	0	0
cTm	1020	0	1	20	0	0	0	1	0	0

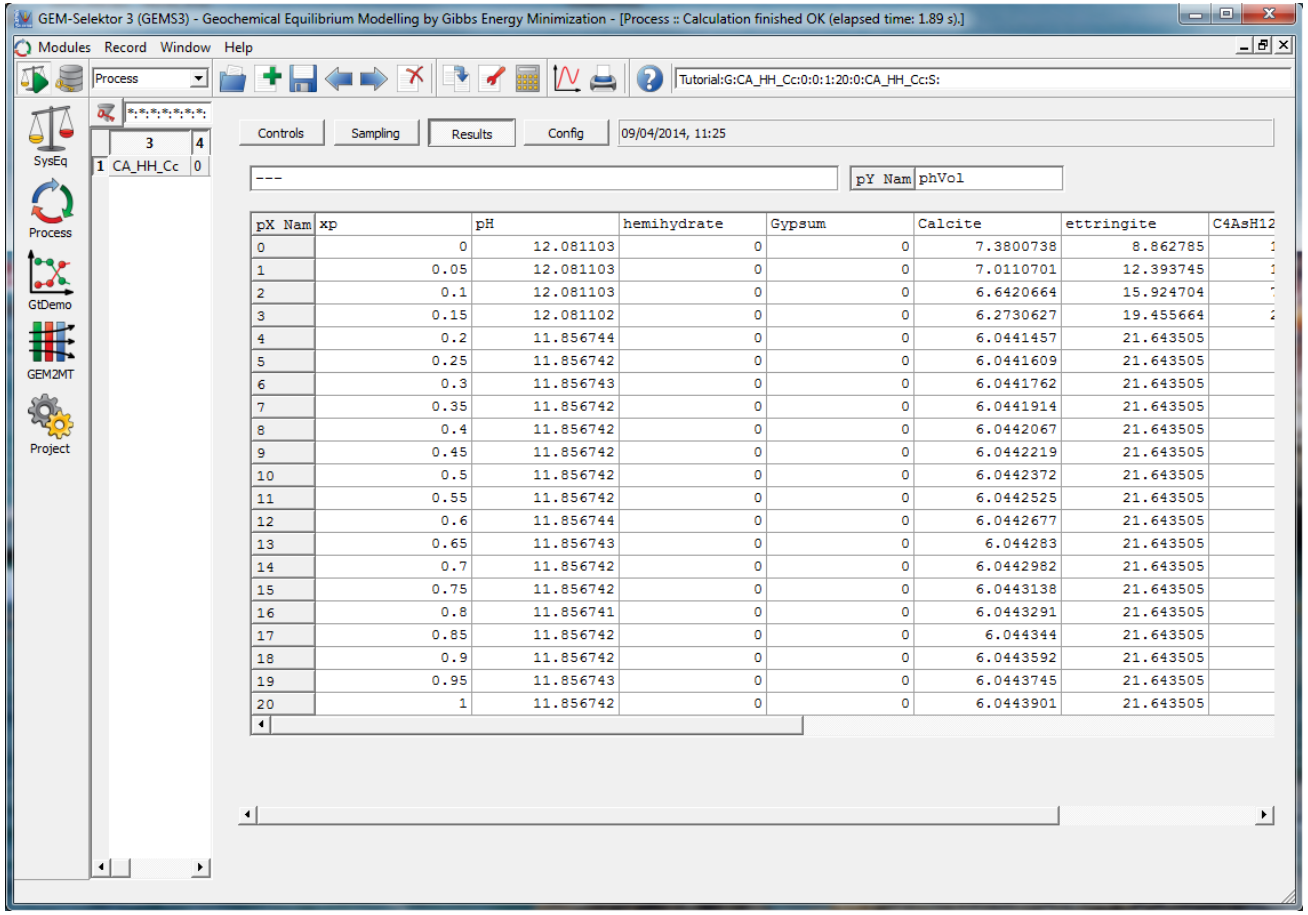
	modC
0	0
1	0.05
2	0.1
3	0.15
4	0.2
5	0.25
6	0.3
7	0.35
8	0.4
9	0.45
10	0.5
11	0.55
12	0.6
13	0.65
14	0.7
15	0.75
16	0.8
17	0.85
18	0.9

Sampling

- Modify the script according to this tutorial

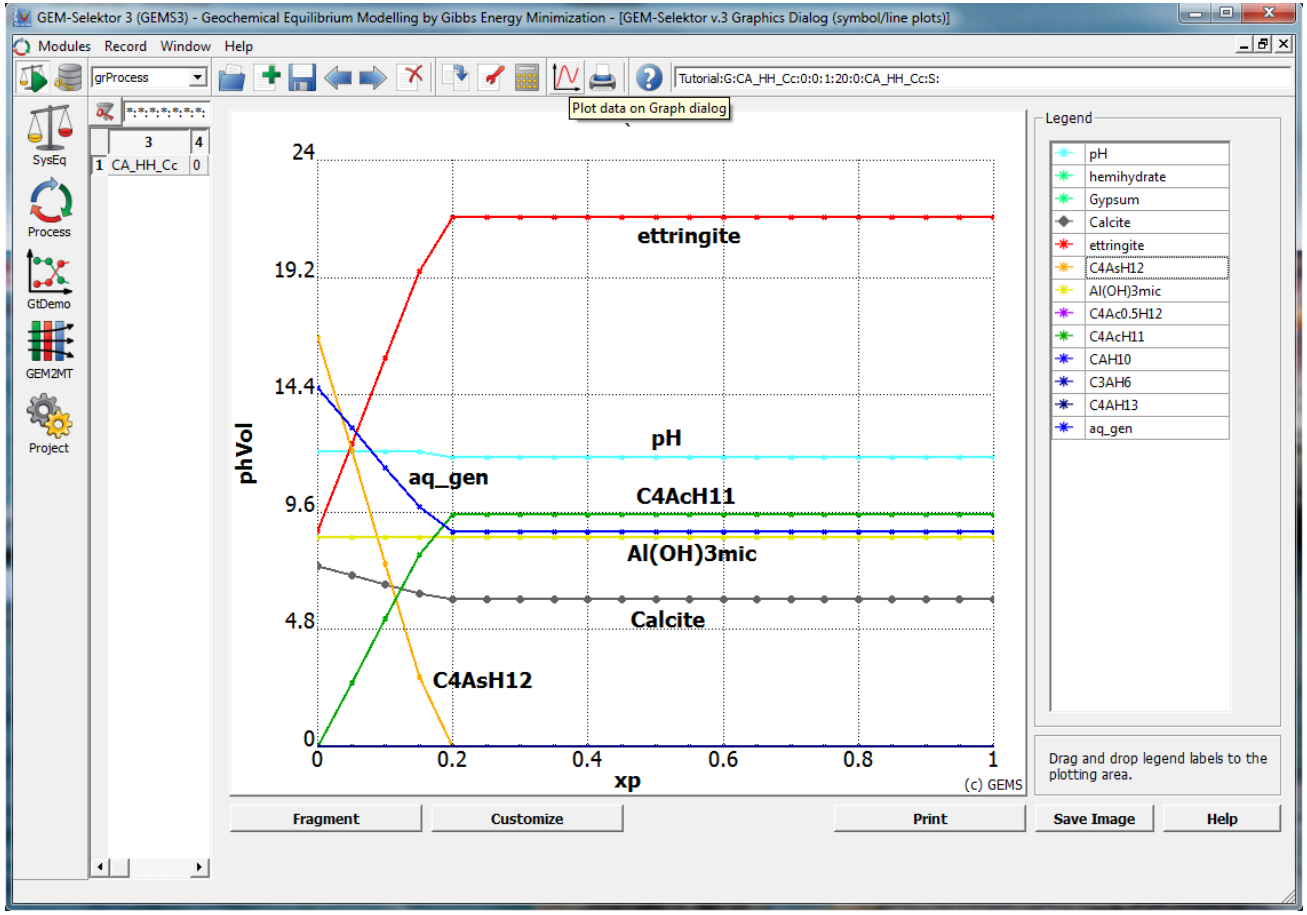


Results

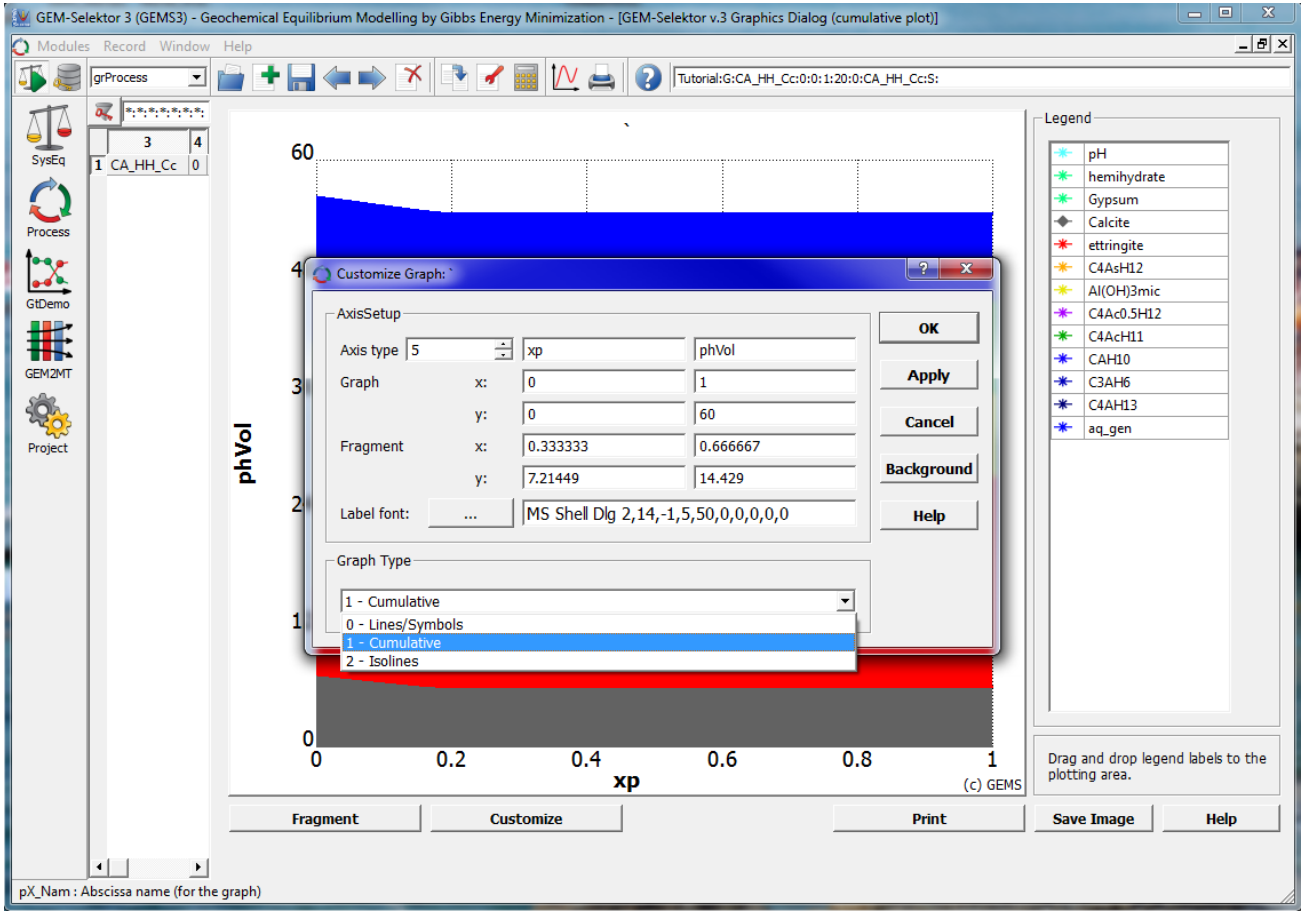


pX Nam	xp	pH	hemihydrate	Gypsum	Calcite	ettringite	C4AsH12
0	0	12.081103	0	0	7.3800738	8.862785	1
1	0.05	12.081103	0	0	7.0110701	12.393745	1
2	0.1	12.081103	0	0	6.6420664	15.924704	1
3	0.15	12.081102	0	0	6.2730627	19.455664	2
4	0.2	11.856744	0	0	6.0441457	21.643505	
5	0.25	11.856742	0	0	6.0441609	21.643505	
6	0.3	11.856743	0	0	6.0441762	21.643505	
7	0.35	11.856742	0	0	6.0441914	21.643505	
8	0.4	11.856742	0	0	6.0442067	21.643505	
9	0.45	11.856742	0	0	6.0442219	21.643505	
10	0.5	11.856742	0	0	6.0442372	21.643505	
11	0.55	11.856742	0	0	6.0442525	21.643505	
12	0.6	11.856744	0	0	6.0442677	21.643505	
13	0.65	11.856743	0	0	6.044283	21.643505	
14	0.7	11.856742	0	0	6.0442982	21.643505	
15	0.75	11.856742	0	0	6.0443138	21.643505	
16	0.8	11.856741	0	0	6.0443291	21.643505	
17	0.85	11.856742	0	0	6.044344	21.643505	
18	0.9	11.856742	0	0	6.0443592	21.643505	
19	0.95	11.856743	0	0	6.0443745	21.643505	
20	1	11.856742	0	0	6.0443901	21.643505	

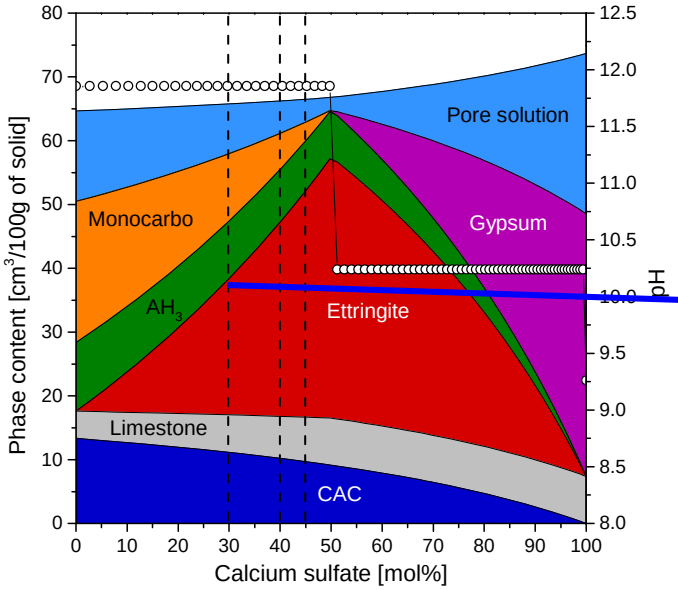
Graph



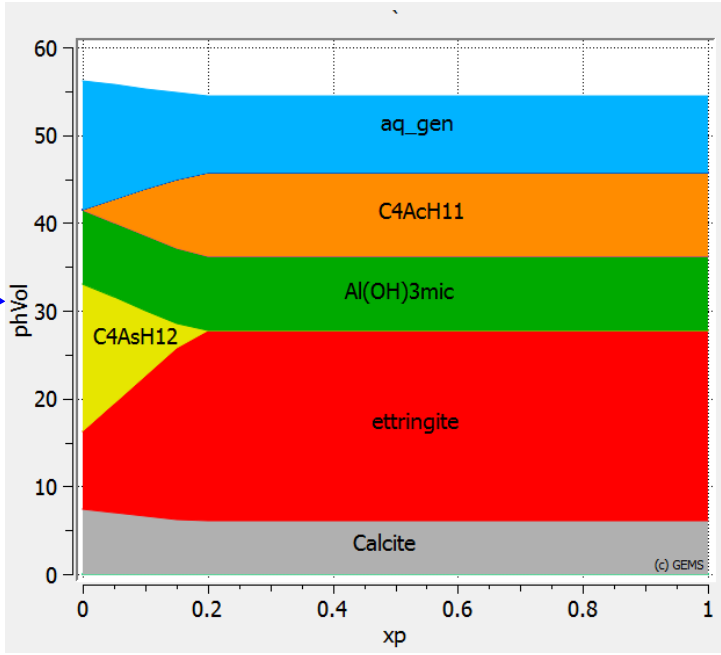
Graph



Conclusions



70CA-30HH system



- From the first study we saw the effect of calcium sulfate on the hydration assuming 100% limestone reaction.
- With your results you can see that by increasing the reacted limestone, the amount of ettringite increases and monosulfate decreases.
- Limestone acts as filler above 20%*0.2=4% in this system.