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

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LABORATORY OF CONSTRUCTION MATERIALS

The project

- Products with special properties like rapid setting, shrinkage compensation

  CAC | CHx | OPC

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

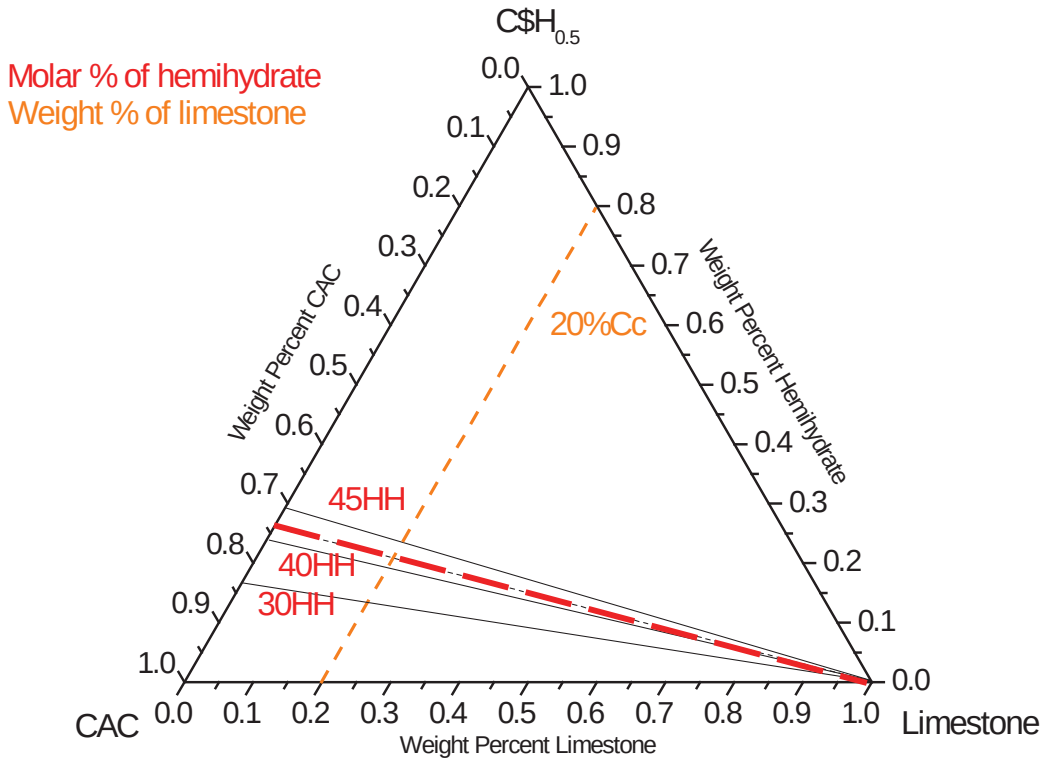
- The novelty of this project is to have a comprehensive study of ternary systems where the OPC is replaced by limestone (reduction of the variability):

  CAC | CHx | Limestone

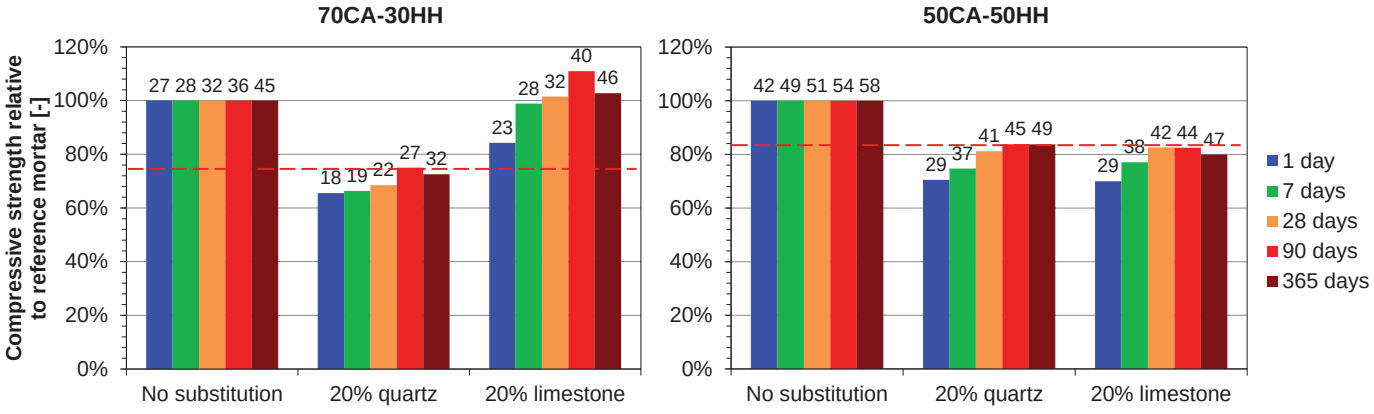
  - Do the limestone act as fillers or it participates in the hydration?

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

Studied systems



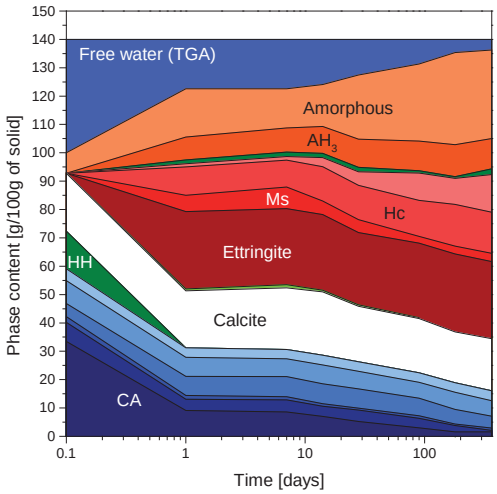
Mechanical properties on mortars



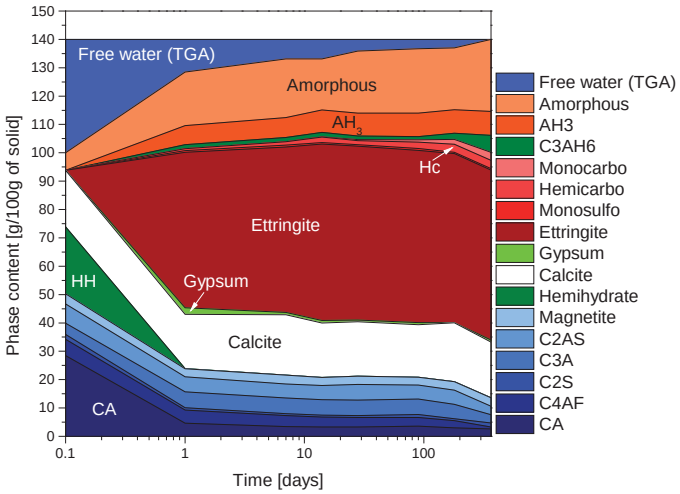
- Limestone enhances the mechanical properties already after 1 day of hydration
- Limestone seems to act as a filler in high sulfate systems

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)

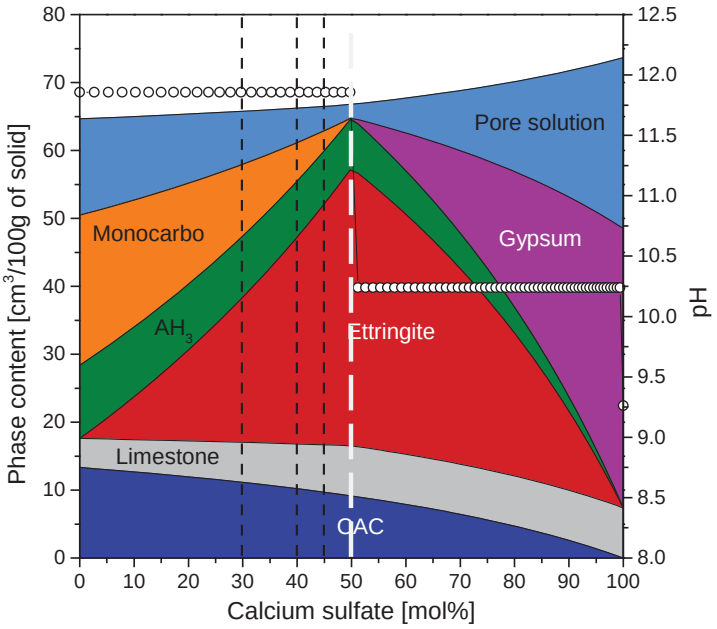
How to “quickly” understand the effect of HH on CA-HH-Cc systems?

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%



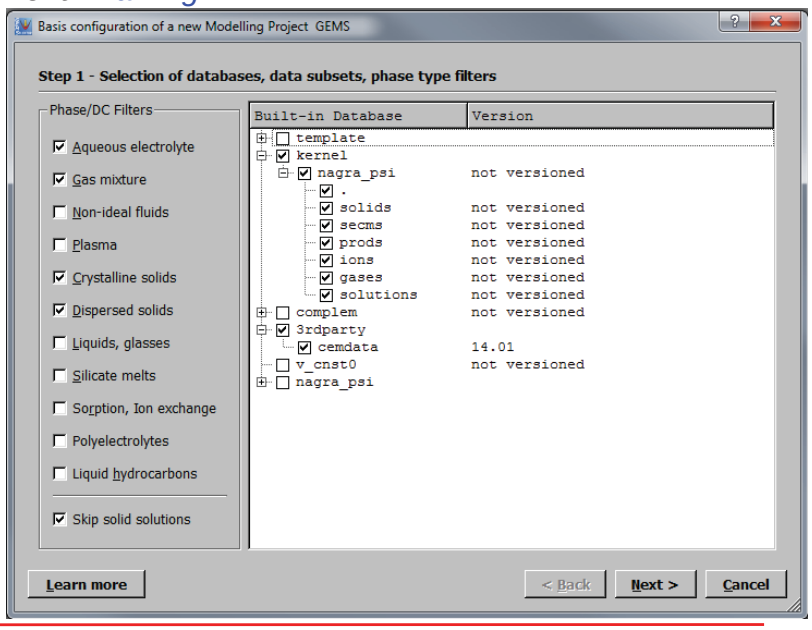
GEMS simulation, variable limestone DH

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

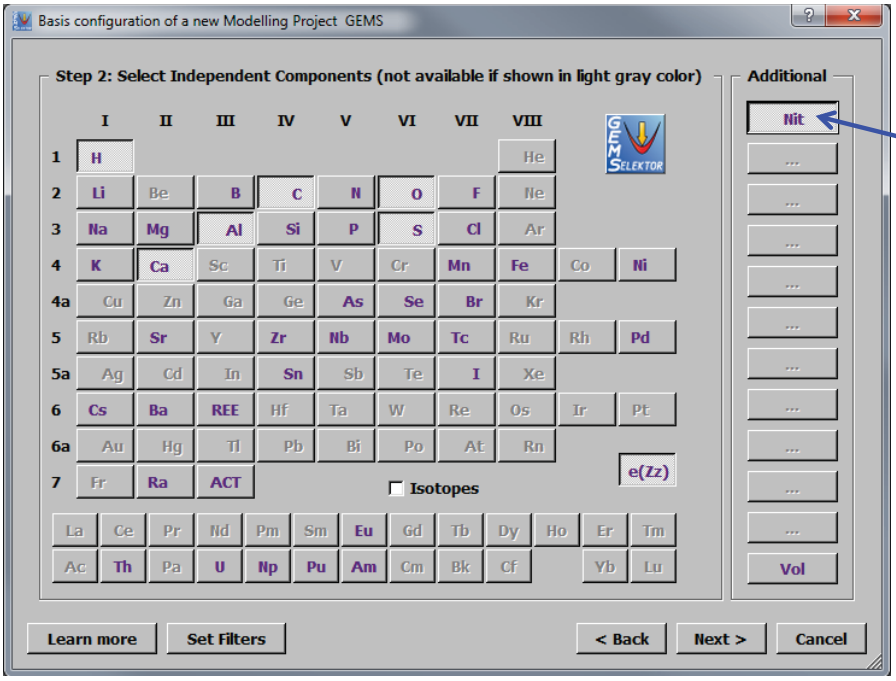
IT's YOUR TURN!

Tutorial: CA-HH-Cc systems

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



Select the elements



Need air for volume variations

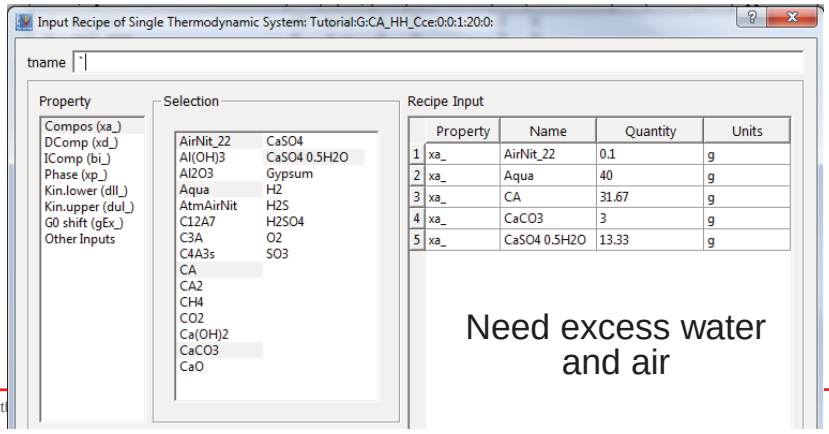
- Select: *Debye-Hueckel (Helgeson) option for aqueous electrolyte model*

SysEq: Enter a new record key

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

Input recipe:

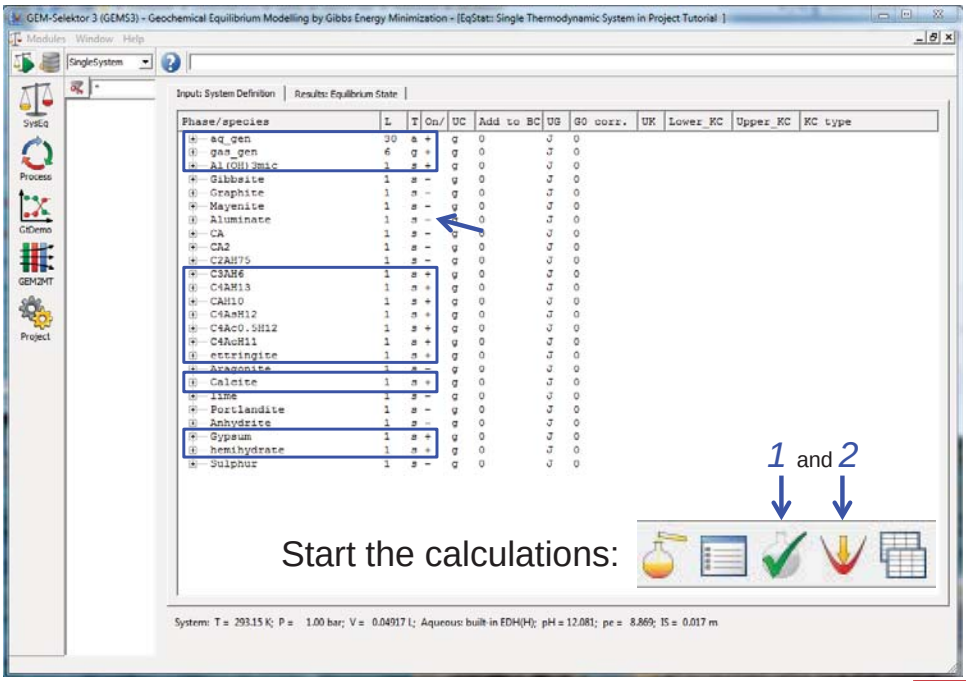
- Name: *CA_HH_Cc*
- DH of CA: 95% — 66.67g *0.5*0.95 = *31.67g*
- DH of hemihydrate: 100% — *23.6g*
- DH of limestone: 15% — 20g *0.15 = *3g*



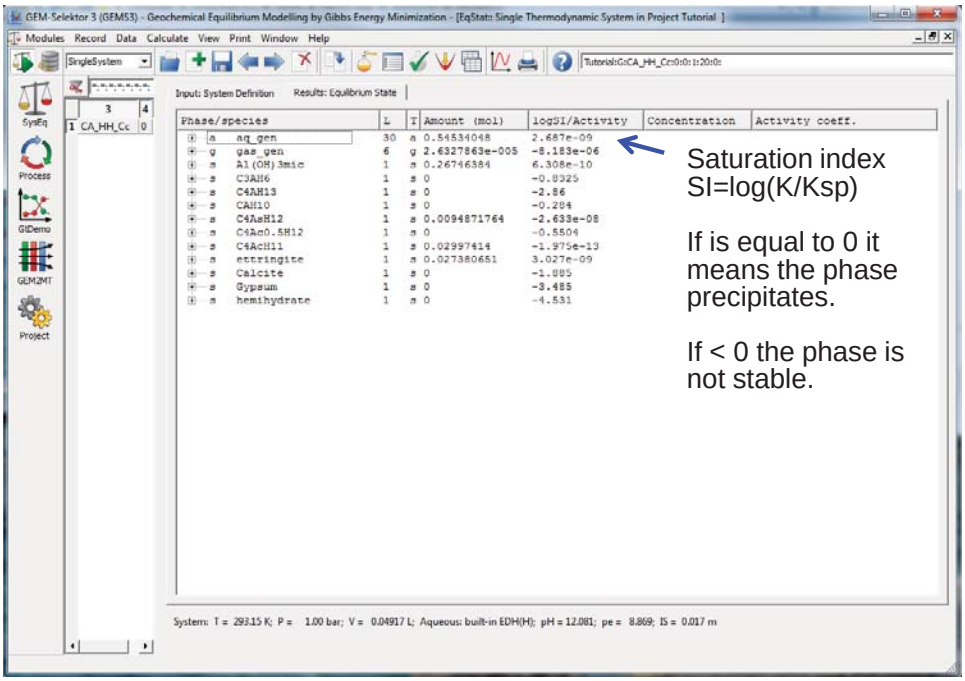
Input: System Definition

SysEq

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



Output: Equilibrium state



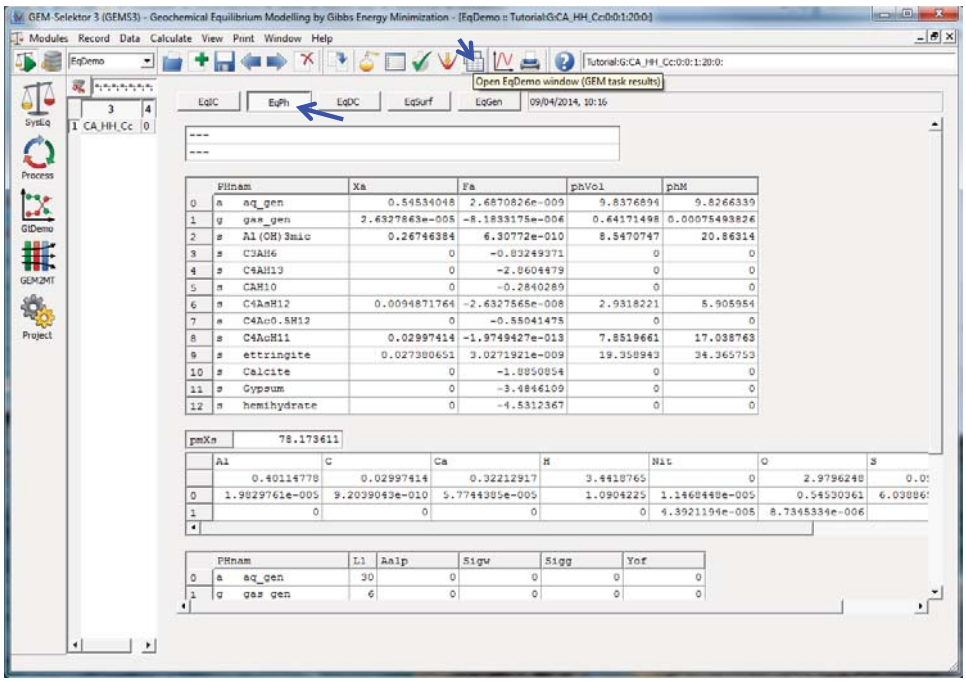
Saturation index SI=log(K/Ksp)

If is equal to 0 it means the phase precipitates.

If < 0 the phase is not stable.

EqDemo: EqPh

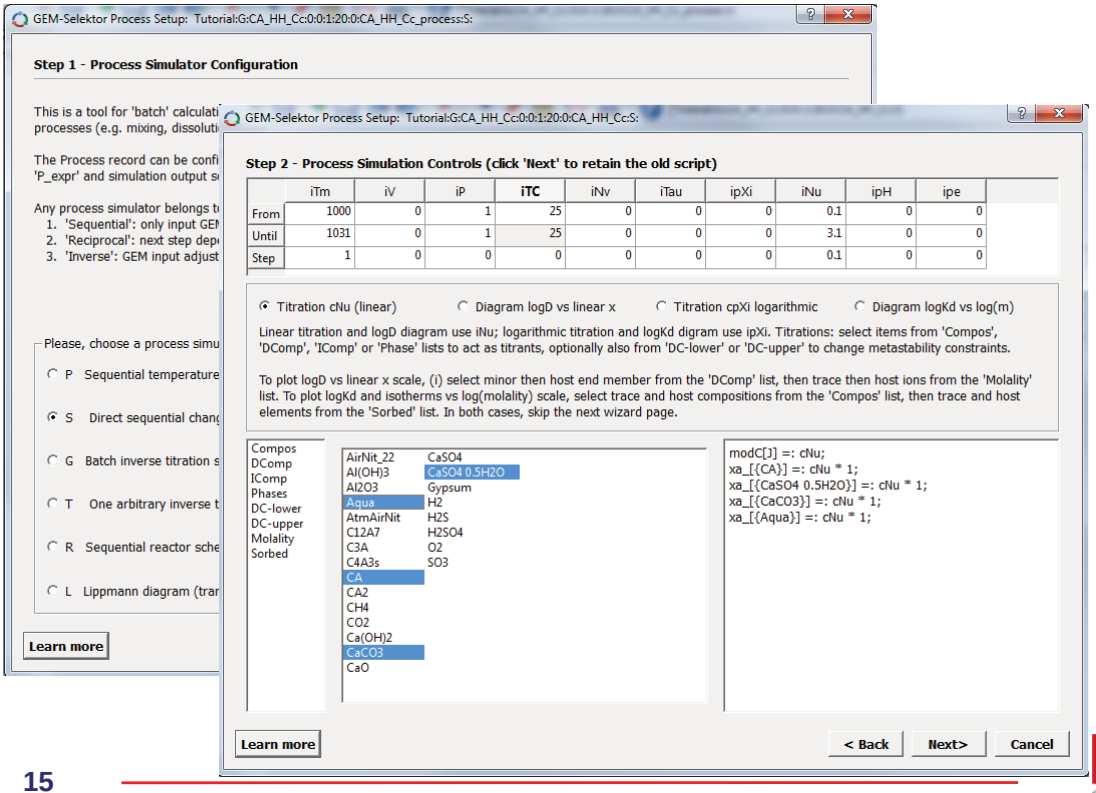
- Comparison between the mass amounts of the different phases measured with XRD Rietveld after 1 year and GEMS



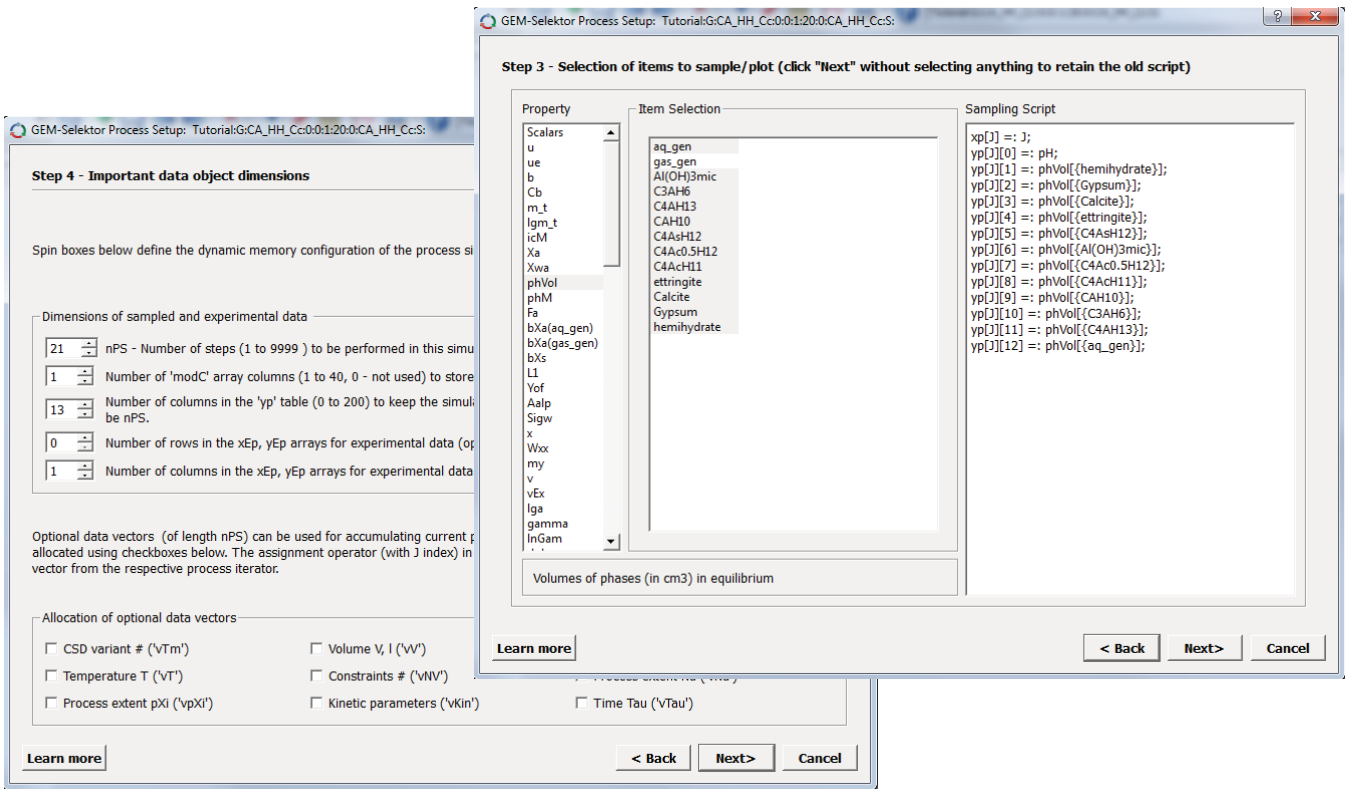
	70CA-30HH-20Cc	
	XRD	GEMS
CA	1.7	1.7
HH	0.0	0.0
CaCO3	18.4	17.0
Gypsum	0.1	0.0
Ettringite	27.1	34.5
Monosulfo	3.0	5.8
Hc	14.4	0.0
Mc	13.3	17.0
C3AH6	2.0	0.0
Gibbsite	10.7	20.8
DH CA		95%
DH HH		100%

Process

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



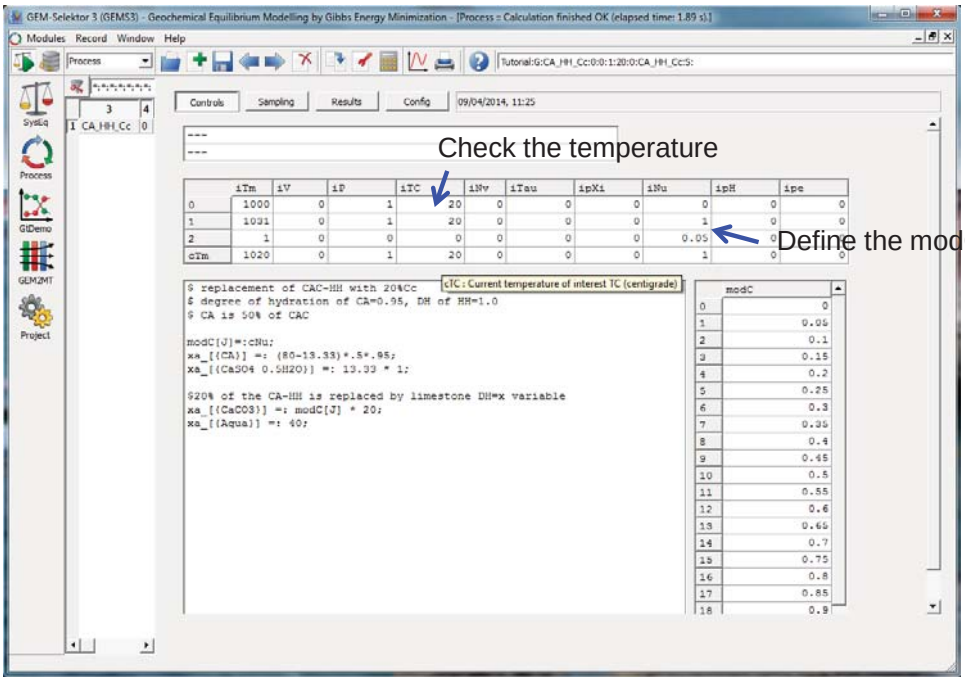
Process



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

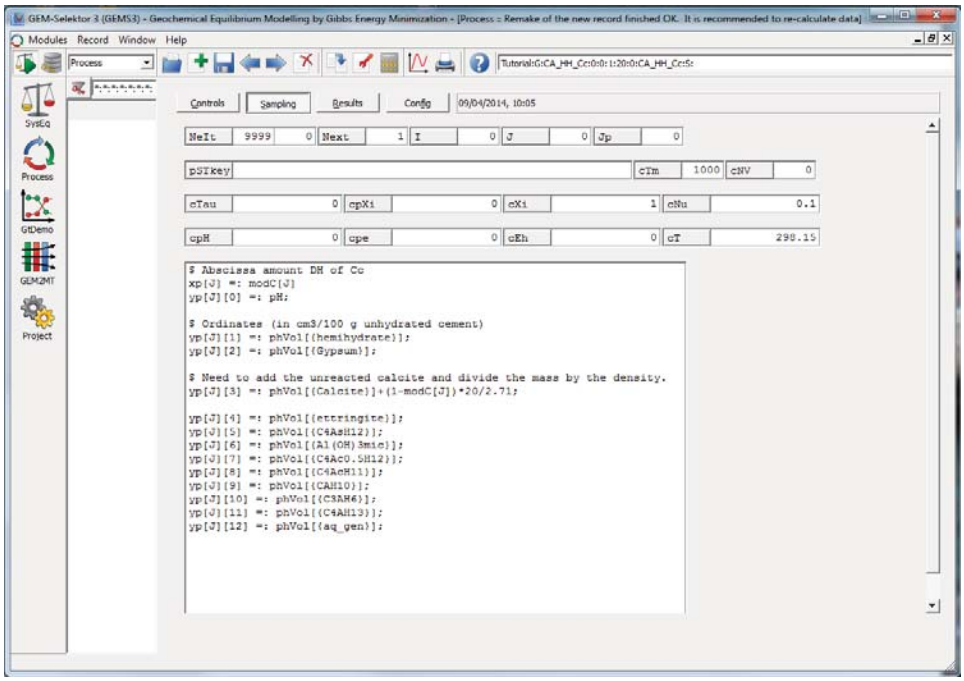
Controls

- Modify the script according to this tutorial

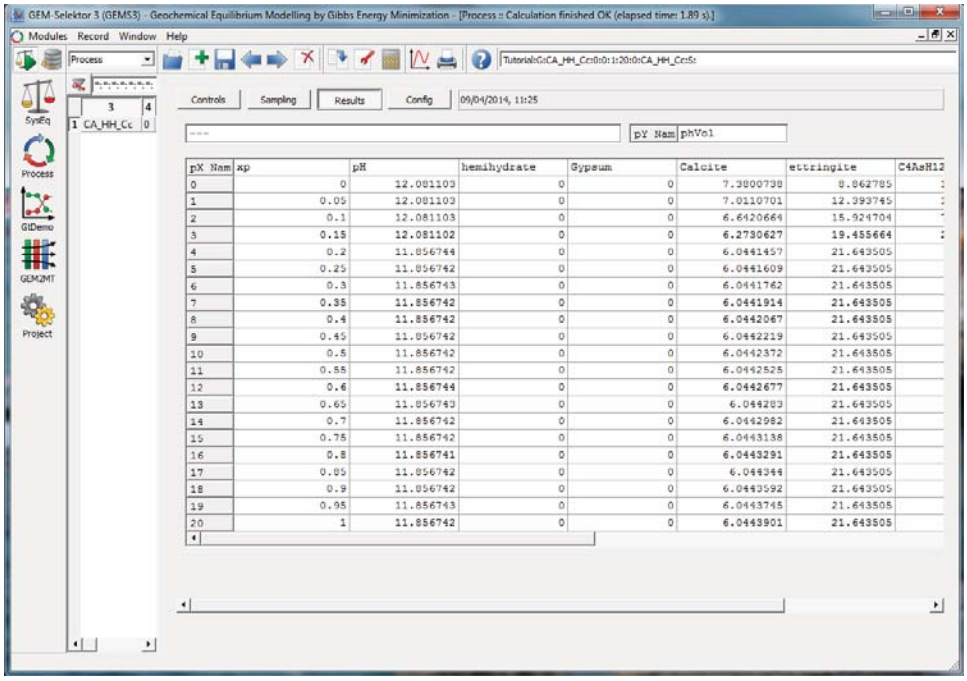


Sampling

- Modify the script according to this tutorial

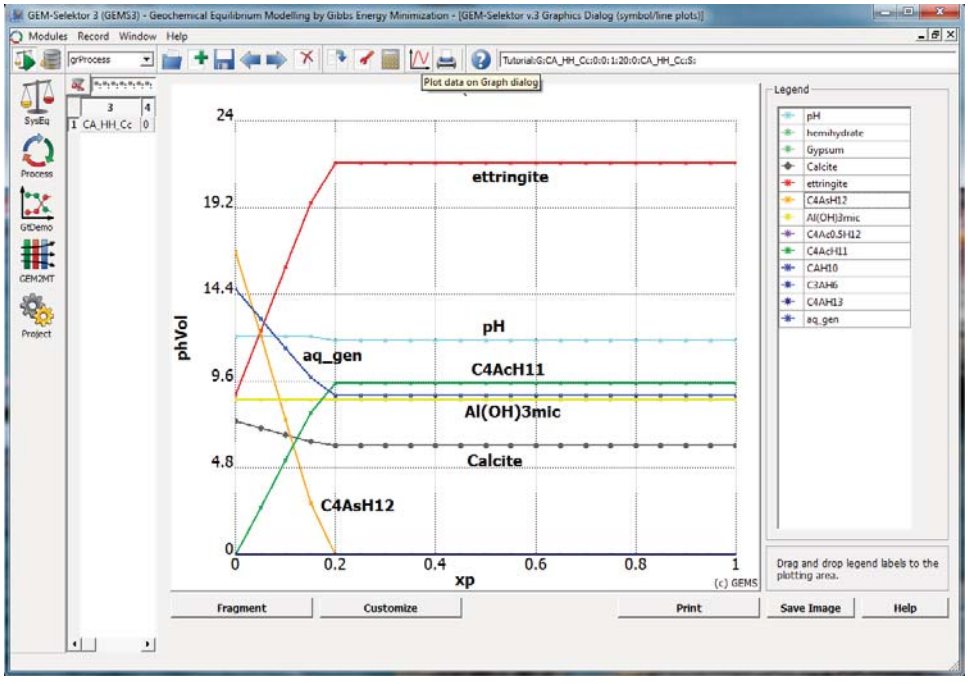


Results

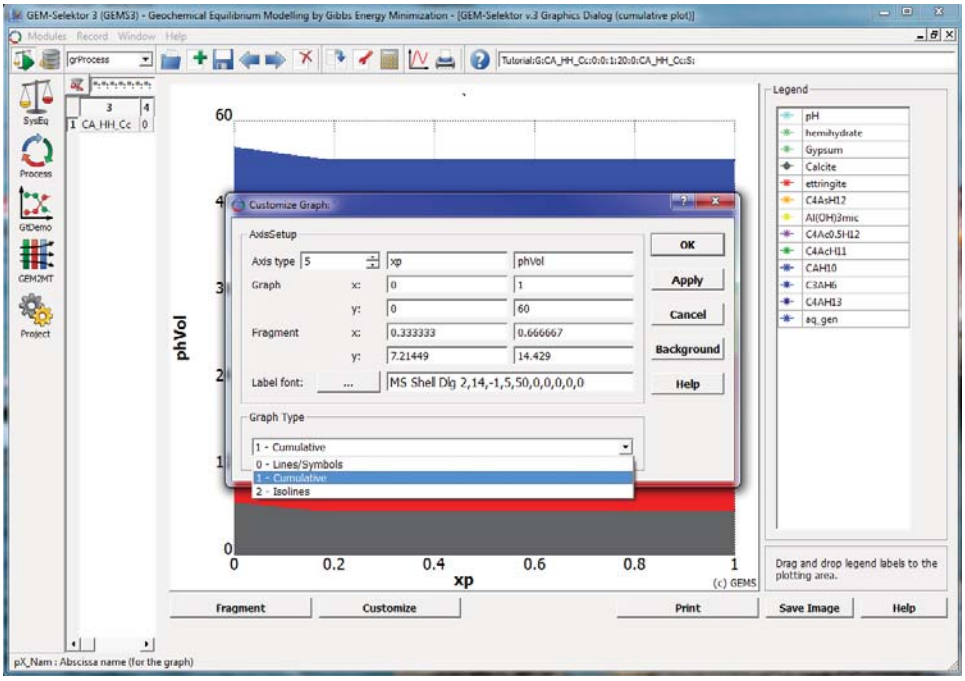


pX Nam	xp	pH	hemihydrate	Gypsum	Calcite	ettringite	C4AsH12
0	0	12.081103	0	0	7.3800738	8.862785	
1	0.05	12.081103	0	0	7.0110701	12.393745	
2	0.1	12.081103	0	0	6.6420664	15.924704	
3	0.15	12.081102	0	0	6.2730627	19.455664	
4	0.2	11.856744	0	0	6.0461457	21.643505	
5	0.25	11.856742	0	0	6.0461609	21.643505	
6	0.3	11.856743	0	0	6.0461762	21.643505	
7	0.35	11.856742	0	0	6.0461914	21.643505	
8	0.4	11.856742	0	0	6.0462067	21.643505	
9	0.45	11.856742	0	0	6.0462219	21.643505	
10	0.5	11.856742	0	0	6.0462372	21.643505	
11	0.55	11.856742	0	0	6.0462525	21.643505	
12	0.6	11.856744	0	0	6.0462677	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	

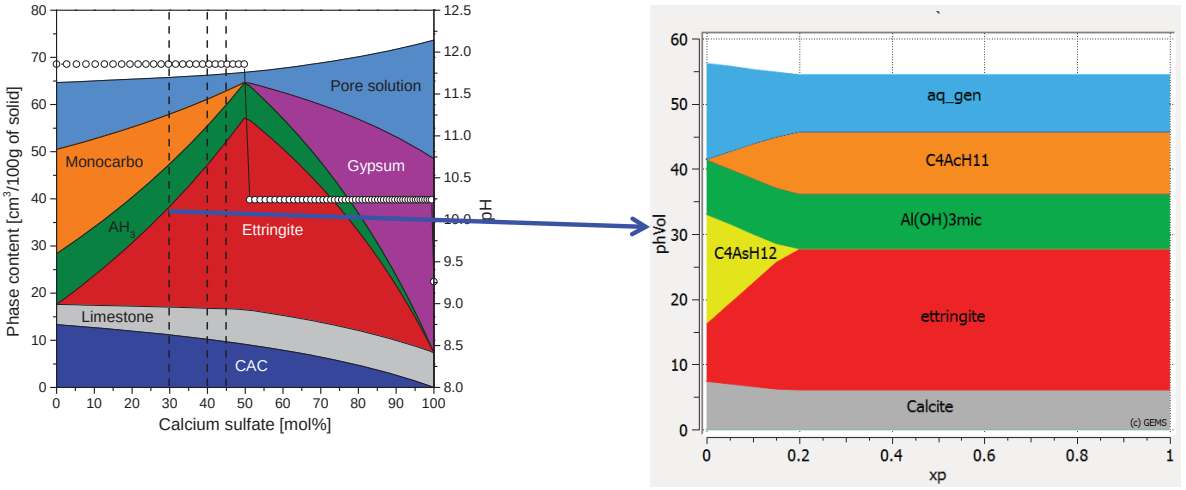
Graph



Graph



Conclusions



- 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.