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## Modelling of $\text{CaO}$ , $\text{Al}_2\text{O}_3$ , $\text{CaSO}_4$ and $\text{CaCO}_3$ systems

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Julien Bizzozero



# The project

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- Products with special properties like rapid setting, shrinkage compensation

CAC

C\$H<sub>x</sub>

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

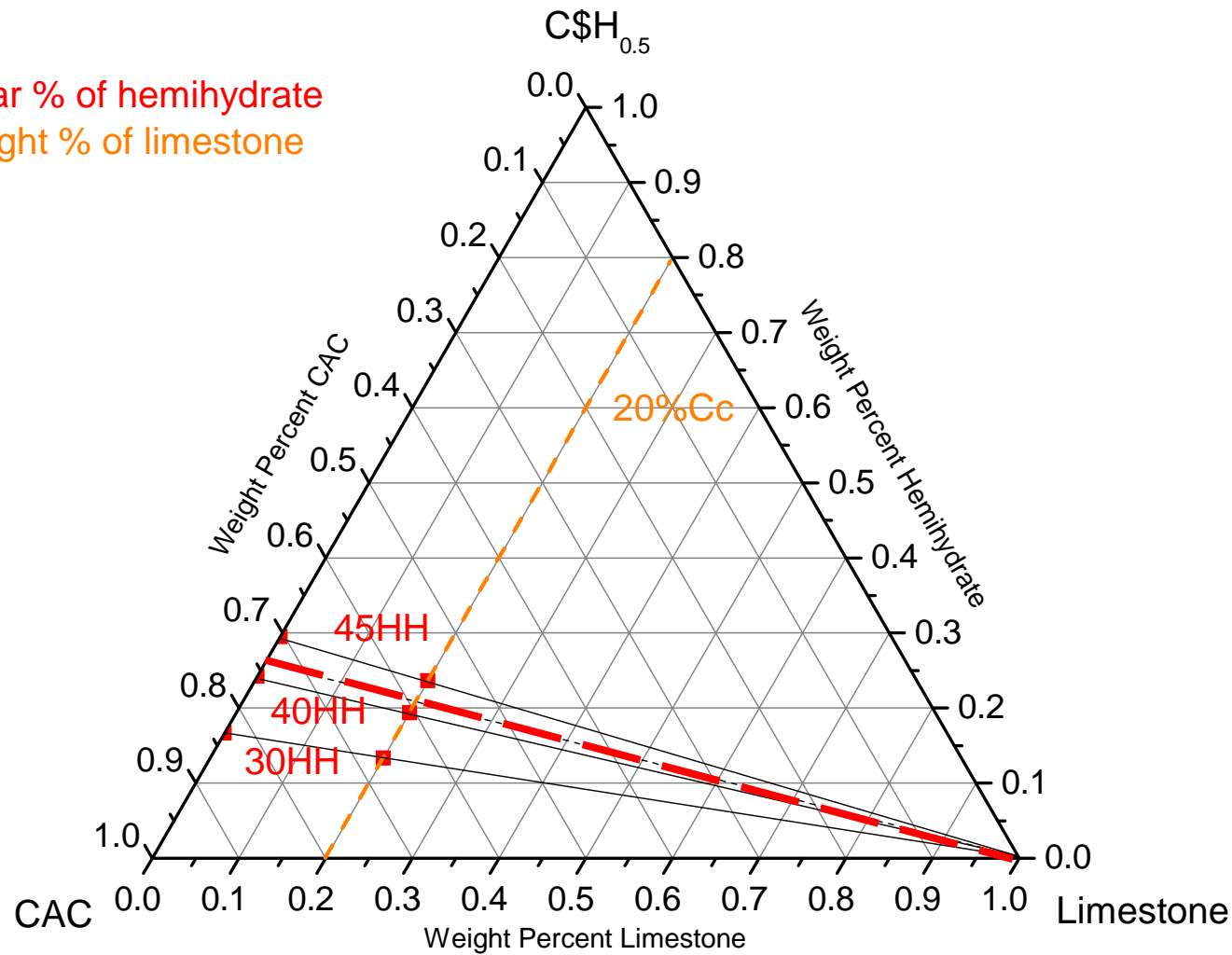
C\$H<sub>x</sub>

Limestone

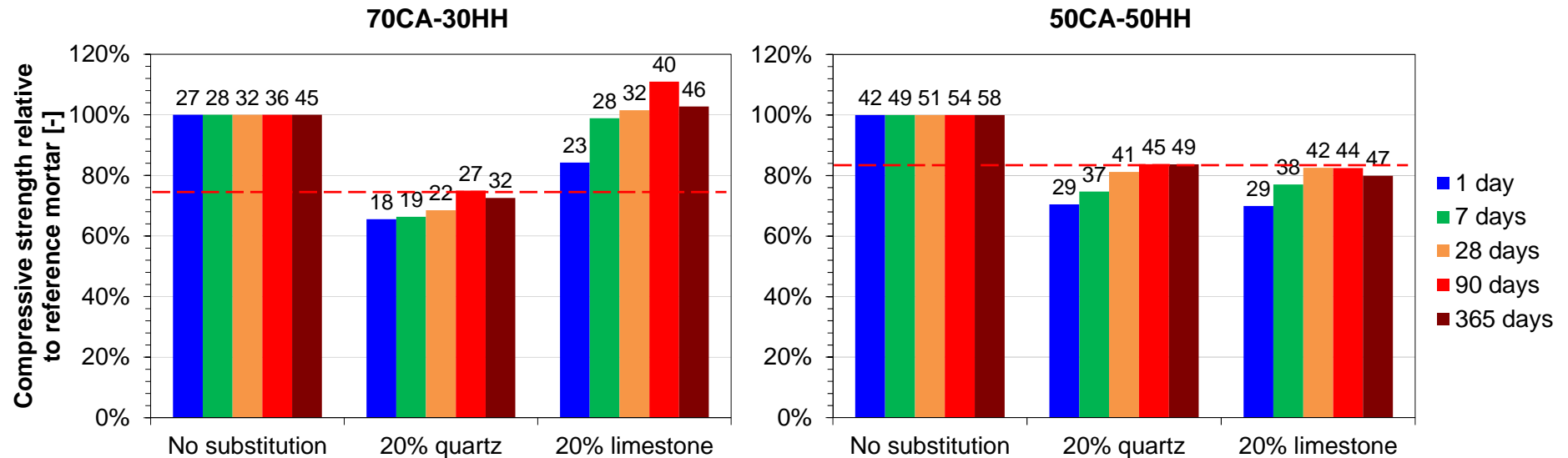
- Do the limestone act as filler or it participates in the hydration?
- Development of new binders
  - Reduction of the CO<sub>2</sub> emissions and energy consumption
  - Reduction of the price

# Studied systems

Molar % of hemihydrate  
Weight % of limestone



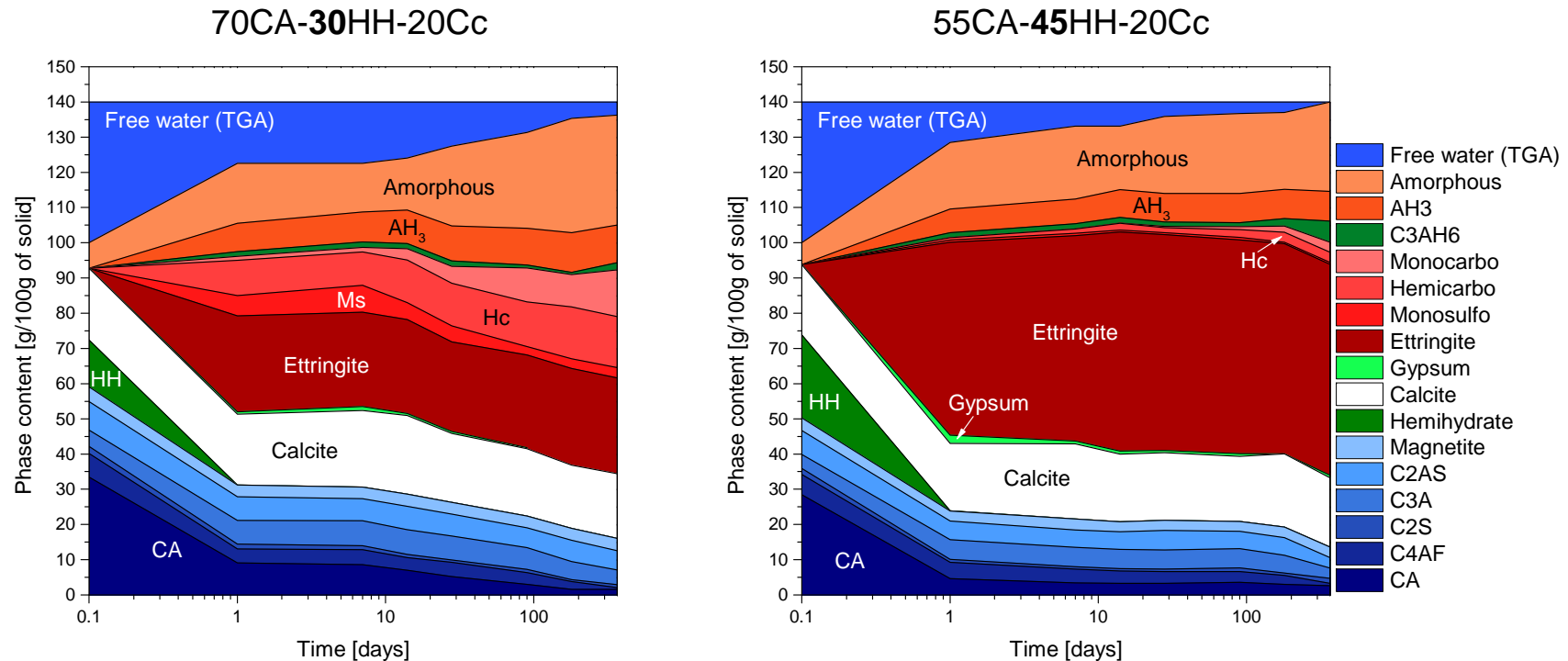
# Mechanical properties on mortars



- 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



- 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<sub>3</sub> (mainly amorphous)

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

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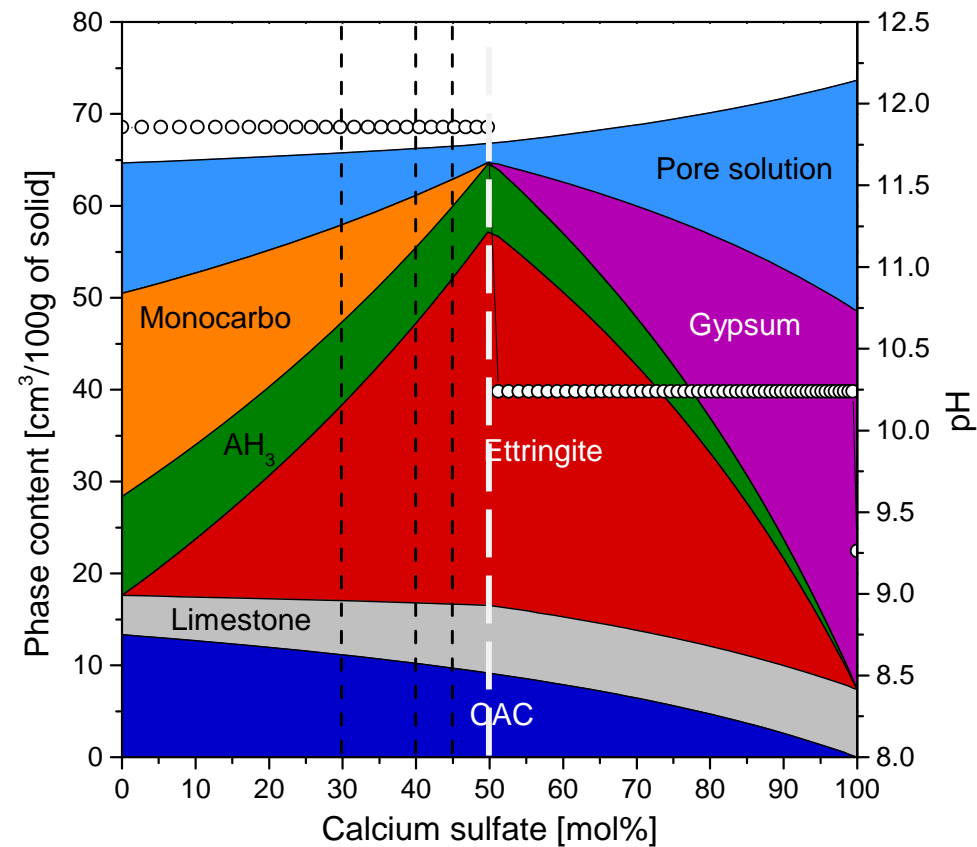
Simply use



<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

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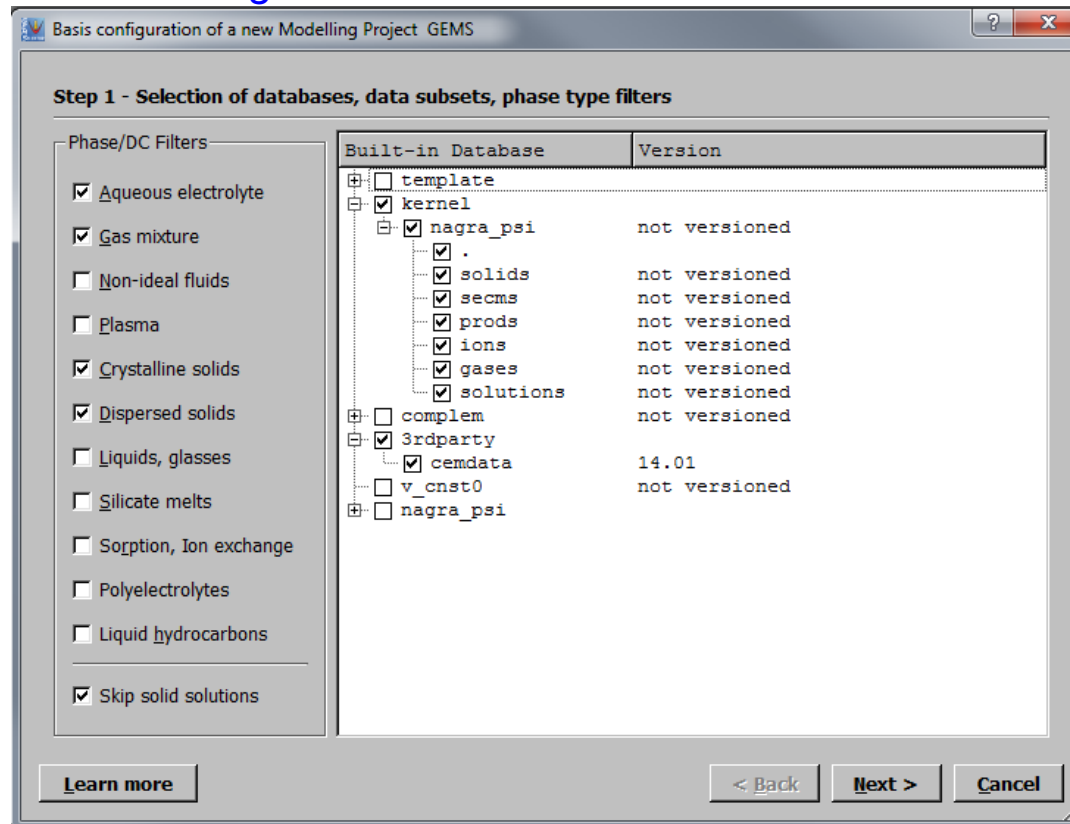
- Now we want to follow the hydrates evolution for variable amount of reacted limestone

IT's YOUR TURN!

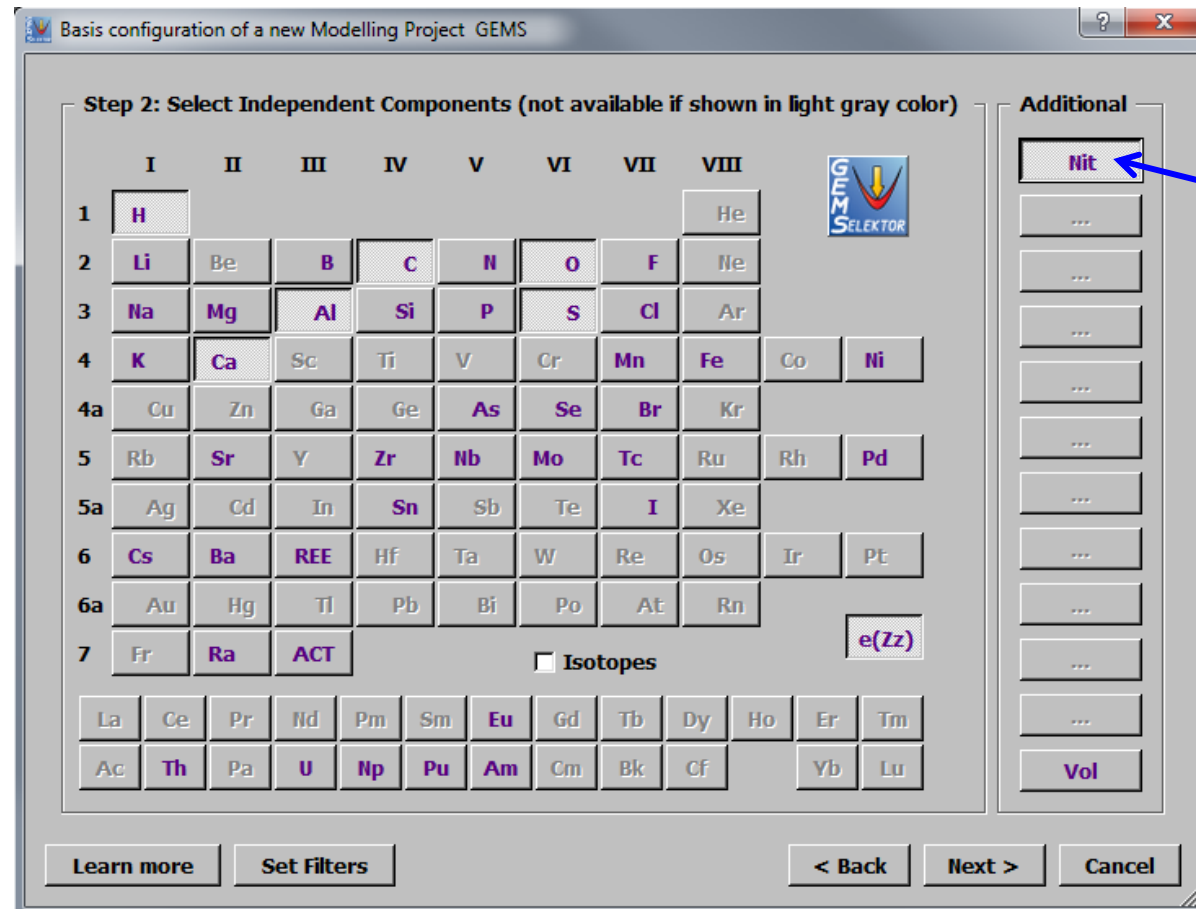


# Tutorial: CA-HH-Cc systems

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



# Select the elements



- 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:  $20^{\circ}C$

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 Recipe of Single Thermodynamic System: Tutorial:G:CA\_HH\_Cce:0:0:1:20:0:

tname |

Property	Selection	Recipe Input
Compos (xa_)	AirNit_22 CaSO4	1 xa_ AirNit_22 0.1 g
DComp (xd_)	Al(OH)3 CaSO4 0.5H2O	2 xa_ Aqua 40 g
IComp (bi_)	Al2O3 Gypsum	3 xa_ CA 31.67 g
Phase (xp_)	Aqua H2	4 xa_ CaCO3 3 g
Kin.lower (dll_)	AtmAirNit H2S	5 xa_ CaSO4 0.5H2O 13.33 g
Kin.upper (dul_)	C12A7 H2SO4	
G0 shift (gEx_)	C3A O2	
Other Inputs	C4A3s SO3	
	CA	
	CA2	
	CH4	
	CO2	
	Ca(OH)2	
	CaCO3	
	CaO	

Need excess water and air

# Input: System Definition



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

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

Modules Window Help

SingleSystem

Input: System Definition Results: Equilibrium State

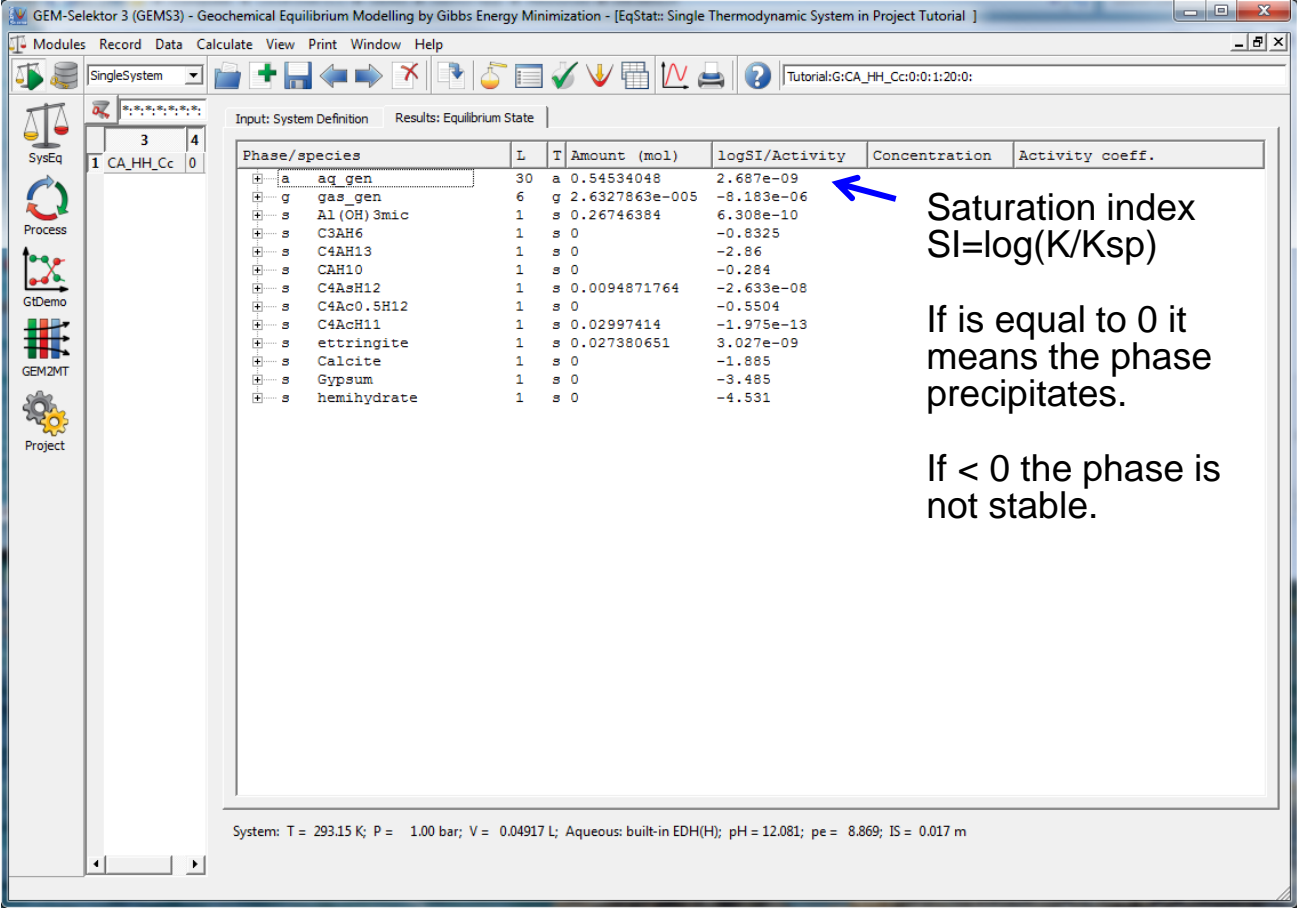
Phase/species	L	T	On/	UC	Add to BC	UG	G0 corr.	UK	Lower_KC	Upper_KC	KC type
aq_gen	30	a	+	g	0	J	0				
gas_gen	6	g	+	g	0	J	0				
Al(OH)3mic	1	s	+	g	0	J	0				
Gibbsite	1	s	-	g	0	J	0				
Graphite	1	s	-	g	0	J	0				
Mayenite	1	s	-	g	0	J	0				
Aluminate	1	s	-	g	0	J	0				
CA	1	s	-	g	0	J	0				
CA2	1	s	-	g	0	J	0				
C2AH75	1	s	-	g	0	J	0				
C3AH6	1	s	+	g	0	J	0				
C4AH13	1	s	+	g	0	J	0				
CAH10	1	s	+	g	0	J	0				
C4AsH12	1	s	+	g	0	J	0				
C4Ac0.5H12	1	s	+	g	0	J	0				
C4AcH11	1	s	+	g	0	J	0				
ettringite	1	s	+	g	0	J	0				
Aragonite	1	s	-	g	0	J	0				
Calcite	1	s	+	g	0	J	0				
lime	1	s	-	g	0	J	0				
Portlandite	1	s	-	g	0	J	0				
Anhydrite	1	s	-	g	0	J	0				
Gypsum	1	s	+	g	0	J	0				
hemihydrate	1	s	+	g	0	J	0				
Sulphur	1	s	-	g	0	J	0				

1 and 2

Start the calculations:

System: T = 293.15 K; P = 1.00 bar; V = 0.04917 L; Aqueous: built-in EDH(H); pH = 12.081; pe = 8.869; IS = 0.017 m

# Output: Equilibrium state



Input: System Definition    Results: Equilibrium State

Phase/species	L	T	Amount (mol)	logSI/Activity	Concentration	Activity coeff.
a aq_gen	30	a	0.54534048	2.687e-09		
g gas_gen	6	g	2.6327863e-005	-8.183e-06		
s Al(OH)3mic	1	s	0.26746384	6.308e-10		
s C3AH6	1	s	0	-0.8325		
s C4AH13	1	s	0	-2.86		
s CAH10	1	s	0	-0.284		
s C4AsH12	1	s	0.0094871764	-2.633e-08		
s C4AcO.5H12	1	s	0	-0.5504		
s C4AcH11	1	s	0.02997414	-1.975e-13		
s ettringite	1	s	0.027380651	3.027e-09		
s Calcite	1	s	0	-1.885		
s Gypsum	1	s	0	-3.485		
s hemihydrate	1	s	0	-4.531		

System: T = 293.15 K; P = 1.00 bar; V = 0.04917 L; Aqueous: built-in EDH(H); pH = 12.081; pe = 8.869; IS = 0.017 m

Saturation index  
 $SI = \log(K/K_{sp})$

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

GEM-Selektor 3 (GEMS3) - Geochemical Equilibrium Modelling by Gibbs Energy Minimization - [EqDemo :: Tutorial:G:CA\_HH\_Cc:0:0:1:20:0]

Modules Record Data Calculate View Print Window Help

EqDemo

Open EqDemo window (GEM task results)

EqIC EqPh EqDC EqSurf EqGen 09/04/2014, 10:16

	PHnam	Xa	Fa	phVol	phM
0	a aq_gen	0.54534048	2.6870826e-009	9.8376894	9.8266339
1	g gas_gen	2.6327863e-005	-8.1833175e-006	0.64171498	0.00075493826
2	s Al (OH) 3mic	0.26746384	6.30772e-010	8.5470747	20.86314
3	s C3AH6	0	-0.83249371	0	0
4	s C4AH13	0	-2.8604479	0	0
5	s CAH10	0	-0.2840289	0	0
6	s C4AsH12	0.0094871764	-2.6327565e-008	2.9318221	5.905954
7	s C4AcO.5H12	0	-0.55041475	0	0
8	s C4AcH11	0.02997414	-1.9749427e-013	7.8519661	17.038763
9	s ettringite	0.027380651	3.0271921e-009	19.358943	34.365753
10	s Calcite	0	-1.8850854	0	0
11	s Gypsum	0	-3.4846109	0	0
12	s hemihydrate	0	-4.5312367	0	0

pmXs 78.173611

	Al	C	Ca	H	Nit	O	S
0	0.40114778	0.02997414	0.32212917	3.4418765	0	2.9796248	0.00
1	1.9829761e-005	9.2039043e-010	5.7744385e-005	1.0904225	1.1468448e-005	0.54530361	6.03886e-006
2	0	0	0	0	4.3921194e-005	8.7345334e-006	0

	PHnam	L1	Aalp	Sigw	Sigg	Yof
0	a aq_gen	30	0	0	0	0
1	g gas gen	6	0	0	0	0

	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' calculation processes (e.g. mixing, dissolution).

The Process record can be configured by the 'P\_expr' and simulation output scale.

Any process simulator belongs to one of the following categories:

1. 'Sequential': only input GEM
2. 'Reciprocal': next step depends on the first
3. 'Inverse': GEM input adjusts to the process

Please, choose a process simulator:

- ☐ P Sequential temperature
- ☒ S Direct sequential change
- ☐ G Batch inverse titration
- ☐ T One arbitrary inverse titration
- ☐ R Sequential reactor scheme
- ☐ L Lippmann diagram (transformation)

[Learn more](#)

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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 diagram 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

The image shows two overlapping windows from the GEM-Selektor software. The background window is 'Step 4 - Important data object dimensions', and the foreground window is 'Step 3 - Selection of items to sample/plot'.

**Step 4 - Important data object dimensions**

Spin boxes below define the dynamic memory configuration of the process simulation:

- nPS - Number of steps (1 to 9999) to be performed in this simulation: 21
- Number of 'modC' array columns (1 to 40, 0 - not used) to store: 1
- Number of columns in the 'yp' table (0 to 200) to keep the simulation: 13
- Number of rows in the xEp, yEp arrays for experimental data (optional): 0
- Number of columns in the xEp, yEp arrays for experimental data (optional): 1

Optional data vectors (of length nPS) can be used for accumulating current process data allocated using checkboxes below. The assignment operator (with J index) in vector from the respective process iterator.

Allocation of optional data vectors:

- ☐ CSD variant # ('vTm')
- ☐ Temperature T ('vT')
- ☐ Process extent pXi ('vpXi')
- ☐ Volume V, l ('vV')
- ☐ Constraints # ('vNV')
- ☐ Kinetic parameters ('vKin')
- ☐ Time Tau ('vTau')

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

Property list:

- Scalars
- u
- ue
- b
- Cb
- m\_t
- lgm\_t
- icM
- Xa
- Xwa
- phVol
- phM
- Fa
- bXa(aq\_gen)
- bXa(gas\_gen)
- bXs
- L1
- Yof
- Aalp
- Sigw
- x
- Wxx
- my
- v
- vEx
- lga
- gamma
- InGam
- ...

Item Selection:

- aq\_gen
- gas\_gen
- Al(OH)3mic
- C3AH6
- C4AH13
- CAH10
- C4AsH12
- C4Ac0.5H12
- C4AcH11
- ettringite
- Calcite
- Gypsum
- hemihydrate

Sampling Script:

```

xp[J] = J;
yp[J][0] = pH;
yp[J][1] = phVol[{hemihydrate}];
yp[J][2] = phVol[{Gypsum}];
yp[J][3] = phVol[{Calcite}];
yp[J][4] = phVol[{ettringite}];
yp[J][5] = phVol[{C4AsH12}];
yp[J][6] = phVol[{Al(OH)3mic}];
yp[J][7] = phVol[{C4Ac0.5H12}];
yp[J][8] = phVol[{C4AcH11}];
yp[J][9] = phVol[{CAH10}];
yp[J][10] = phVol[{C3AH6}];
yp[J][11] = phVol[{C4AH13}];
yp[J][12] = phVol[{aq_gen}];
    
```

Learn more

< Back Next> Cancel

- Step 5: select only the first option (*Use 'P\_expr'*)



# Controls

- Modify the script according to this tutorial

Check the temperature

	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	0	1	0
2	1	0	0	0	0	0	0	0	0.05	0
cTm	1020	0	1	20	0	0	0	0	1	0

Define the modC vector

modC
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18

```
$ replacement of CAC-HH with 20%Cc
$ degree of hydration of CA=0.95, DH of HH=1.0
$ CA is 50% of CAC

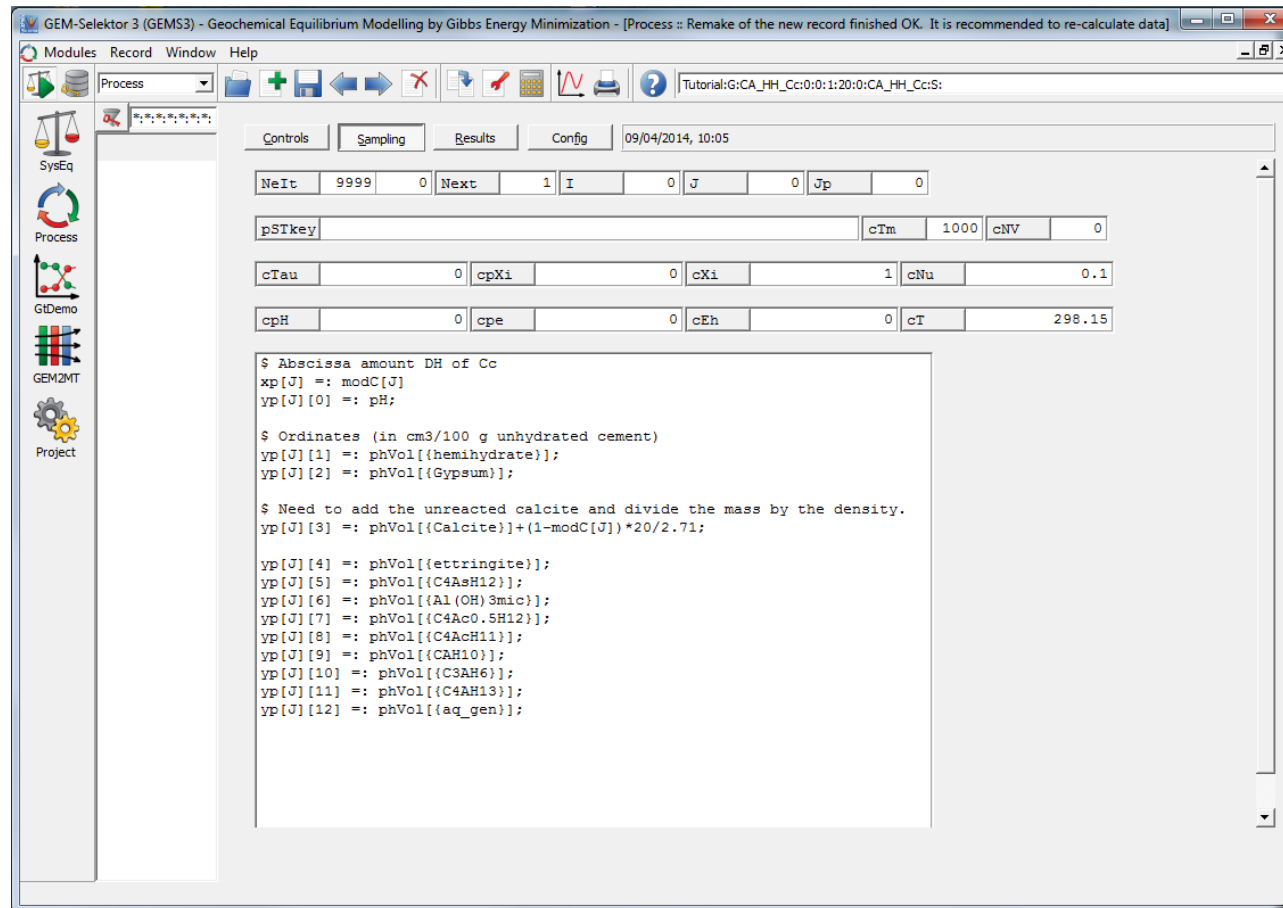
modC[J]=:cNu;
xa_[{CA}] =: (80-13.33)*.5*.95;
xa_[{CaSO4 0.5H2O}] =: 13.33 * 1;

$20% of the CA-HH is replaced by limestone DH=x variable
xa_[{CaCO3}] =: modC[J] * 20;
xa_[{Aqua}] =: 40;
```

cTC: Current temperature of interest TC (centigrade)

# Sampling

- Modify the script according to this tutorial



# Results

GEM-Selektor 3 (GEMS3) - Geochemical Equilibrium Modelling by Gibbs Energy Minimization - [Process :: Calculation finished OK (elapsed time: 1.89 s)]

Modules Record Window Help

Process

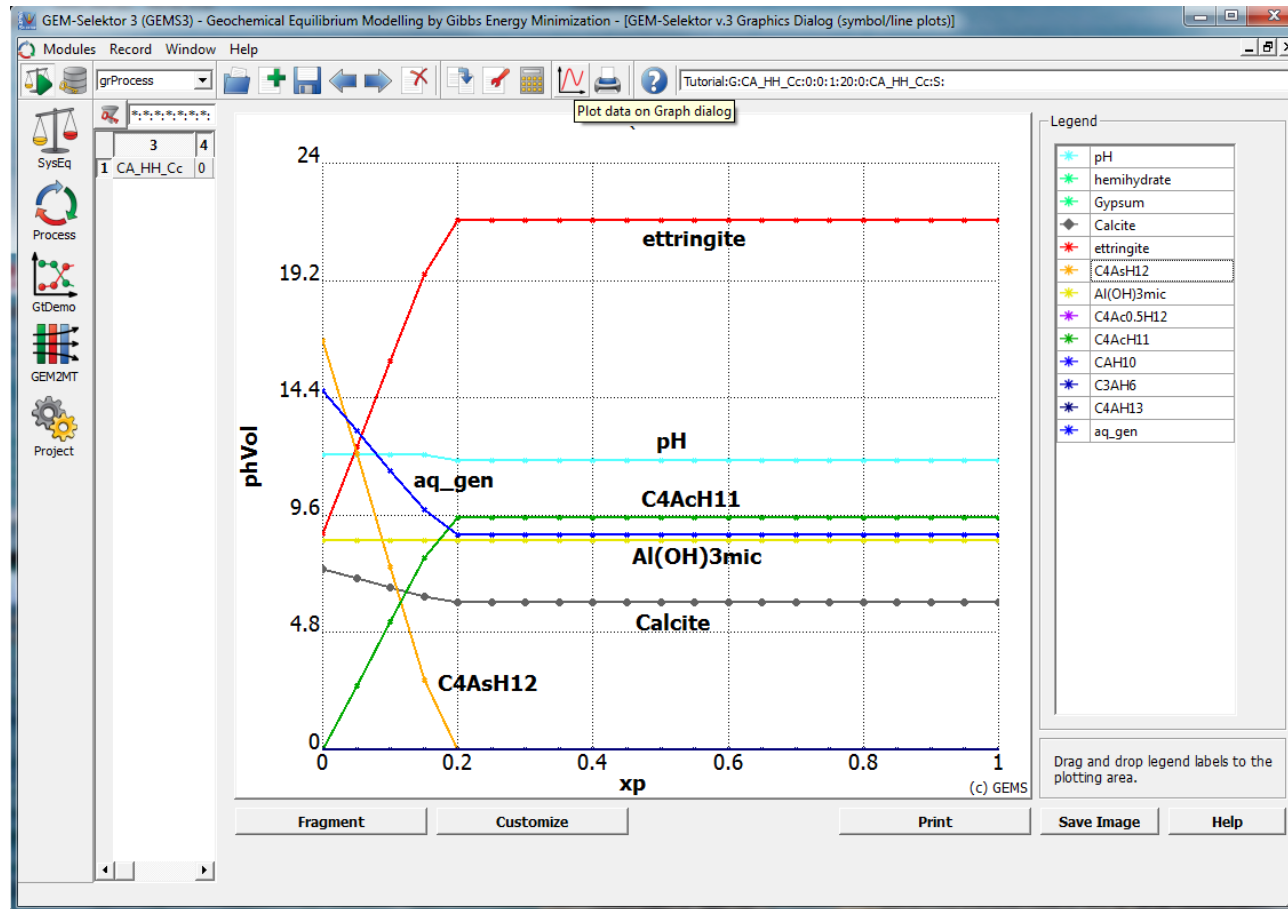
3 4  
1 CA\_HH\_Cc 0

Controls Sampling Results Config 09/04/2014, 11:25

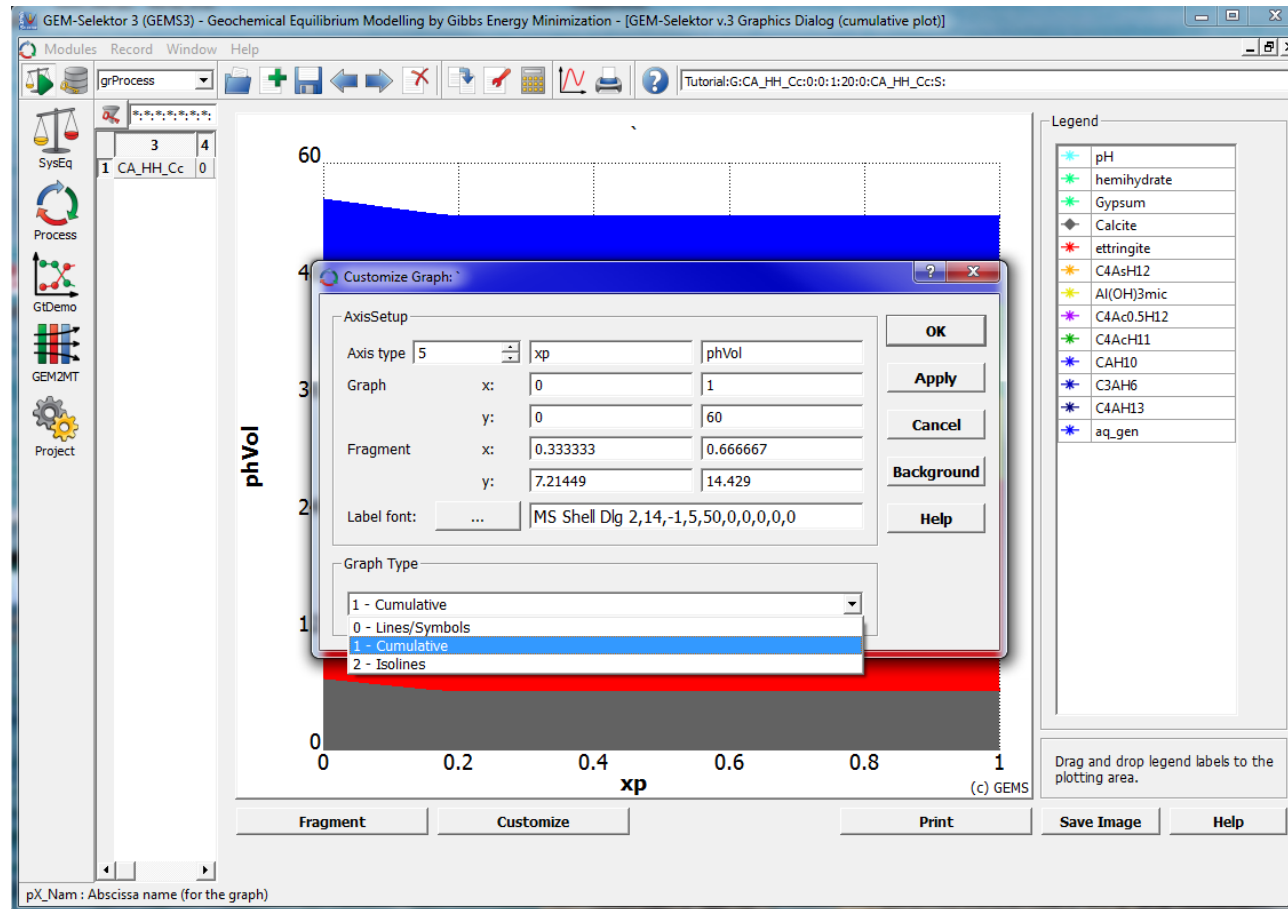
--- pY Nam phVol

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	

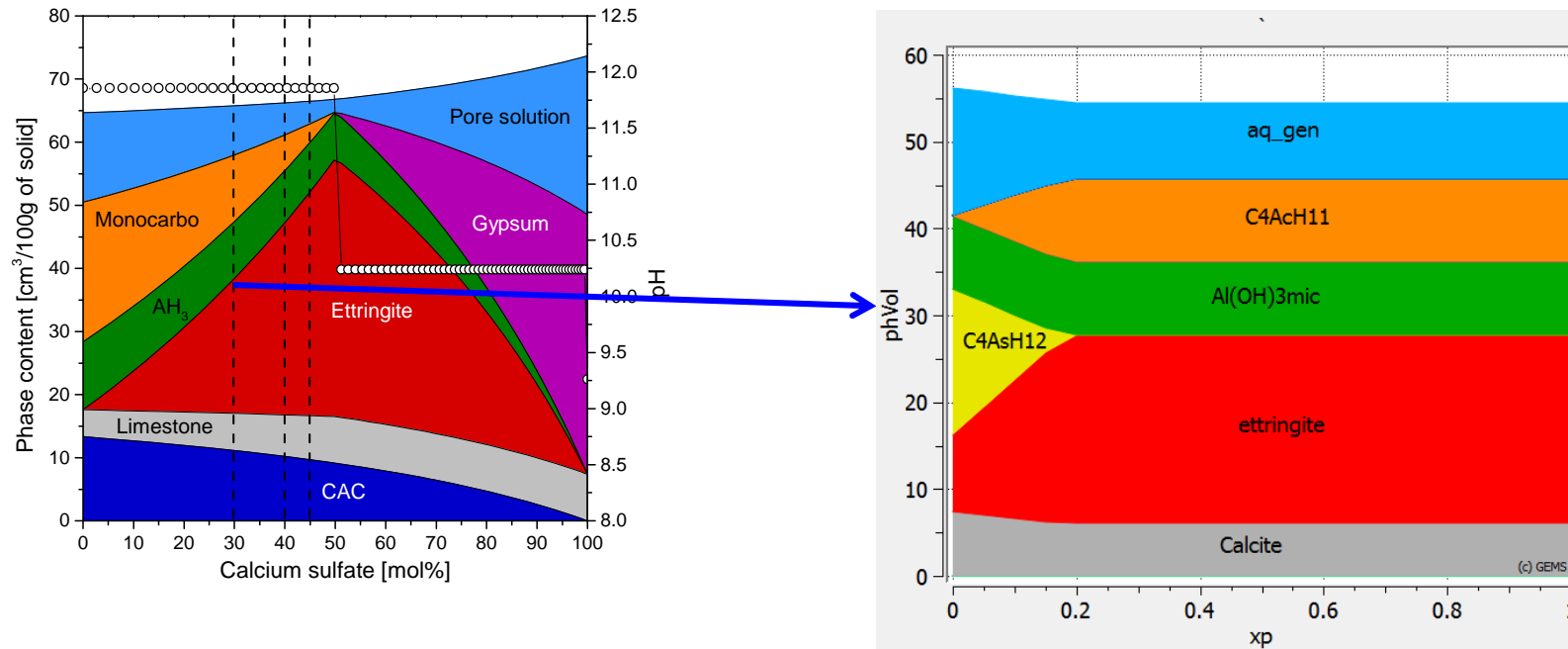
# Graph



# Graph



# Conclusions



- 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  $20\% \cdot 0.2 = 4\%$  in this system.