

Modelling of CaO , Al_2O_3 , CaSO_4 and CaCO_3 systems

Julien Bizzozero



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

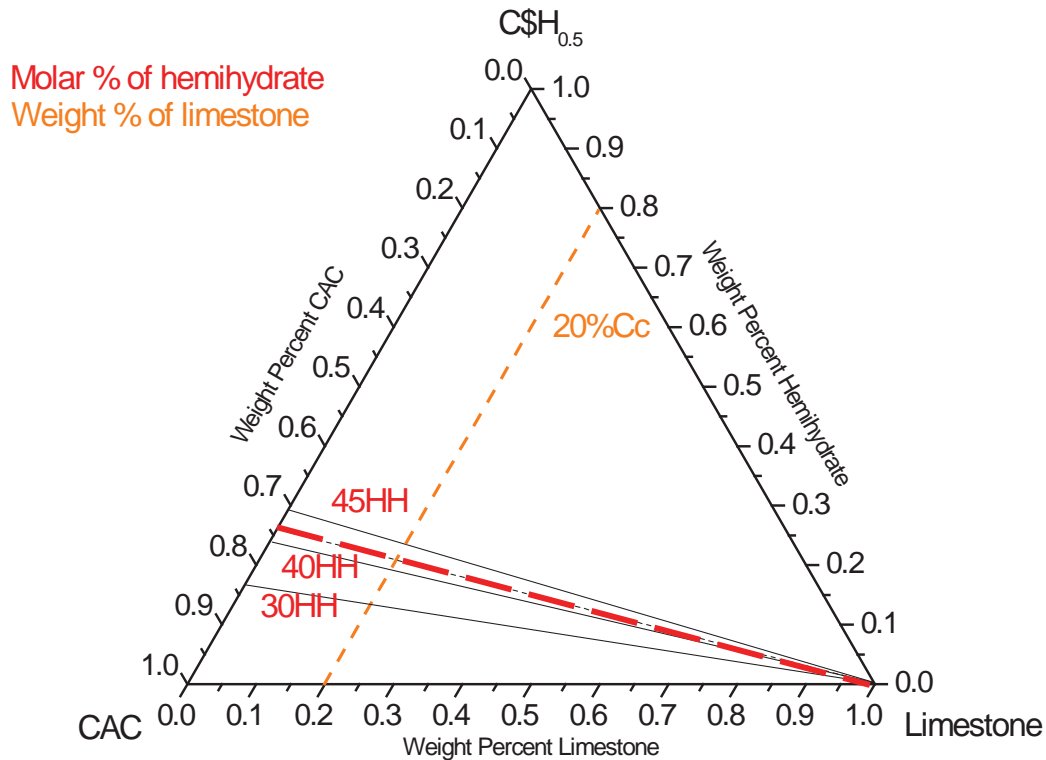
C\$H_x

Limestone

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

- Development of new binders
 - Reduction of the CO₂ emissions and energy consumption
 - Reduction of the price

Studied systems

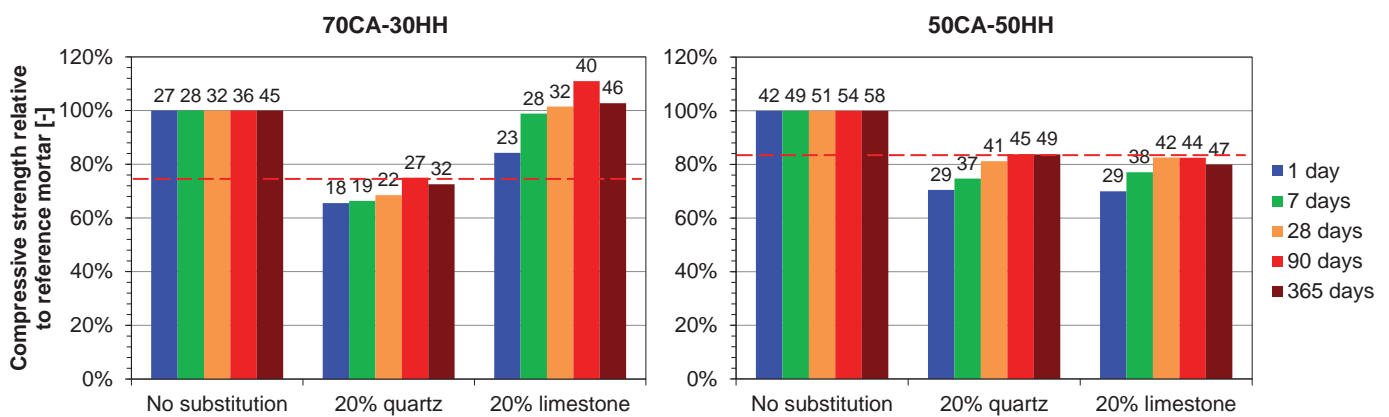


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Mechanical properties on mortars



- Limestone enhances the mechanical properties already after 1 day of hydration

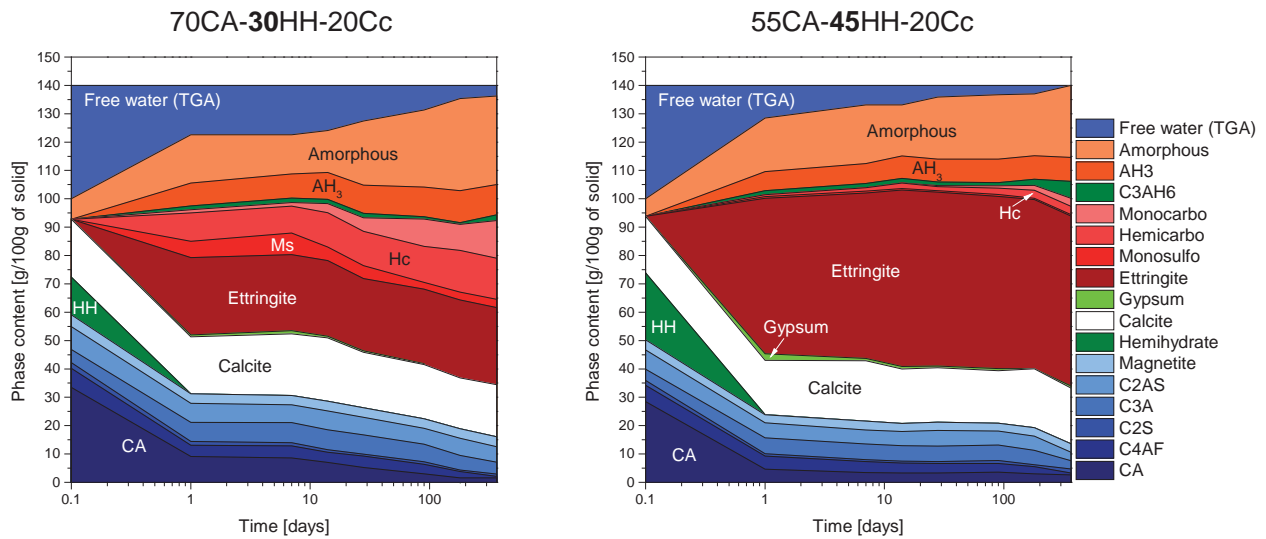
- Limestone seems to act as a filler in high sulfate systems

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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 AH₃ (mainly amorphous)

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

Simply use



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

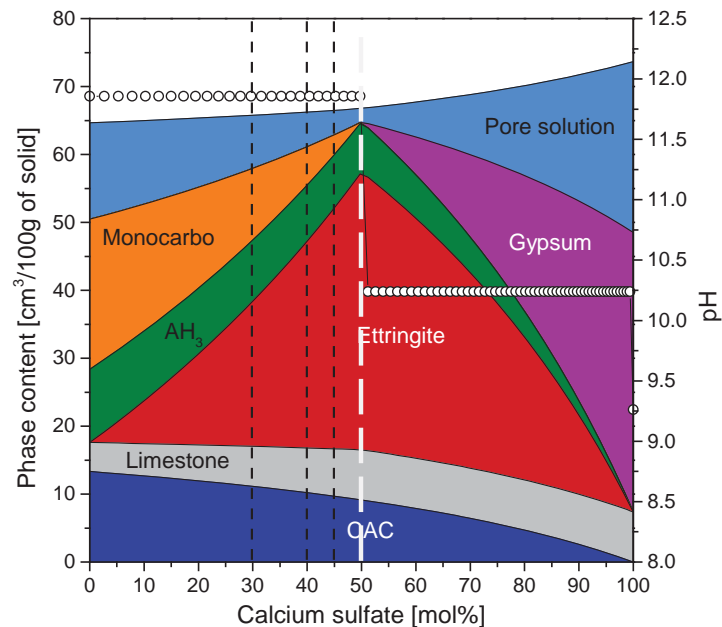
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GEMS simulation

- 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%



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GEMS simulation, variable limestone DH

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

IT's YOUR TURN!

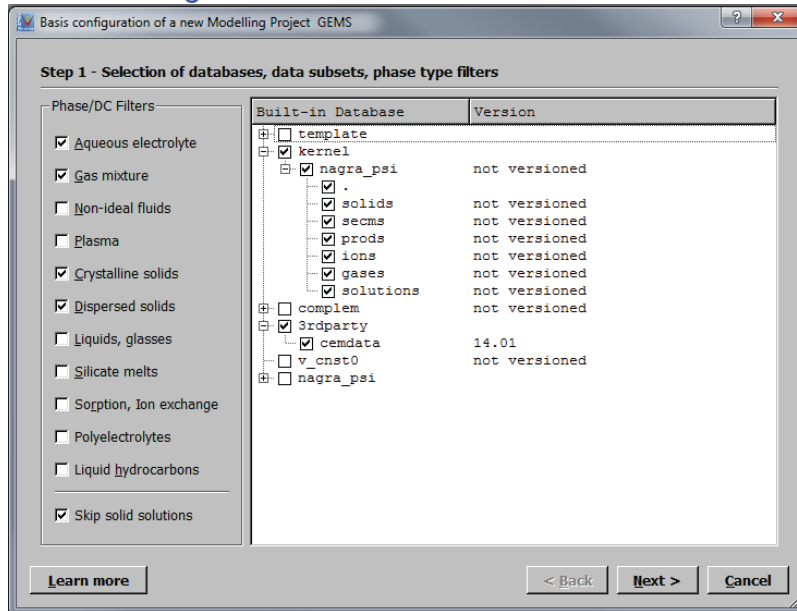
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Tutorial: CA-HH-Cc systems

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

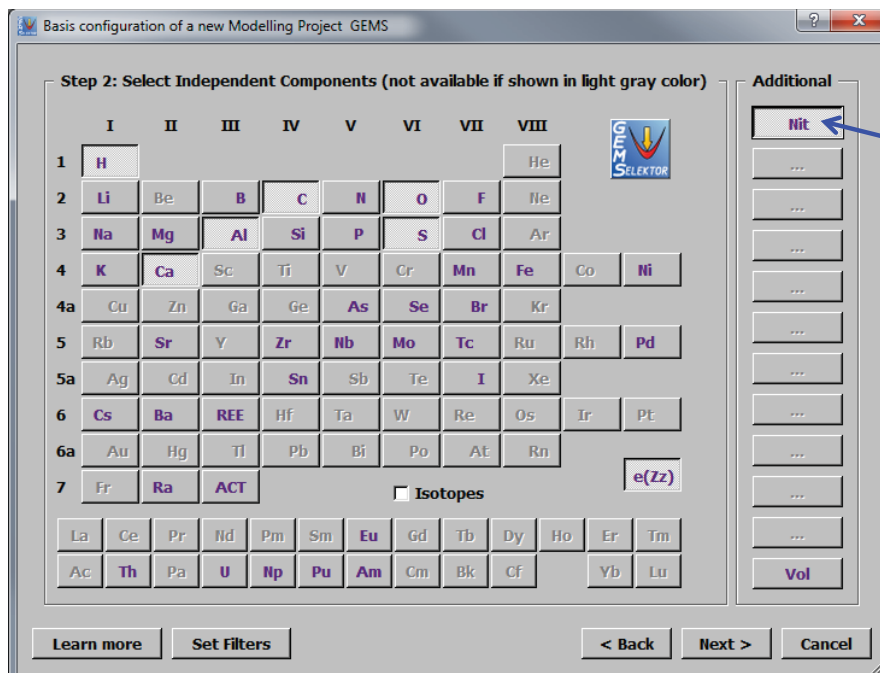


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Select the elements



Need air for volume variations

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

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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% $66.67\text{g} * 0.5 * 0.95 = 31.67\text{g}$
- DH of hemihydrate: 100% 23.6g
- DH of limestone: 15% $20\text{g} * 0.15 = 3\text{g}$

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4th



Input: System Definition

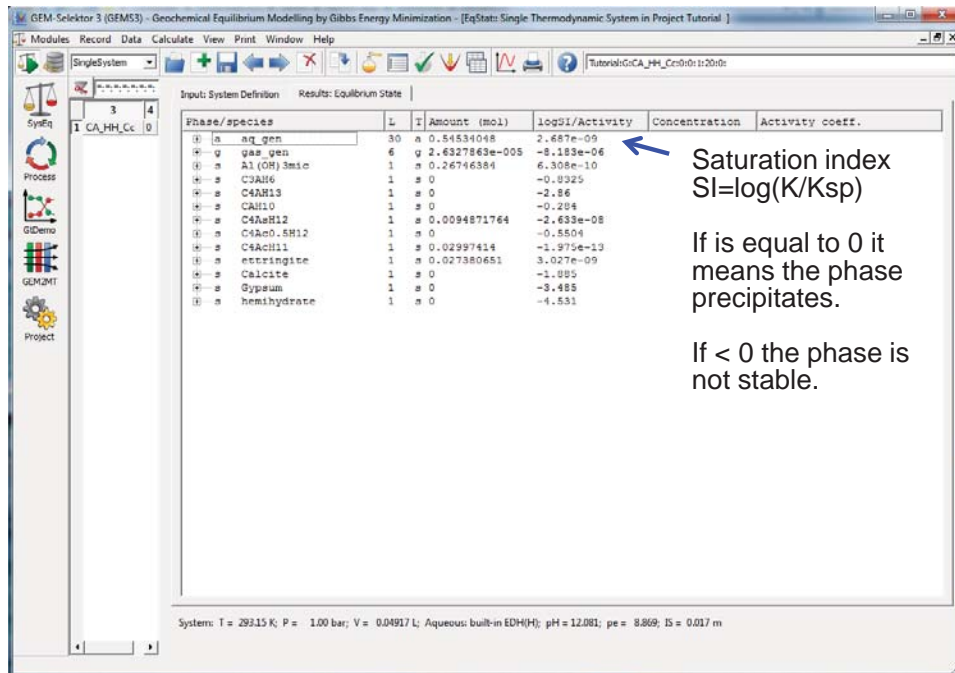


- Turn off the phases with —
- With the new database you don't need to create the CA phase!

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Output: Equilibrium state



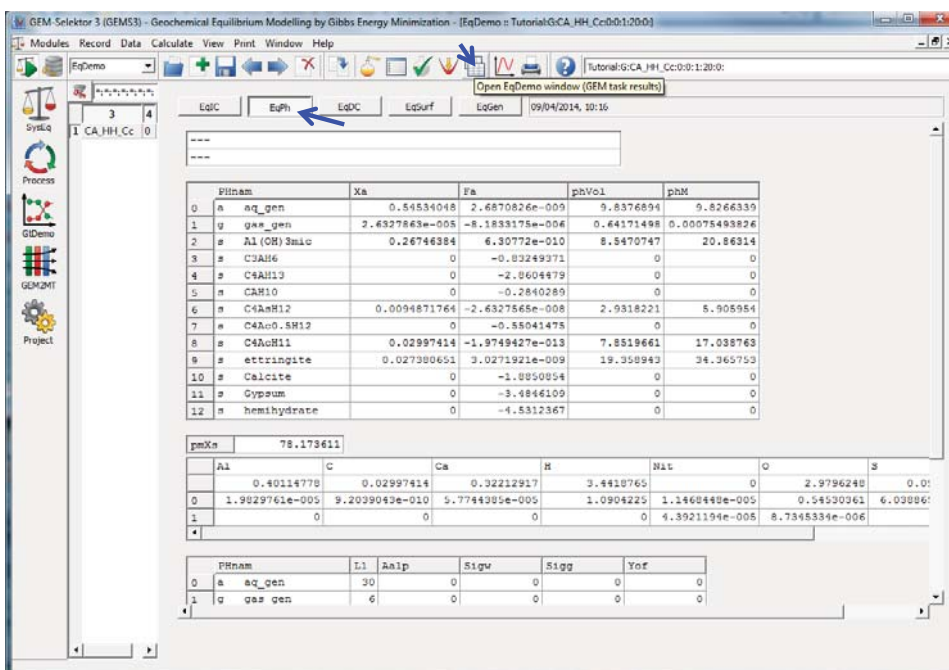
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EqDemo: EqPh

- 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%

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

GEM-Selektor Process Setup: TutorialG:CA_HH_Cc:0:1:20:0:CA_HH_Cc:0:S:

Step 1 - Process Simulator Configuration

This is a tool for 'batch' calculation of processes (e.g. mixing, dissolution). The Process record can be configured by 'P_expr' and simulation output settings.

Any process simulator belongs to one of the following categories:

- 'Sequential': only input GEM
- 'Reciprocal': next step depends on the previous one
- 'Inverse': GEM input adjusts to the process output

Please, choose a process simulator:

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

[Learn more](#)

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, (1) 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

- AirNit_22
- Al(OH)3
- Al2O3
- Aqua
- AtmAirNit
- C12A7
- C3A
- C4A3s
- CA
- CA2
- CH4
- CO2
- Ca(OH)2
- CaCO3
- CaO

DComp

- CaSO4
- CaSO4 0.5H2O
- Gypsum
- H2
- H2S
- H2SO4
- O2
- SO3

modC[] =: cNu;
 xa_[]([CA]) =: cNu * 1;
 xa_[]([CaSO4 0.5H2O]) =: cNu * 1;
 xa_[]([CaCO3]) =: cNu * 1;
 xa_[]([Aqua]) =: cNu * 1;

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GEM-Selektor Process Setup: TutorialG:CA_HH_Cc:0:1:20:0:CA_HH_Cc:0:S:

Step 4 - Important data object dimensions

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

Dimensions of sampled and experimental data

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

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

Allocation of optional data vectors

- ☐ CSD variant # ('VTm')
- ☐ Volume V, I ('Vv')
- ☐ Temperature T ('VT')
- ☐ Constraints # ('VNV')
- ☐ Process extent pXi ('VpXi')
- ☐ Kinetic parameters ('VKin')
- ☐ Time Tau ('vTau')

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Step 5 - Selection of items to sample/plot (click 'Next' without selecting anything to retain the old script)

Property

- Scalars
- u
- ue
- b
- Cb
- m_t
- Igm_t
- icM
- Xa
- Xwa
- phVol
- phM
- Fa
- bKa(aq_gen)
- bKa(gas_gen)
- bXs
- L1
- Yof
- Aalp
- Sigw
- x
- Wox
- my
- v
- vEx
- Iga
- 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;
yp[][] =: J;
yp[][] =: pH;
yp[][] =: phVol[(hemihydrate)];
yp[][] =: phVol[(Gypsum)];
yp[][] =: phVol[(Calcite)];
yp[][] =: phVol[(ettringite)];
yp[][] =: phVol[(C4AsH12)];
yp[][] =: phVol[(Al(OH)3mic)];
yp[][] =: phVol[(C4Ac0.5H12)];
yp[][] =: phVol[(C4AcH11)];
yp[][] =: phVol[(CAH10)];
yp[][] =: phVol[(C3AH6)];
yp[][] =: phVol[(C4AH13)];
yp[][] =: phVol[(aq_gen)];

```

Volumes of phases (in cm3) in equilibrium

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

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Controls

- Modify the script according to this tutorial

Check the temperature

Define the modC vector

	iTm	iV	iP	iTC	iTv	iTau	ipXi	ihu	ipH	ipe
0	1000	0	1	20	0	0	0	0	0	0
1	1001	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	0	1	0

modC

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

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Sampling

- Modify the script according to this tutorial

Check the temperature

Define the modC vector

	iTm	iV	iP	iTC	iTv	iTau	ipXi	ihu	ipH	ipe
0	1000	0	1	20	0	0	0	0	0	0
1	1001	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	0	1	0

modC

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

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Results

GEM-Seltor 3 (GEM53) - Geochemical Equilibrium Modelling by Gibbs Energy Minimization - [Process - Calculation finished OK (elapsed time: 1.89 s)]

Modules: Record Window Help

Process: Tutorial:G:\CA_HH_Cc\0:1:20:0:CA_HH_Cc:5

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

1 CA_HH_Cc 0

px Nam xp pH hemihydrate Gypsum Calcite ettringite C4AsH12

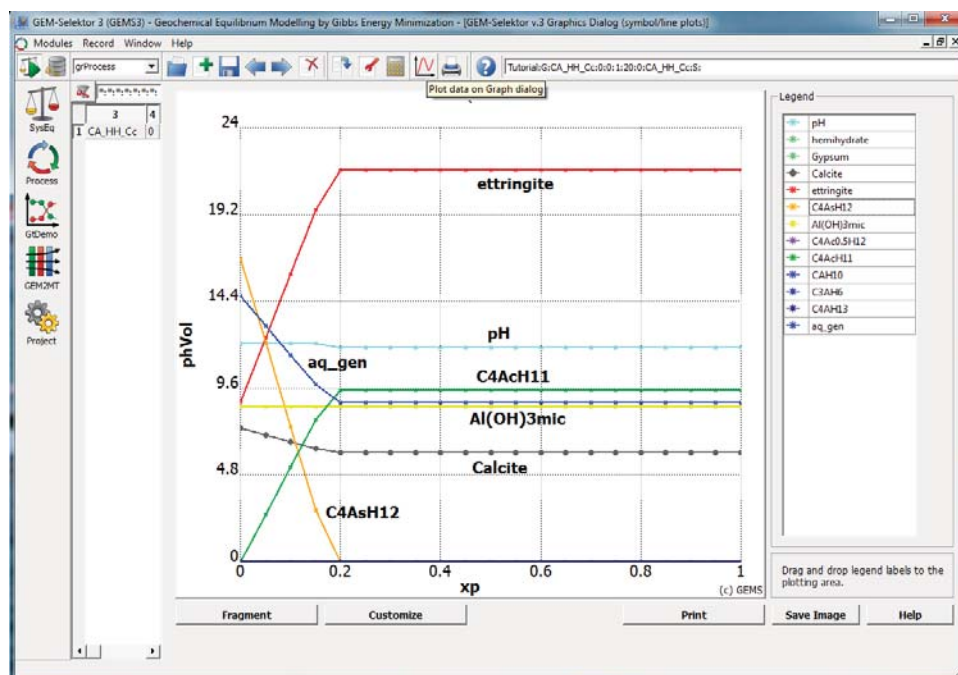
0		0	12.081103	0	0	7.3800738	8.062705	:
1		0.05	12.081103	0	0	7.0110701	12.392745	:
2		0.1	12.081103	0	0	6.6420664	15.924704	:
3		0.15	12.081102	0	0	6.2730627	19.455664	:
4		0.2	11.856744	0	0	6.0441457	21.643505	:
5		0.25	11.856742	0	0	6.0441609	21.643505	:
6		0.3	11.856743	0	0	6.0441762	21.643505	:
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	6.0443135	21.643505	:
16		0.8	11.856741	0	0	6.0443287	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	:

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Graph

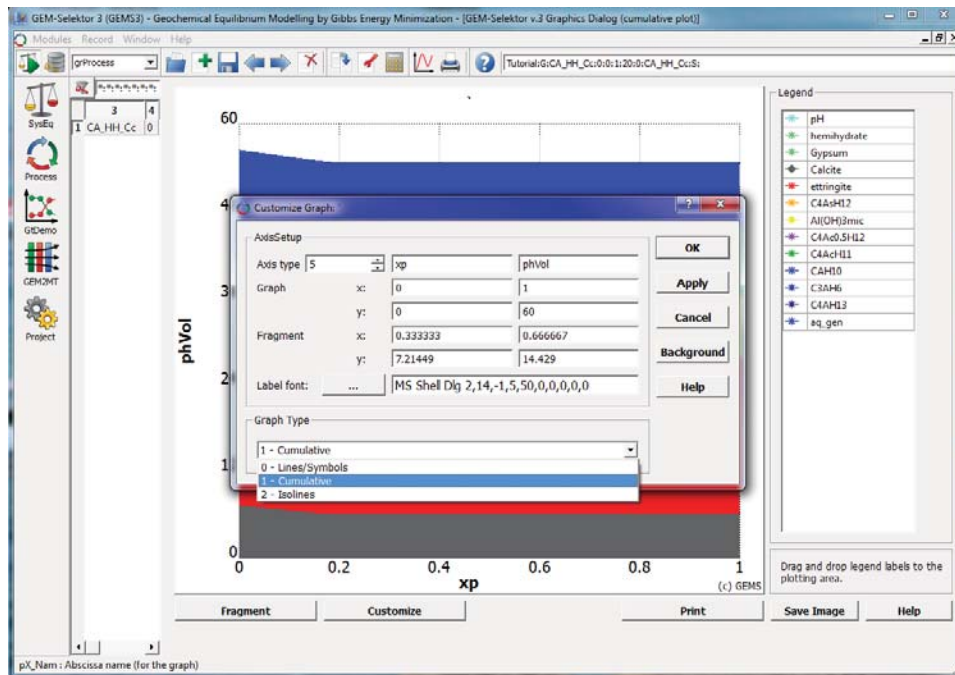


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Graph

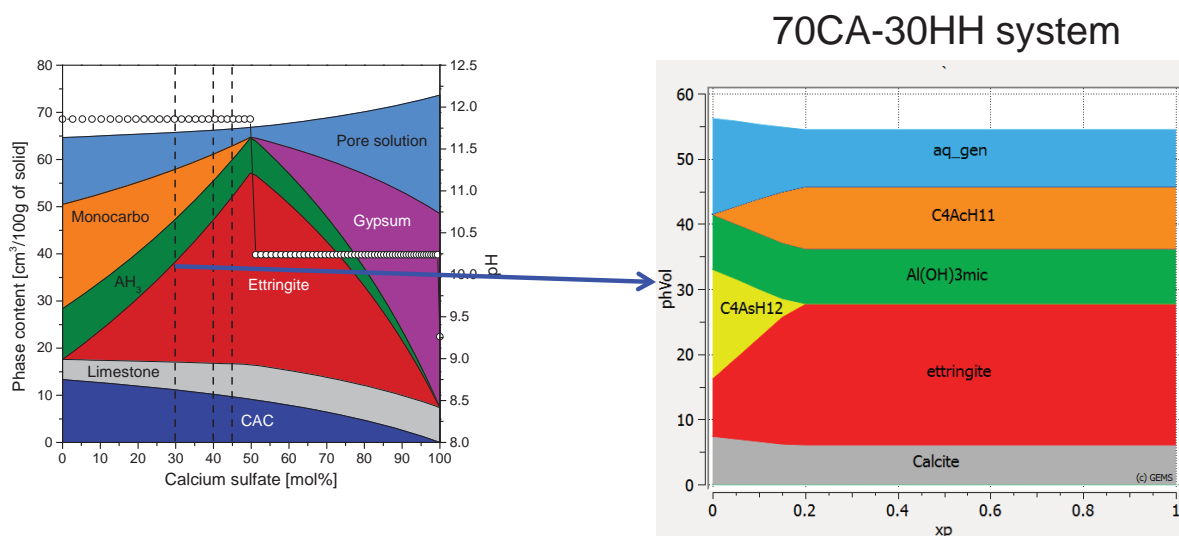


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Conclusions



- 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.

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