Oregon State University

NTNU – Trondheim
Norwegian University of Science and Technology

Empa
Materials Science and Technology

Lecture 02
Single system – hydration of C_3A

1) Simulation of reaction $C_3A + CaO + CaSO_4$
2) Simulation of reaction $C_3A + CaO + CaCO_3$
3) Simulation of reaction $C_3A + CaCO_3$
4) Simulation of reaction $C_3A + C + CaSO_4 + CaCO_3$

Ellina Bernard

GEMS SELEKTOR

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PAUL SCHERRER INSTITUT
PSI

Version GEMS 3.9.6 (June 2023)

First Tutorial – single systems: hydration of C_3A

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Hydration of C_3A ($Ca_3Al_2O_6$)*

1) Simulation of reaction $C_3A + CaO + CaSO_4$ — Guided tutorial

2) Simulation of reaction $C_3A + CaO + CaCO_3$

3) Simulation of reaction $C_3A + CaCO_3$

4) Simulation of reaction $C_3A + C + CaSO_4 + CaCO_3$

Individual work

See Seligmann & Greening ICCC 1969 and various papers by Kuzel et al. (Kuzel & Pöllmann CCR 1991, Kuzel et. al CCR 1996) for experimental verification

* cement notation

C => CaO	A => Al_2O_3
S => SiO_2	H => H_2O
s => SO_3	c=> CO_2

Hydration of C_3A + CaO + $CaSO_4$ – project setup

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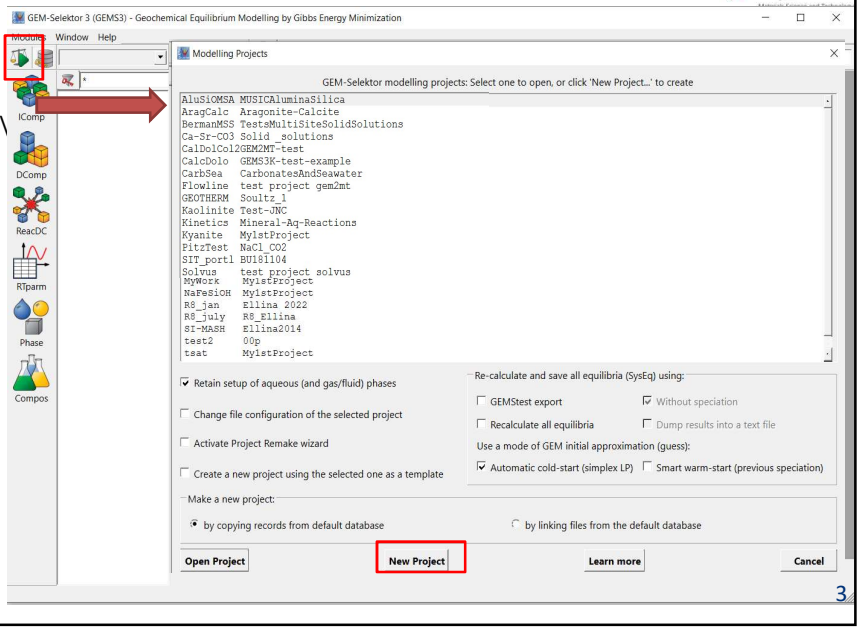

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Hydration of C_3A + CaO + $CaSO_4$ – project setup

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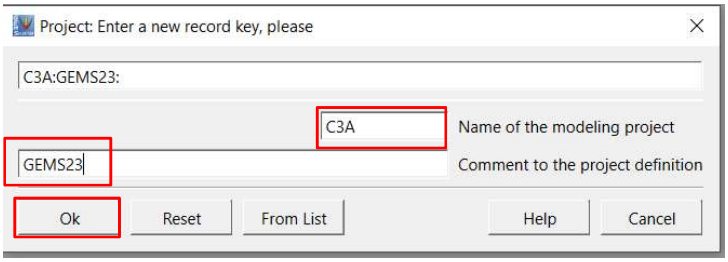

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Hydration of C_3A + CaO + $CaSO_4$ – project setup

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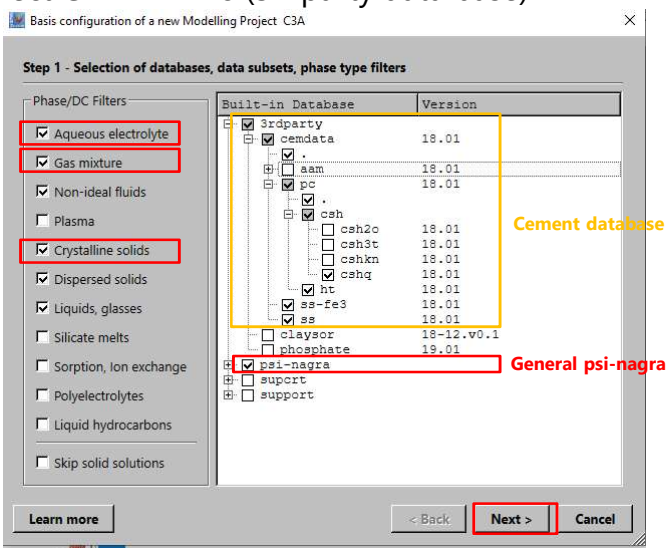
Select CEMDATA18 (3rd party data base)



Recommended selection for PC and blended cements

Hydration of C_3A + CaO + $CaSO_4$ – project setup

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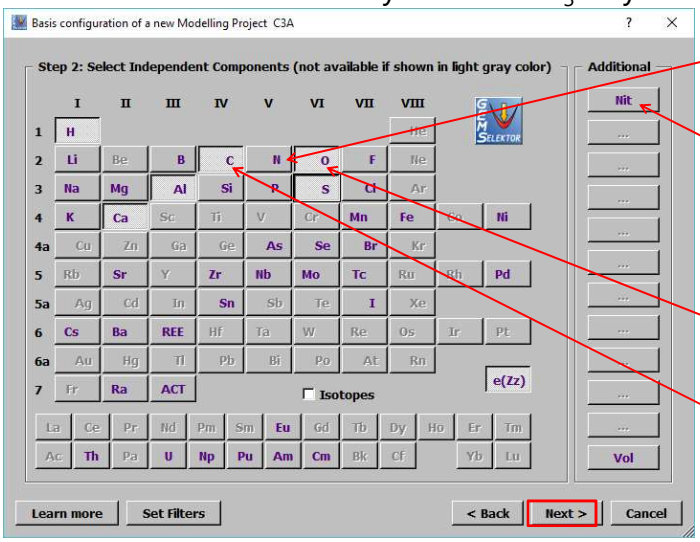
Select elements necessary to model C_3A hydration



„reactive N“ (don‘t use here)

Air: O_2, N_2, etc. (no reducing conditions, N_2 not reactive)

we can also use just oxygen (O_2)

needed for parts 2+3 of the tutorial

Hydration of C_3A + CaO + $CaSO_4$ – project setup

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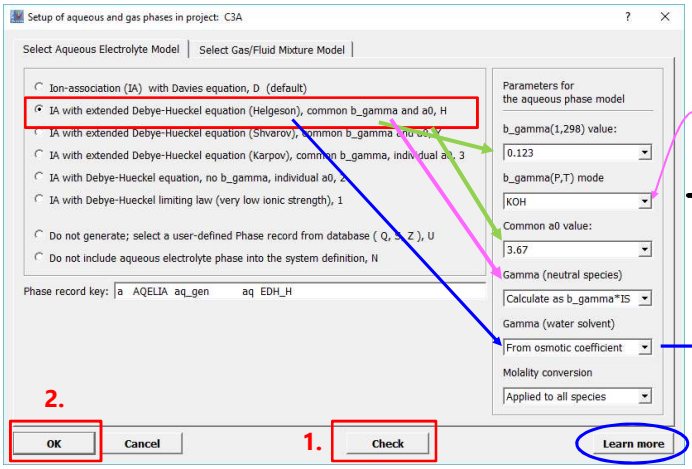
Select model for calculation of the aqueous phase



1) KOH good for cements
2) f(pressure, temp) -> electrolyte

a0=3.67 for KOH
b0= 0.123

Calculates activity of water

More details

Activity coefficients

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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

Hydration of C_3A + CaO + $CaSO_4$ – project setup

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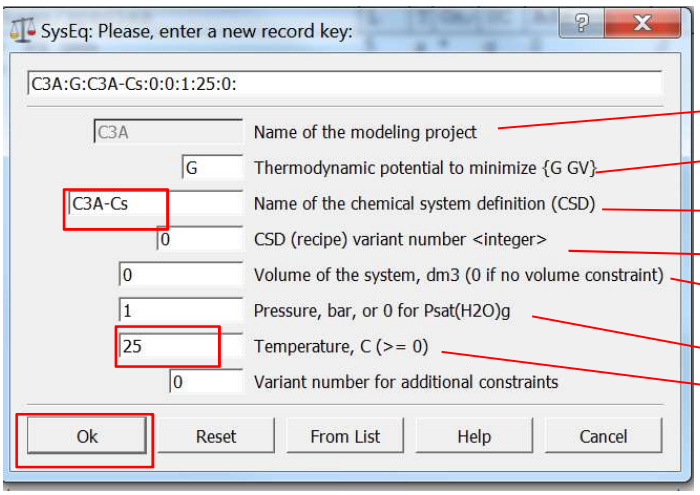

Project name

Method (Gibbs free energy minimization)

System definition

Integer (default 0)

System volume unconstrained

Pressure (bar)

Temperature (°C)

Avoid special signs such as $ & % ä ö ü æ å ø 好 ...

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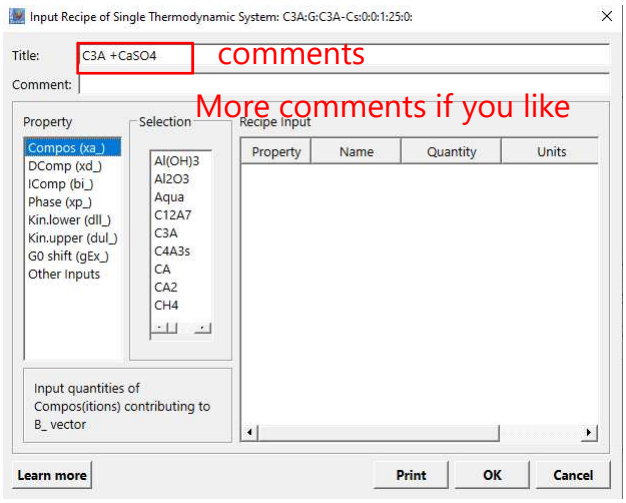
Hydration of C_3A + CaO + $CaSO_4$ – system creation (recipe)

We need a receipe



Hydration of C_3A + CaO + $CaSO_4$ – system creation (recipe)

1 Reaction of C_3A with calcium sulfate

5 g C_3A + 2.52 g $CaSO_4$ + 2.5 g CaO + 50 g H_2O

+ 0.1 g O_2 (oxidizing conditions, CO_2-free = no carbonation)

molar ratio SO_3/Al_2O_3 = 1, molar ratio CO_2/Al_2O_3 = 0

Reaction products?

Expectation: monosulfate
$Ca_4Al_2O_6SO_4$ $12H_2O$
No ettringite
$Ca_6Al_2O_8S_3O_{12}$ $32H_2O$

> Recipe >

> Equilibrium speciation

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Hydration of C_3A + CaO + $CaSO_4$ – system creation (recipe)

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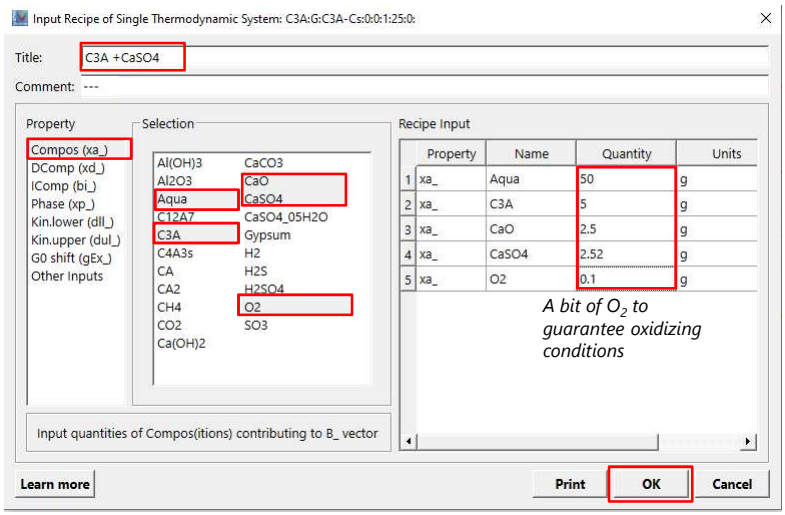

Hydration of C_3A + CaO + $CaSO_4$ – system creation (recipe)

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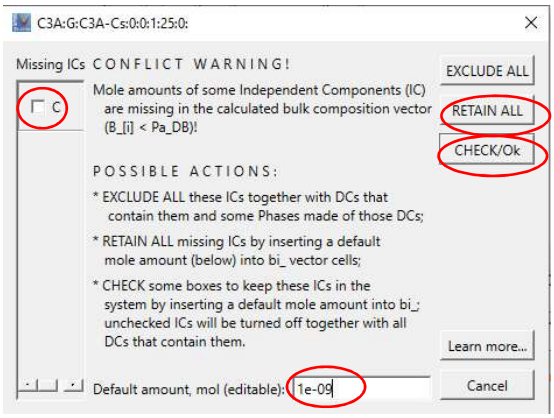
Check system definition



we keep carbonate in this example

=> adds a very small amount of C (10^{-9} M), has a negligible effect

GEMS interface

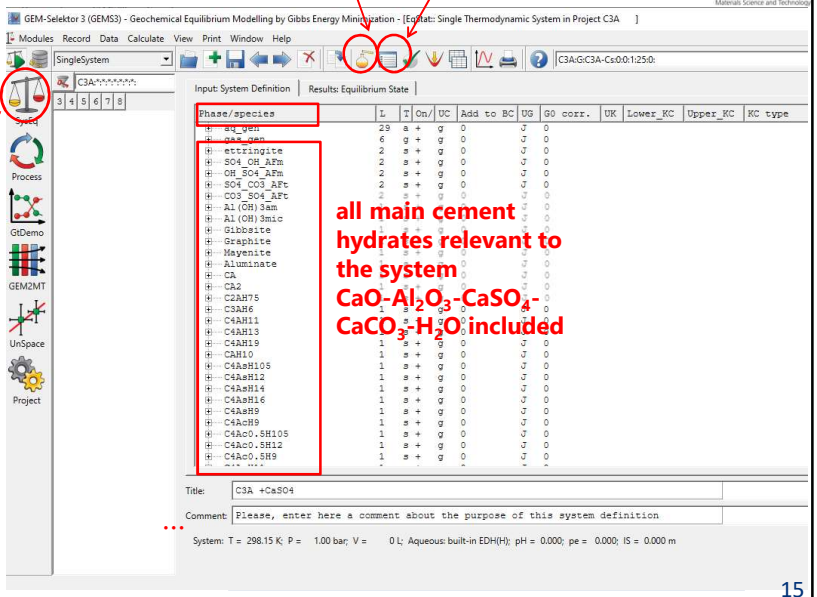
2 equivalent input options

Recipe wizard (previous page)

Detailed input recipe

Brings you always back to this screen

all main cement hydrates relevant to the system CaO-Al_2O_3-$CaSO_4$-$CaCO_3$-H_2O included



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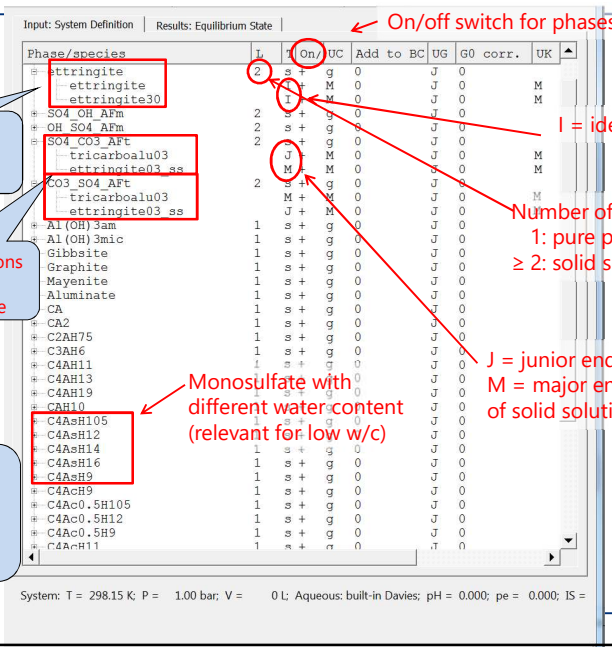
Hydration of C_3A + CaO + $CaSO_4$ – system creation (input)



SO_4-AFt solid solution 30-32 H_2O

2 AFt solid solutions containing sulfate+carbonate

SO_4-AFt with less water (metaettringite; for low water content

I = ideal solid solution

Number of components
1: pure phase
≥ 2: solid solutions

J = junior end-member
M = major end-member
of solid solution

Monosulfate with different water content (relevant for low w/c)

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Hydration of C_3A + CaO + $CaSO_4$ – system creation (recipe)

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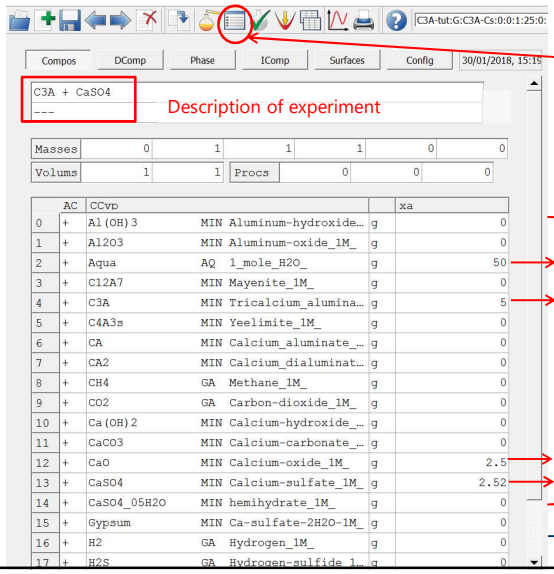
Experimental conditions: React 5 g C_3A, 2.52 g $CaSO_4$ and 2.5 g CaO with 50 g water (add 1 g O_2 to simulate gas phase)



	AC	CCvp			xa
0	+	Al(OH)3	MIN	Aluminum-hydroxide… g	0
1	+	Al2O3	MIN	Aluminum-oxide_1M_ g	0
2	+	Aqua	AQ	1_mole_H2O_ g	50
3	+	C12A7	MIN	Mayenite_1M_ g	0
4	+	C3A	MIN	Tricalcium_alumina… g	5
5	+	C4A3s	MIN	Yeelimite_1M_ g	0
6	+	CA	MIN	Calcium_aluminate_… g	0
7	+	CA2	MIN	Calcium_dialuminat… g	0
8	+	CH4	GA	Methane_1M_ g	0
9	+	CO2	GA	Carbon-dioxide_1M_ g	0
10	+	Ca(OH)2	MIN	Calcium-hydroxide_… g	0
11	+	CaCO3	MIN	Calcium-carbonate_… g	0
12	+	CaO	MIN	Calcium-oxide_1M_ g	2.5
13	+	CaSO4	MIN	Calcium-sulfate_1M_ g	2.52
14	+	CaSO4_05H2O	MIN	hemihydrate_1M_ g	0
15	+	Gypsum	MIN	Ca-sulfate-2H2O-1M_ g	0
16	+	H2	GA	Hydrogen_1M_ g	0
17	+	H2S	GA	Hydrogen-sulfide_1… g	0

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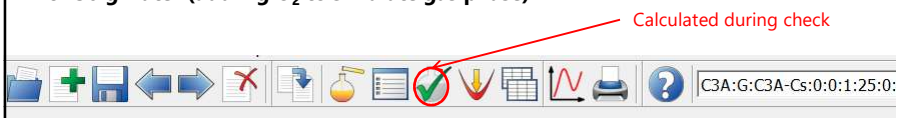
Hydration of C_3A + CaO + $CaSO_4$ – system creation (recipe)

Empa

Experimental conditions: React 5 g C_3A, 2.52 g $CaSO_4$ and 2.5 g CaO with 50 g water (add 1 g O_2 to simulate gas phase)



	IC	ICvp			B		bi
0	+	Al	e	Aluminum_	0.037010516	M	0
1	+	C	e	Carbon_	1e-009	M	1e-009
2	+	Ca	e	Calcium_	0.11860702	M	0
3	+	H	h	Hydrogen_	5.5508373	M	0
4	+	O	o	Oxygen_	3.0113217	M	
5	+	S	e	Sulfur_	0.018510003	M	
6	+	Zz	z	Electric_cha…	0	M	0

$Al/SO_3 = 2$
$A/S = Al_2O_3/SO_3 = 1$

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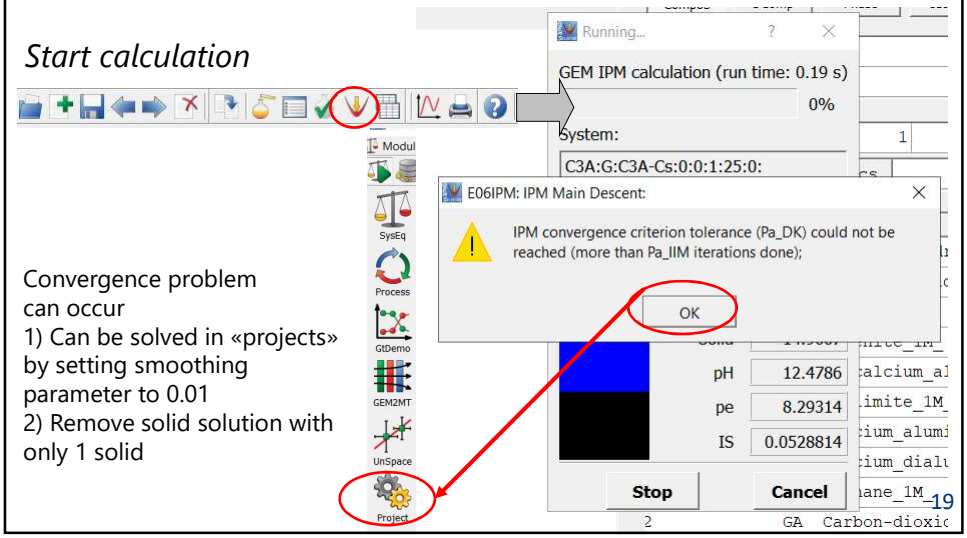
Hydration of C_3A + CaO + $CaSO_4$ – calculation of equilibrium

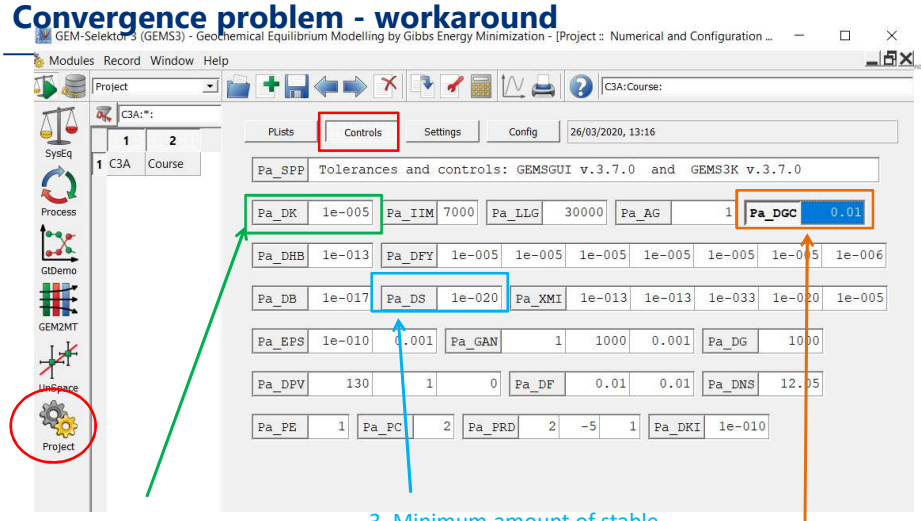
Experimental conditions: **React 5 g C_3A, 2.52 g $CaSO_4$ and 2.5 g CaO with 50 g water (add 1 g O_2 to simulate gas phase)**

Start calculation



Convergence problem can occur
1) Can be solved in «projects» by setting smoothing parameter to 0.01
2) Remove solid solution with only 1 solid

Convergence problem - workaround



2. Covergence tolerance parameter:
use higher value, e.g. 1e-004,
maximum seems to be 5e-003

3. Minimum amount of stable phases:
use lower value, e.g. 1e-023

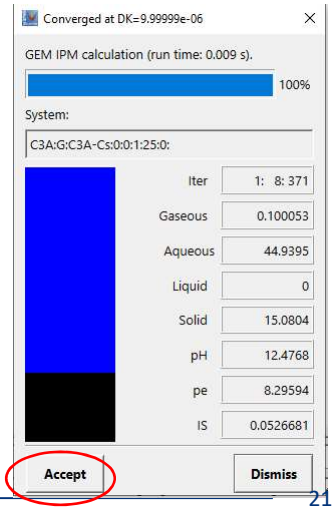
1. Smoothing parameter:
use low positive value, e.g. 0.01
=> 0.01 works

Do not touch the other ~~values~~ !!!

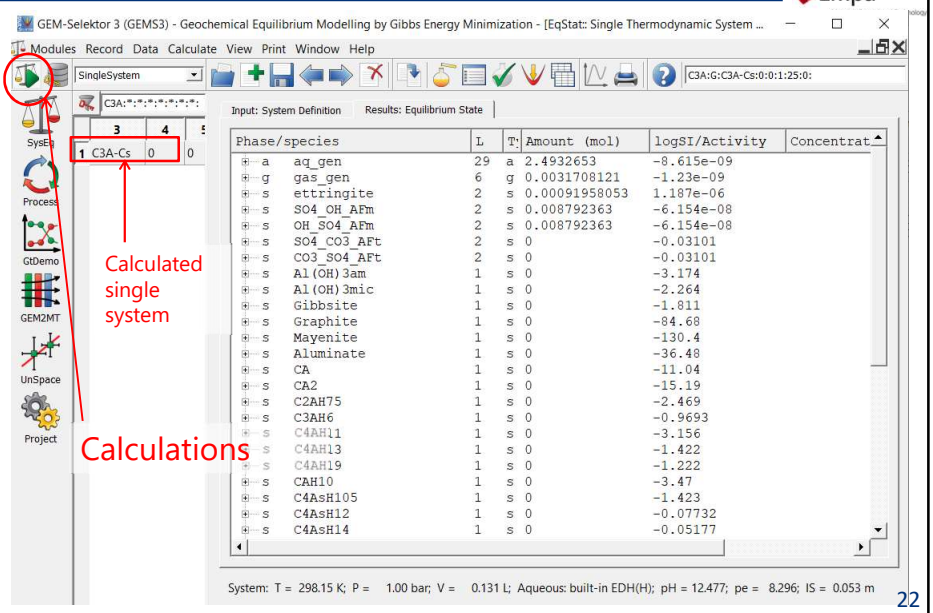
Hydration of C_3A + CaO + $CaSO_4$ – calculation of equilibrium

Experimental conditions: React 5 g C_3A, 2.52 g $CaSO_4$ and 2.5 g CaO with 50 g water (add 1 g O_2 to simulate gas phase)

Start calculation



Hydration of C_3A + CaO + $CaSO_4$ – results



Hydration of C_3A + CaO + $CaSO_4$ – results

Name of single system

2.5 mol aqueous phase (water + dissolved ions)

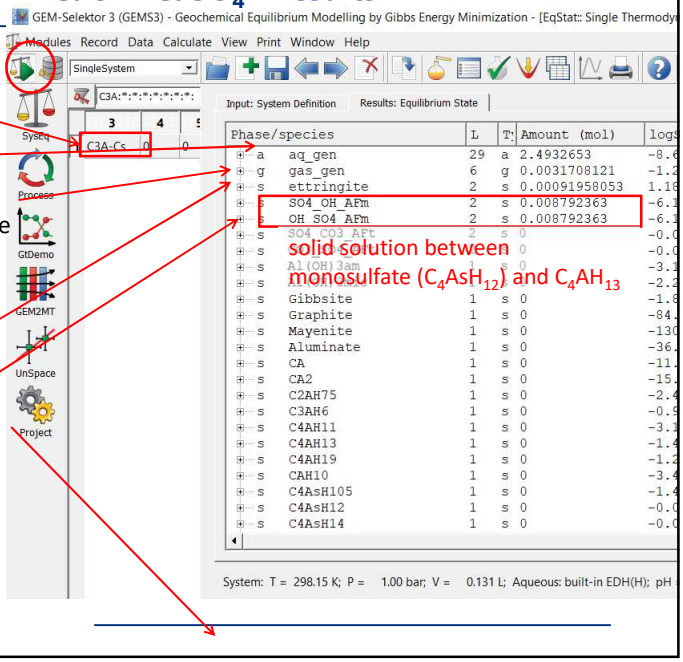
0.0032 mol gaseous phase

Solid products:

0.0009 mol ettringite

0.0176 mol monosulfate

0.0418 mol portlandite



solid solution between monosulfate (C_4AsH_{12}) and C_4AH_{13}

Hydration of C_3A + CaO + $CaSO_4$ – results

Solid solutions

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Phase/species	L	T	Amount (mol)	logSI/Activity	Concentration	Activity coeff.
a aq_gen	29	a	2.49326	-3.448e-09		
g gas_gen	6	g	0.003171698	-1.957e-09		
s ettringite	2	s	0.0009199661	4.729e-07		
ettringite		I	0.0007356808	0.799683	0.7996826	1
ettringite30		I	0.0001842852	0.200318	0.2003174	1
s SO4_OH_AFm	2	s	0.00879217	-2.421e-08		
C4AH13		J	0.0009172862	0.037881	0.1043299	0.3630883
monosulphate12		M	0.007874883	0.836829	0.8956701	0.9343053
s OH_SO4_AFm	2	s	0.00879217	-2.421e-08		
C4AH13		M	0.0009172862	0.037881	0.1043299	0.3630883
monosulphate12		J	0.007874883	0.836829	0.8956701	0.9343053
s SO4_CO3_AFt	2	s	0	-0.031		
tricarboalu03		J	0	0.00247516	0	1
ettringite03_ss		M	0	0.92992	0	1
s CO3_SO4_AFt	2	s	0	-0.031		
tricarboalu03		M	0	0.00247516	0	1
ettringite03_ss		J	0	0.92992	0	1
s Al(OH)3am	1	s	0	-3.174		
s Al(OH)3mic	1	s	0	-2.264		
s Gibbsite	1	s	0	-1.811		

ideal solid solution:

80 mol-% ettringite-32H_2O
20 mol-% ettringite-30 H_2O

Non ideal solid solution:
10 mol-% C_4AH_{13}
90 mol-% C_4AsH_{12}

Incomplete solid solution (hardly any CO_3 endmember; normally not stable, can be deactivated:

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Hydration of C_3A + CaO + $CaSO_4$ – system creation (recipe)

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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
ettringite	2	s	+	g	0	J	0				
SO4_OH_AFm	2	s	+	g	0	J	0				
OH_SO4_AFm	2	s	+	g	0	J	0				
SO4_CO3_AFt	2	s	-	g	0	J	0				
tricarboalu03		J	-	M	0	J	0	M	0	1000000	B
ettringite03_ss		M	-	M	0	J	0	M	0	1000000	B
CO3_SO4_AFt	2	s	-	g	0	J	0				
tricarboalu03		M	-	M	0	J	0	M	0	1000000	B
ettringite03_ss		J	-	M	0	J	0	M	0	1000000	B
Al(OH)3am	1	s	+	g	0	J	0				
Al(OH)3mic	1	s	+	g	0	J	0				
Gibbsite	1	s	+	g	0	J	0				

As we have very little carbonate in the system in the first calculation we may switch off the carbonate-sulfate AFt solid solutions
(In the input page)

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Hydration of C_3A + CaO + $CaSO_4$ – results

GEM-Selektor 3 (GEMS3) - Geochemical Equilibrium Modelling by Gibbs Energy Minimization - [EqStat:: Single Thermodynamic System in Project C3A ...

Modules Record Data Calculate View Print Window Help

SingleSystem | C3A:G:C3A-Cs:0:0:1:25:0:

Input: System Definition | Results: Equilibrium State

Phase/species	L	T	Amount (mol)	logSI/Activity	Concentration	Acti
a aq_gen	29	a	2.49326	-3.448e-09		
g gas_gen	6	g	0.003171698	-1.987e-09		
s ettringite	2	s	0.0009199661	4.729e-07		
s SO4_OH_AFm	2	s	0.00879217	-2.421e-08		
s OH_SO4_AFm	2	s	0.00879217	-2.421e-08		
s SO4_CO3_AFt	2	s	0	-0.031		
s CO3_SO4_AFt	2	s	0	-0.031		
s Al(OH)3am	1	s	0	-3.174		
s Al(OH)3mic	1	s	0	-2.264		
s Gibbsite	1	s	0	-1.811		
s Graphite	1	s	0	-84.68		
s Mayenite	1	s	0	-92.94		
s Aluminate	1	s	0	-36.48		
s CA	1	s	0	-11.04		
s CA2	1	s	0	-15.19		
s C2AH75	1	s	0	-2.469		
s C3AH6	1	s	0	-0.9692		
s C4AH11	1	s	0	-3.156		
s C4AH13	1	s	0	-1.422		
s C4AH19	1	s	0	-1.221		

View detailed results

Title: C3A +CaSO4

Comment: Please, enter here a comment about the purpose of this system definition

System: T = 298.15 K; P = 1.00 bar; V = 0.131 L; Aqueous: built-in EDH(H); pH = 12.477; pe = 8.296; IS = 0.053 m

General information: pH, ionic strength, redox, …

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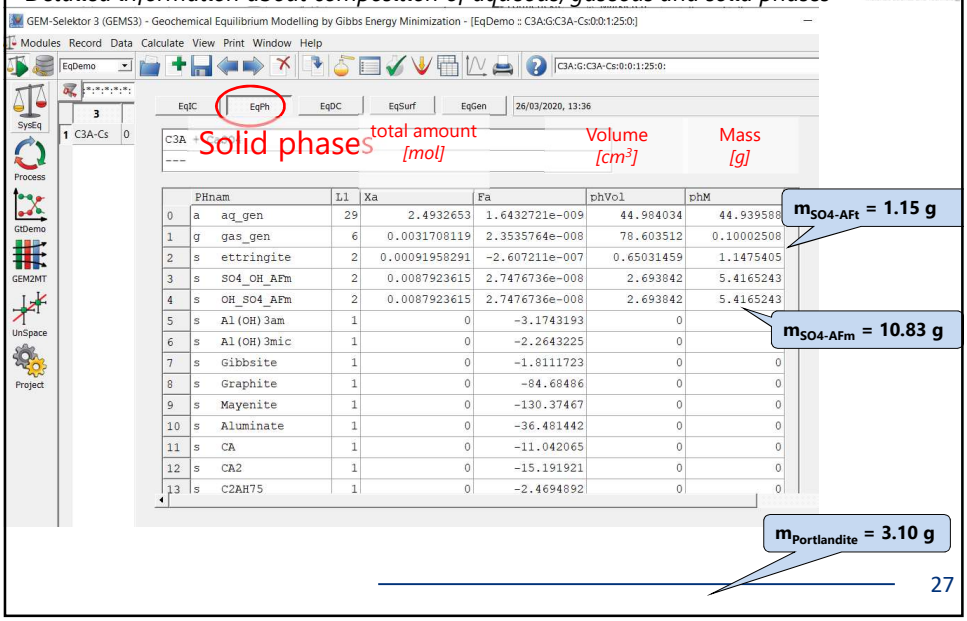
Hydration of C_3A + CaO + $CaSO_4$ – results

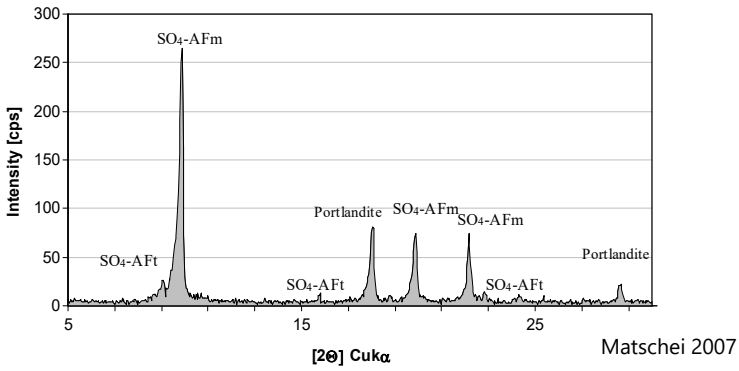
Detailed information about composition of aqueous, gaseous and solid phases



Hydration of C_3A + CaO + $CaSO_4$ – results

Comparison to experiments:

Hydration of C_3A at SO_3/Al_2O_3 = 1, cured 28 d at 25°C, solid phases by XRD



Matschei 2007

Qualitatively very good agreement between experimental and calculated results
Phase assemblage SO_4-AFm - SO_4-AFt - portlandite - aq. predicted and observed.
Quantification with help of GEMS possible.

Hydration of C_3A + CaO + $CaSO_4$ – results

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Composition of aqueous phase

EqIC | EqPh | EqDC | EqSurf | EqGen | 09/06/2023, 16:21

C3A +CaSO4

Please, enter here a comment about the purpose of this system de…

Output: total molalities in aqueous phase (mol/kg H_2O)

	ICnam		b	Cb	u	lgm t	m t	ICnam	
0	Al	e	0.03701052	1.387779e-17	-324.928	-4.372027	4.245927e-05	Al	e
1	C	e	1e-09	3.797537e-26	-194.9822	-7.651954	2.22867e-08	C	e
2	Ca	e	0.118607	-2.081668e-17	-266.1541	-1.690528	0.02039259	Ca	e
3	H	h	5.550837	-2.872702e-15	-47.8309	-1.390111	0.0407276	H	h
4	O	o	3.011322	1.249001e-16	-0.01647609	-1.36302	0.04334909	O	o
5	S	e	0.01851	6.938894e-18	-275.1372	-5.122594	7.540599e-06	S	e
6	Zz	z	0	-4.012578e-19	19.1021	0	-2.480751e-18	Zz	z

total mol in system (input)

Log_{10} of total molalities

Tutorial – single systems: hydration of C_3A

Empa

Hydration of C_3A

1) Simulation of reaction C_3A + CaO + $CaSO_4$ Guided tutorial

2) Simulation of reaction C_3A + CaO + $CaCO_3$

3) Simulation of reaction C_3A + $CaCO_3$

4) Simulation of reaction C_3A + CaO + $CaSO_4$ + $CaCO_3$

Individual work