Oregon State University

Empa
Materials Science and Technology

Lecture 06
Database, solubility,

saturation indices

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Empa
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Thermodynamic data

1. **Databases**
   a. **Cement database cemdata18**
   b. **PC and alkali activated system**
   c. **GEMS – PHREEQC**
   d. **«How to» in GEMS**

2. Solubility and speciation
3. Saturation indices
4. Hydrates in cement
5. *Details on how to manage thermodynamic data in GEMS*

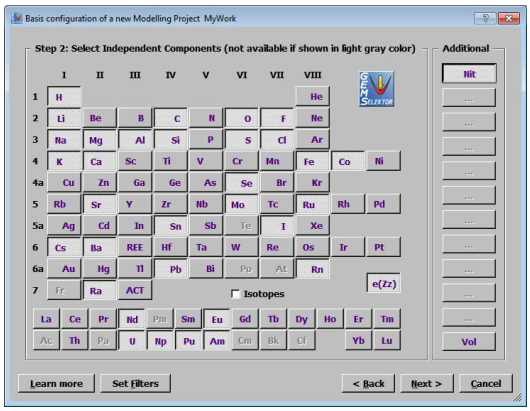
   => Self study

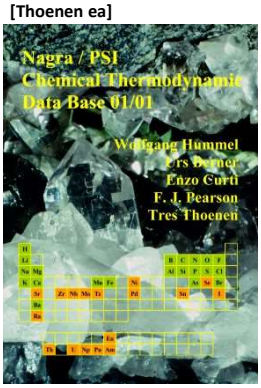
Default ThermoDynamic Databases

Empa

New modeling projects can easily be created using default TDBs.

PSI/Nagra 12/07 TDB [Thoenen ea]





log*K* at 1 bar 25 C , enhanced with *T,P* corrections from SUPCRT

3rd-party: Cemdata'18

www.empa.ch/cemdata

3rd-party: HERACLES

www.psi.ch/heracles/heracles

Complementary: SUPCRT (Slop98)

www.asu.edu/geopig

3

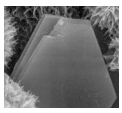
Thermodynamic databases

Empa

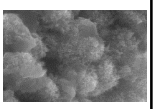
Generic data

general-TDB

- Aqueous phase (Ca^{2+}, $Ca(OH)^{+}$, …)
- Gaseous phase (e.g. CO_2 (g), …)
- Minerals (calcite, gypsum, portlandite, …)



Cemdata 18



AFm

SO_4-AFm ⇕ solid solution OH-AFm

CO_3-AFm

hemicarb.

strätlingite

Al-AFm ⇕ solid solution Fe-AFm

AFt

SO_4-AFt ⇕ solid solution CO_3-AFt

thaumasite

Fe-AFt ⇕ solid solution Al-AFt

hydrogarnet

C_3AH_6

$C_3AS_{0.84}H_{4.32}$ ⇕ solid solution $C_3FS_{0.84}H_{4.32}$

C-S-HQ

$Ca_{0.67}SiH_{1.5}$ ⇕ $C_{0.83}S_{0.67}H_{1.8}$ ⇕ $C_{1.3}SH_{2.17}$ ⇕ $C_{1.5}S_{0.67}H_{2.5}$

Cemdata18 additions: Cl_2-, NO_3-, NO_2-AFm, relative humidity, M-S-H, zeolites, C-N-A-S-H, …

Data based on solubility measurements at different temperatures + solid phasec haracterisation

4

Database 1

- **Geochemical database** (generally integrated in software)
  - Complex formation: $CaOH^+$, $CaHCO_3^+$, …
  - Solubility products: gypsum, calcite, ….
- **Specific cement database**
  - Babushkin et al. (1985) Thermodynamics of Silicates, Springer
  - Reardon, E.J. (1992) Waste Management 12, 221-239; Atkins et al. (1992) CCR 22, 241-246.
  - **CEMDATA07**: Matschei et al. (2007) CCR, Lothenbach et al. (2008) CCR
  - Blanc et al. (2010) CCR 40, 851-866; 1360-1374
  - **CEMDATA18**: Lothenbach et al. (2019) CCR 115, 472-506:
    - ***Friedel's salt:*** *Balonis ea (2010) CCR 40,1009-1022*
    - ***NO_2- and NO_3-AFm:*** *Balonis ea (2011) Adv Cem Res, 23 (2011) 129-143*
    - ***CO_3-hydrotalcite:*** *Rozov ea (2010, 2011)*
    - ***C-S-H models****: Kulik (2011) CCR 41, 477-495*
    - ***Fe-hydrates:*** *Dilnesa ea (2011, 2012, 2014a, 2014b), CCR*
    - ***C-A-S-H for alkali activated cements:*** *Myers (2014) CCR 66, 27-47*
    - ***Relative humidity:*** *Baquerizo ea (2015, 2016a, b) CCR*
    - ***M-S-H:*** *Nied ea (2016) CCR 79, 323-332*
    - ***Na- /Ca-zeolites****: Lothenbach ea (2017) J Phys. Chem. Earth 99, 77-94*

5

Cemdata18

Cemdata18 database: Standard thermodynamic properties at 25 °Ca and 1 atm. Update of Cemdata07

The data are fully compatible with the GEMS version of the PSI/Nagra thermodynamic database [6, 7].

	log K_{S0}^*	$\Delta_f G°$ [kJ/mol]	$\Delta_f H°$ [kJ/mol]	S° [J/K/mol]	a_0 [J/K/mol]	a_1	a_2	a_3	V° [cm^3/mol]	Ref
(Al-)ettringite[a,b,c]	-44.9	-15205.94	-17535	1900	1939	0.789			707	[3, 4]
$C_6As_3H_{30}$[c]		-14728.1	-16950.2	1792.4	1452	2.156			708	[8]
$C_6As_3H_{13}$		-10540.6	-11530.3	1960.4	970.7	1.483			411	[8]
$C_6As_3H_9$		-9540.4	-10643.7	646.6	764.3	1.638			361	[8]
tricarboaluminate[a]	-46.5	-14565.64	-16792	1858	2042	0.559	$-7.78\cdot10^6$		650	[3, 4]
Fe-ettringite[b]	-44.0	-14282.36	-16600	1937	1922	0.855	$2.02\cdot10^6$		717	[3, 9]
Thaumasite	-24.75	-7564.52	-8700	897.1	1031	0.263	$-3.40\cdot10^6$		330	[10]
C_3AH_6[d]	-20.50	-5008.2	-5537.3	422	290	0.644	$-3.25\cdot10^6$		150	[11, 12]
$C_3AS_{0.41}H_{5.18}$[**d]	*-25.35*	*-5192.9*	*-5699*	*399*	*310*	*0.566*	*$-4.37\cdot10^6$*		*146*	*[12]*
$C_3AS_{0.84}H_{4.32}$[**e]	*-26.70*	*-5365.2*	*-5847*	*375*	*331*	*0.484*	*$-5.55\cdot10^6$*		*142*	*[12]*
C_3FH_6[***]	*-26.30*	*-4122.8*	*-4518*	*870*	*330*	*1.237*	*$-4.74\cdot10^6$*		*155*	*[12]*
$C_3FS_{0.84}H_{4.32}$[e,f]	-32.50	-4479.9	-4823	840	371	0.478	$-7.03\cdot10^6$		149	[12]
$C_3A_{0.5}F_{0.5}S_{0.84}H_{4.32}$[e]	-30.20	-4926.0	-5335	619	367	0.471	$-8.10\cdot10^6$		146	[12]
$C_3FS_{1.34}H_{3.32}$	-34.20	-4681.1	-4994	820	395	0.383	$-8.39\cdot10^6$		145	[12]
C_4AH_{19}[g]	-25.45	-8749.9	-10017.9	1120	1163	1.047		-1600	369	[11, 13]
C_4AH_{13}		-7325.7	-8262.4	831.5	208.3	3.13			274	[13]
C_4AH_{11}		-6841.4	-7656.6	772.7	0.0119	3.56	$1.34\cdot10^{-7}$		257	[13]
$C_2AH_{7.5}$	-13.80	-4695.5	-5277.5	450	323	0.728			180	[11]
CAH_{10}	-7.60	-4623.0	-5288.2	610	151	1.113		3200	193	[11]
C_4AsH_{16}		-8726.8	-9930.5	975.0	636	1.606			351	[13, 14]
C_4AsH_{14}[g]		-8252.9	-9321.8	960.9	1028.5				332	[13, 14]
C_4AsH_{12}[h]		-7778.4	-8758.6	791.6	175	2.594			310	[13, 14]
$C_4AsH_{10.5}$		-7414.9	-8311.9	721	172	2.402			282	[13, 14]
C_4AsH_9		-7047.6	-7845.5	703.6	169	2.211			275	[13, 14]
C_4AcH_{11}	-31.47	-7337.46	-8250	657	618	0.982	$-2.59\cdot10^6$		262	[3, 4]
C_4AcH_9		-6840.3	-7618.6	640.6	192.4	2.042			234	[13]
$C_4Ac_{0.5}H_{12}$	-29.13	-7335.97	-8270	713	664	1.014	$-1.30\cdot10^6$	-800	285	[3, 4]
$C_4Ac_{0.5}H_{10.5}$		-6970.3	-7813.3	668.3	0.0095	2.836	$1.07\cdot10^{-7}$		261	[13]
$C_4Ac_{0.5}H_9$		-6597.4	-7349.7	622.5	0.0088	2.635	$9.94\cdot10^{-8}$		249	[13]

Database: Cemdata18

- **PC:**
  Focus on **Portland cements and Portland-blends**
  - **CSHQ** (Kulik): Ca/Si 0.67 – 2.2 (portlandite limits to Ca/Si **≈ 1.6**)
  - $(KOH)_{2.5}SiO_2H_2O$) and $(NaOH)_{2.5}SiO_2H_2O$) to **estimate** alkali uptake
  - Very stable hydrotalcite from Atkins: $Mg_4Al_2O_{10}$ $10H_2O$
- **AAM18**
  Focus on **alkali activated materials**
  - CSHT (Kulik) with Na uptake and Al-uptake (in bridging site) (Myers ea 2014)
    Ca/Si **0.67 – 1.5**
  - Less stable hydrotalcite, variable Mg/Al (Myers ea 2015)
    $Mg_4Al_2O_{10}$ $10H_2O$, $Mg_6Al_2O_{12}$ $12H_2O$, $Mg_8Al_2O_{14}$ $14H_2O$

Cannot be used at the same time !

Further CSH models activated by introducing additional solid solutions in «Phase»:

- Tob-jennite (Kulik and Kersten 2001, Lothenbach and Winnefeld 2006)
- CSHT (Kulik 2011)

All details in Lothenbach et al. (2019) CCR 115, 472-506

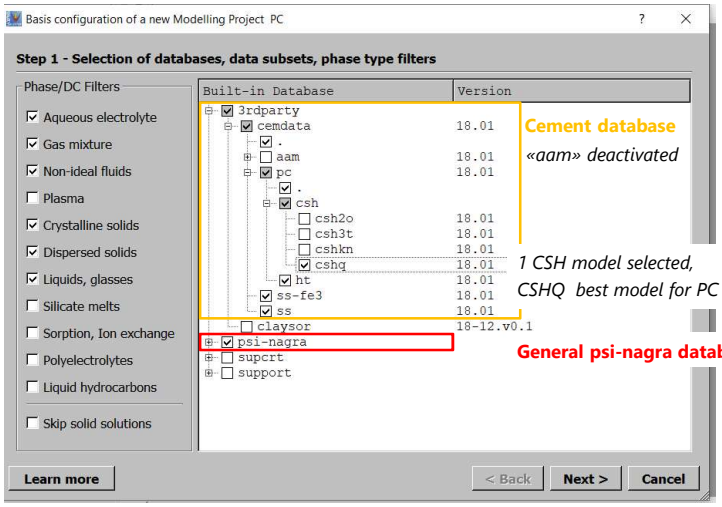
New CSH model with alkali and earth alkali uptake in preparation:

Kulik ea (2022) CCR 151, 106585, Miron ea (2022) CCR 152, 106667; M&S 55(8) 212

Al and sulfate in preparation

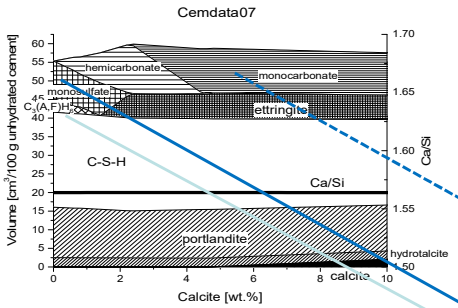
7

Recommended selection for PC and blended cements

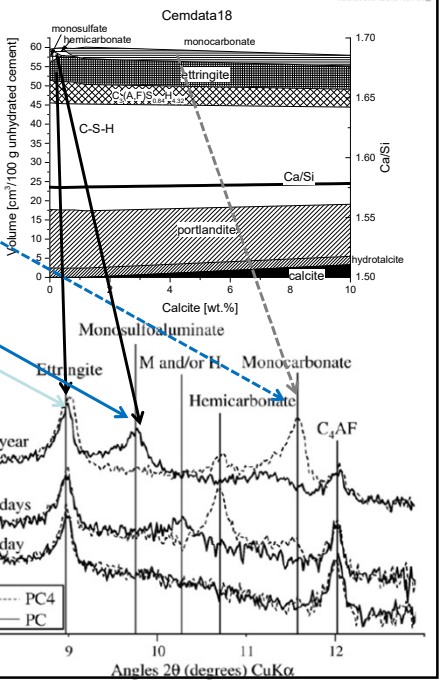


8

Cemdata 07 ⇔ Cemdata18 ?



Lothenbach et al. 2008



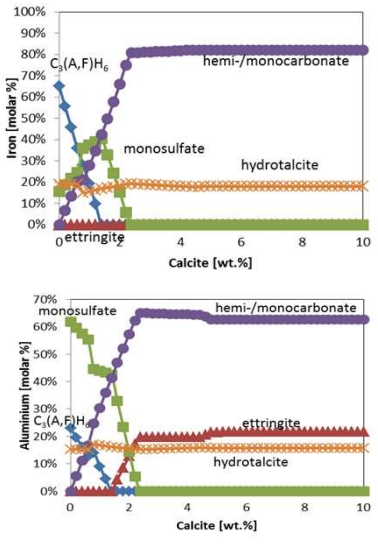
Cemdata18: $C_3(A,F)S_{0.84}H_{4.32}$

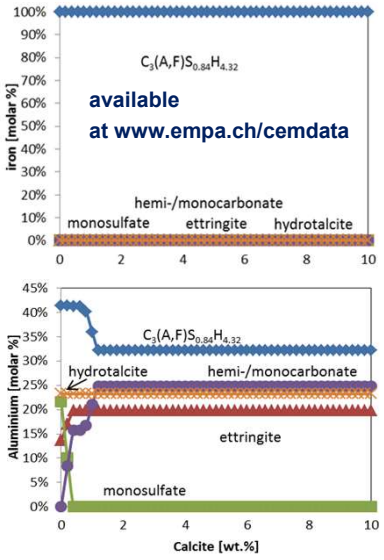
=> Some **Al in Si-hydrogarnet**

- No calcite: Ettringite, less monosulfate as all Fe and some Al in Si-hydrogarnet
- Calcite: less monocarbonate as some Al in Si-hydrogarnet, less strong volume effect of limestone

Cemdata07 | Cemdata18

main effect on Al and Fe distribution





No calcite: More ettringite, less monosulfate as all Fe and some Al in Si-hydrogarnet

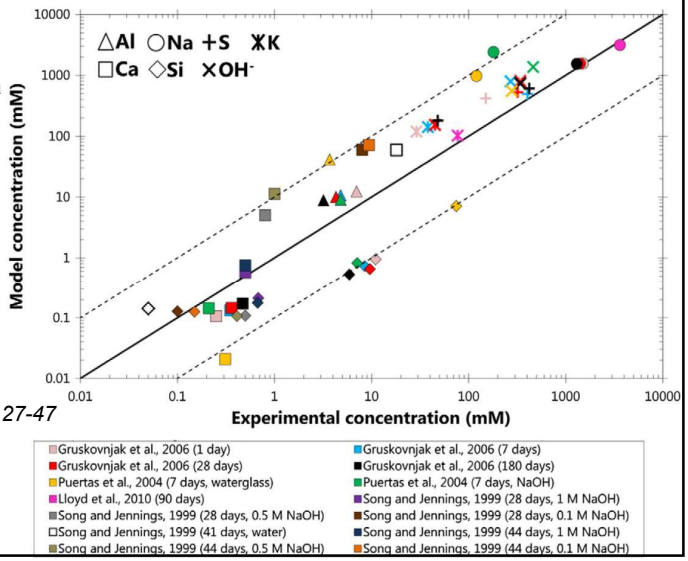
Calcite: less monocarbonate as some Al in Si-hydrogarnet

Cemdata18 for AAM

For alkali activated materials

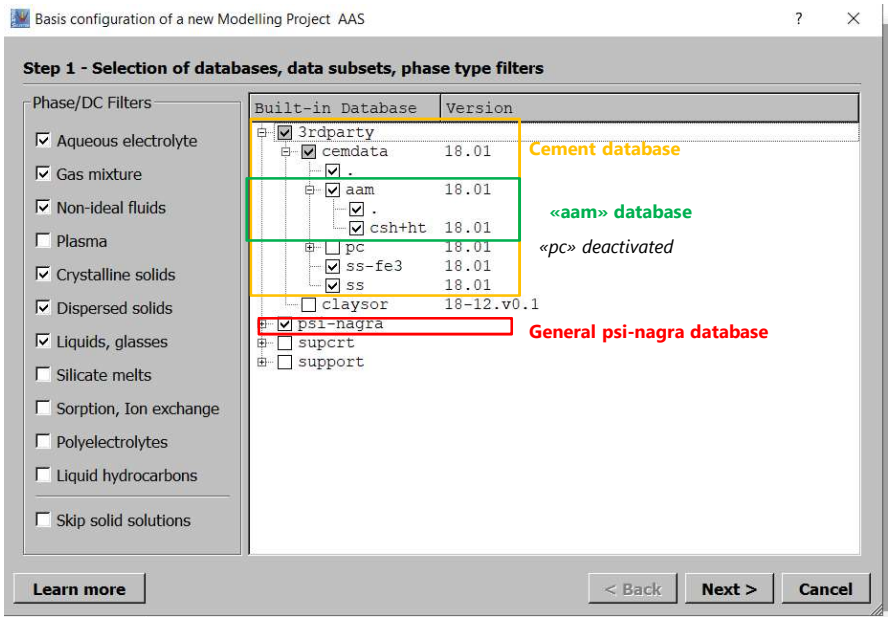
Same data as in Cemdata18 for PC with the following exceptions

CNASH model (Myers ea 2014): Ca/Si = 0.67 to 1.5; **uptake of Al and Na**



Myers ea (2014) CCR 66, 27-47

Recommended selection for alkali activated materials



GEMS versus PHREEQC

Cemdata18 also available in PHREEQC format *(uses log K instead of $G_f°$):*

Details see Lothenbach et al. (2019) CCR 115, 472-506:

CEMDATA18.1-16-01-2019-phaseVol.dat - Editor

Datei Bearbeiten Format Ansicht ?

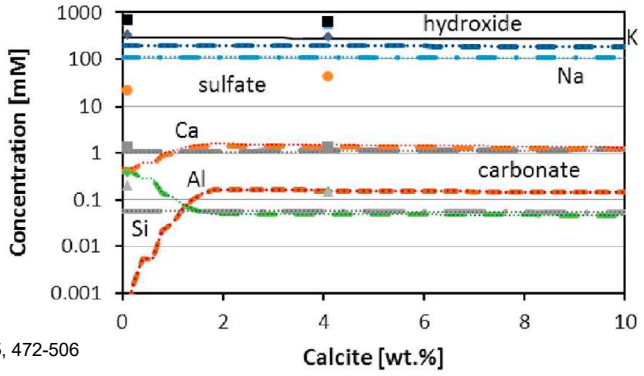
```
# Cemdata18: A chemical thermodynamic database for hydrated Portland cements and alkali-activated
# Authors: Barbara Lothenbach, Dmitrii Kulik, Thomas Matschei, Magdalena Balonis, Luis Baquerizo,
# Published in Cement and Concrete Research, 2018, in press
#
# Based on CEMDATA18 version 01 (09.10.2017) and PSI/Nagra 12/07 GEM format
#
# Exported to PHREEQC format using ThermoMatch (https://bitbucket.org/gems4/thermomatch) reactions
#
# Temperature dependence described by three-term analytical model
# Valid range : 0 - 100°C
#
#
# Phreeqc version date: 08.05.2018
# update 03.12.2018 - added missing phases: zeoliteP_Ca, chabazite, M075SH, M15SH, zeoliteX, natro
# update 08.01.2019 - corrected INFCNA formula and reaction
# update 16.01.2019 - fixed a3 parameter from the logK analytical function (wrong converted from A
# phreeqc A[3]*log10(T); for phases aded in update update 03.12.2018)
#
# for questions contact: Barbara Lothenbach (barbara.lothenbach@empa.ch); G. Dan Miron (dan.miron@

SOLUTION_MASTER_SPECIES

#
#  elemen     species   alk   gfw_formula element_gfw atomic number
#

Al              AlO2-   0.0     AlO2    26.981541       # 13
C               CO3-2   0.0     CO3     12.0108         # 6
# C(0)          SCN-    0.0     SCN                     #
# C(-1)         HCN     0.0     HCN                     #
C(+4)           CO3-2   2.0     CO3                     #
C(-4)           CH4     0.0     CH4                     #
Alkalinity      CO3-2   1.0     Ca0.5(CO3)0.5   50.05   #
```

Solid solution to be defined by user!

GEMS versus PHREEQC

Cemdata18 also available in PHREEQC format *(uses log K instead of G°):*

```
C3AH6
        Ca3Al2O6(H2O)6 + 4H+ = 3Ca+2 + 2AlO2- + 8H2O
        -Vm     149.702
        -analytical_expression  6.92717 0 11498.865007 -4.036936 0 0 0
        -log_K  35.500282
```



Identical results

GEMS: dashed - - -

PHREEQC: dotted …
(ideal solid solution)

Lothenbach et al. (2019) CCR 115, 472-506

Database 3

- Geochemical database and specific cement database have to be consistent!
- Use the specific cement database only with the correct geochemical database!

- Data formats:
  - Log K values (PHREEQC, GEMS, MINEQL, …)
  - ΔG_f° (Gibbs free energy of formation) (GEMS, MTDATA, …)
  - convertible: $K = e^{-\frac{\Delta G_r^\circ}{RT}}$

$$\Delta G_r^\circ = \sum_i \nu_i \Delta G_f^\circ$$

15

Thermodynamic modelling: Limits

- **Thermodynamic data**
  - **Small differences in data -> other solids stable small errors can lead to wrong results**
  - **Gaps in database: Al-K-Na uptake in C-S-H, …**
- **Kinetics: some phases are metastable**
  - **C-S-H metastable (jennite, tobermorite, …)**
  - **Hydrated cement thermodynamically unstable**
  - **Slow kinetics**
- **Kinetics: some phases do not form at ambient conditions and in the timeframe considered**
  - **Quartz, dolomite, goethite, hematite, gibbsite, talc, thaumasite (only at low temp), ...**

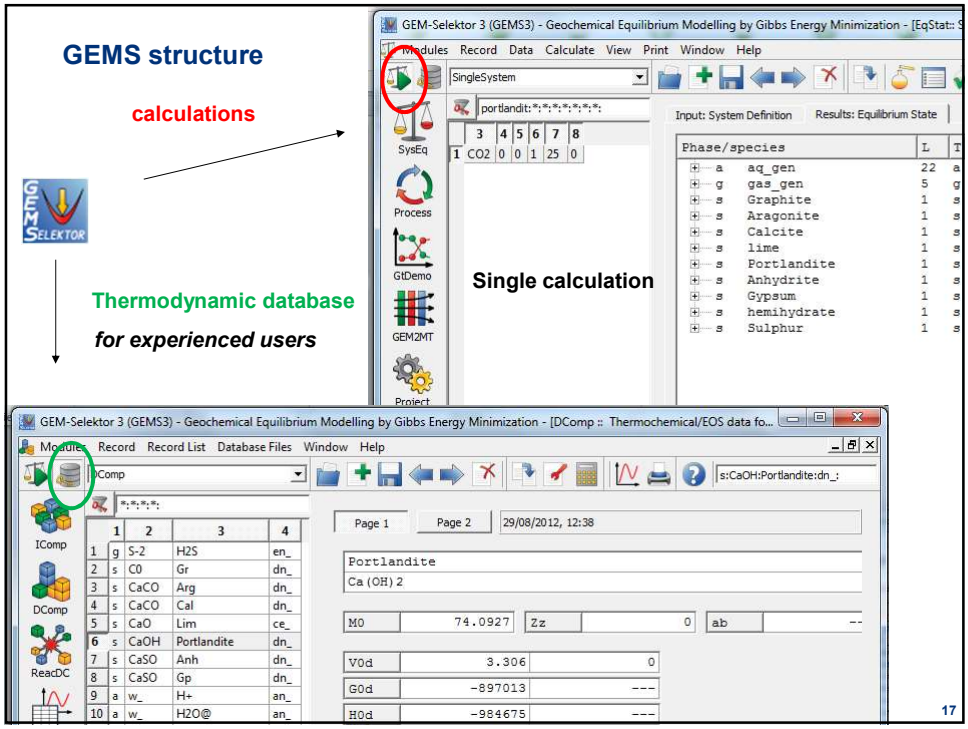
16

GEMS structure

calculations

Thermodynamic database

for experienced users



Thermodynamic database

Empa

Independent components (chemical elements: Ca)

Dependent components: e.g. Ca^{2+}, $Ca(OH)_2$, …

2 input options: both equally valid

Reaction of dependent components (log K)

e.g. $Ca^{2+} + 2OH^- \Leftrightarrow Ca(OH)_2$

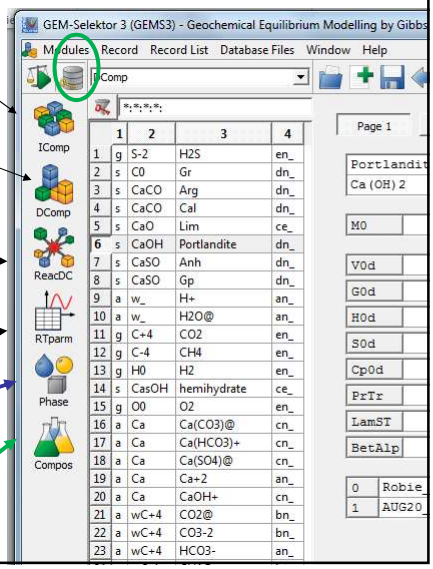
Calculation and plotting of T/P dependency

Solids phases

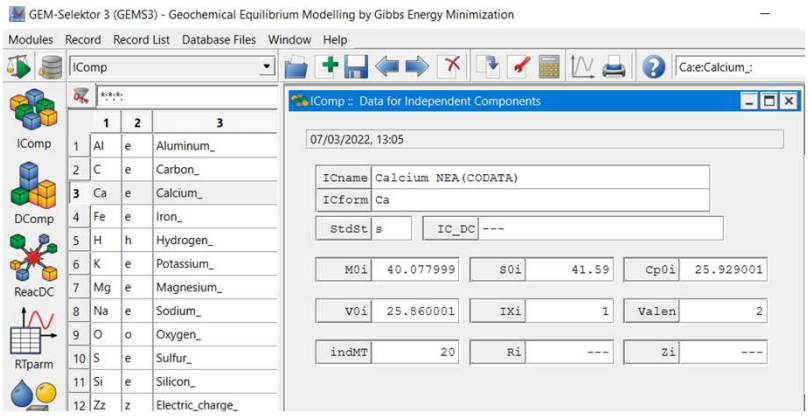
single phases / solid solutions

Predefined compositions:

e.g. air, PC, slag, …



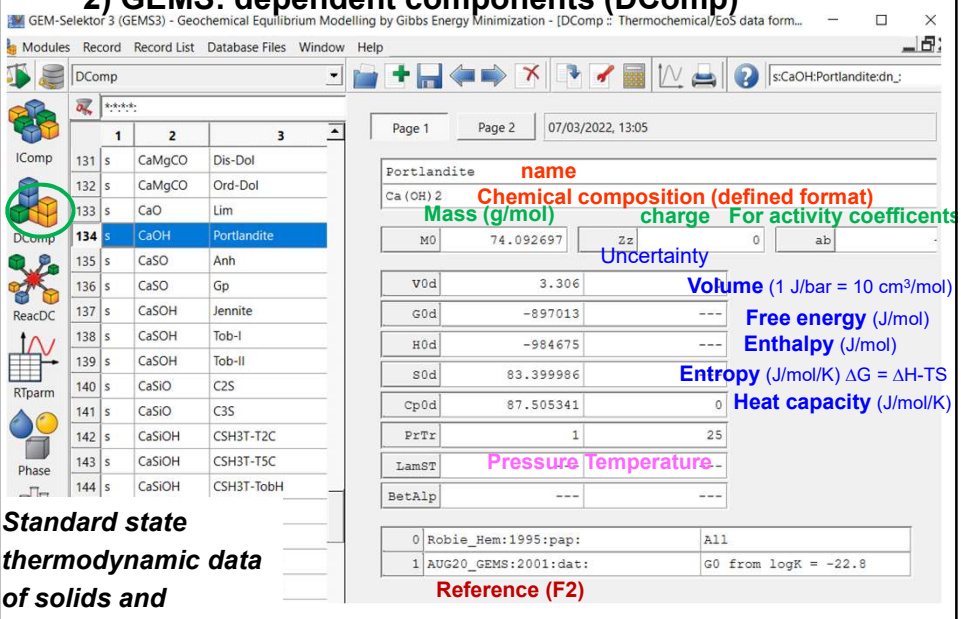
1) GEMS: independent components



Contains basic properties of elements (e.g. molar weight, standard state entropy, valence number)

19

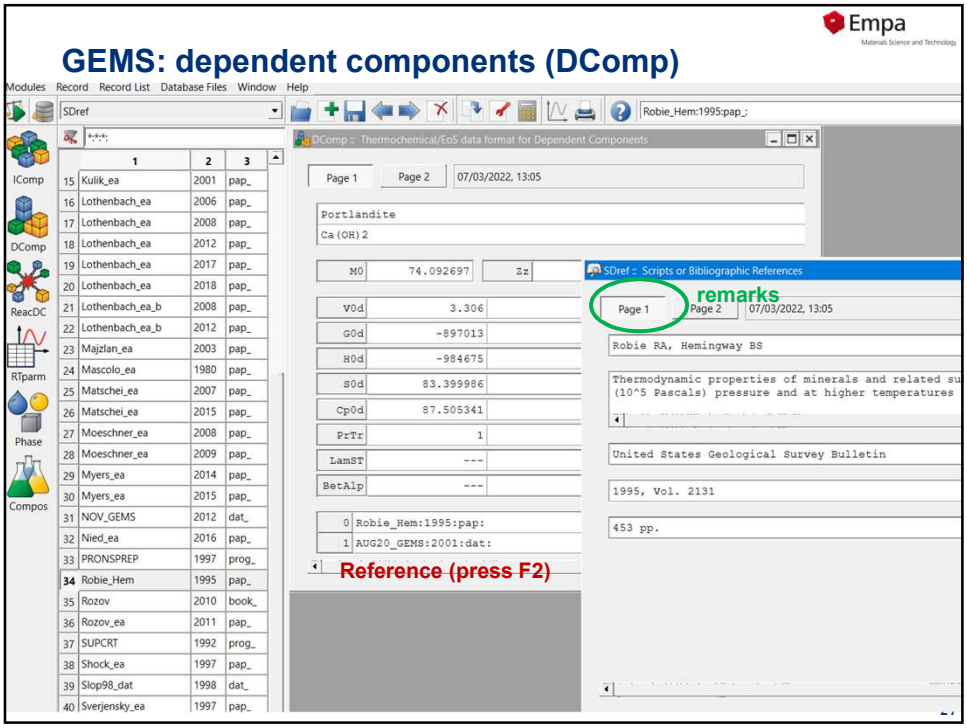
2) GEMS: dependent components (DComp)



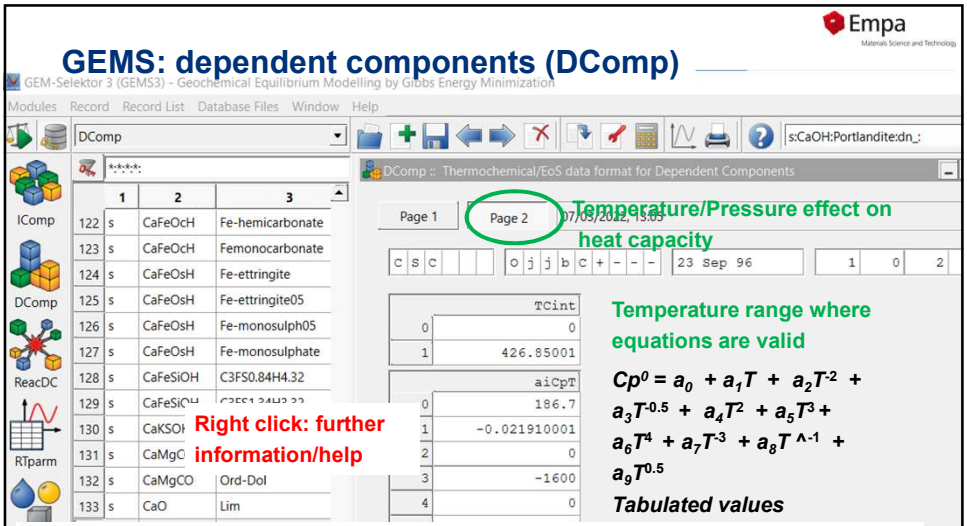
Standard state thermodynamic data of solids and aqueous species

20

GEMS: dependent components (DComp)



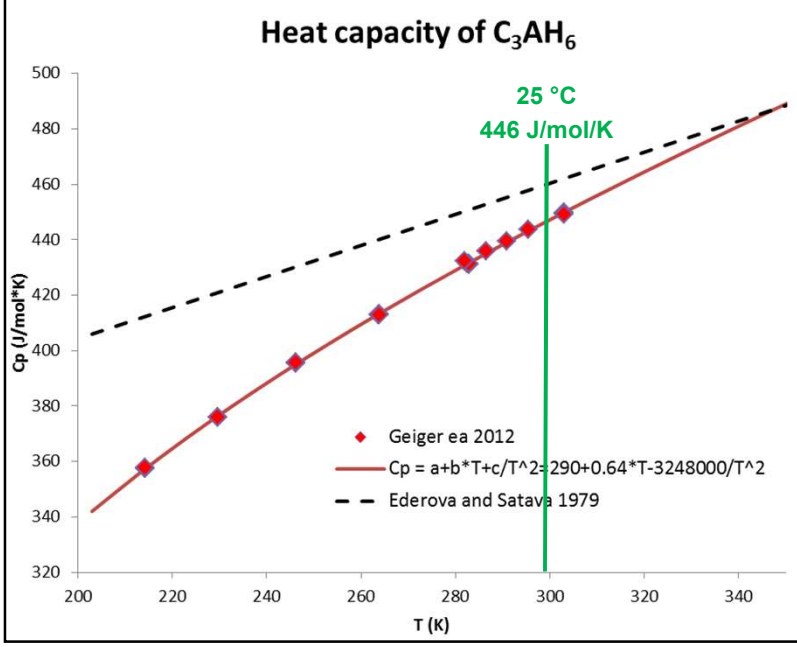
GEMS: dependent components (DComp)



	log K_{S0}^{*}	a_0 [J/K/mol]	a_1	a_2	a_3	V° [cm^3/mol]	Ref
(Al-)ettringite[a,b,c]	-44.9	1939	0.789			707	[3, 4]
CH (portlandite)	-5.2	187	-0.022		-1600	33	[6, 7]
$SiO_{2,am}$	1.476	47	0.034	$-1.13 \cdot 10^6$		29	[3, 4]

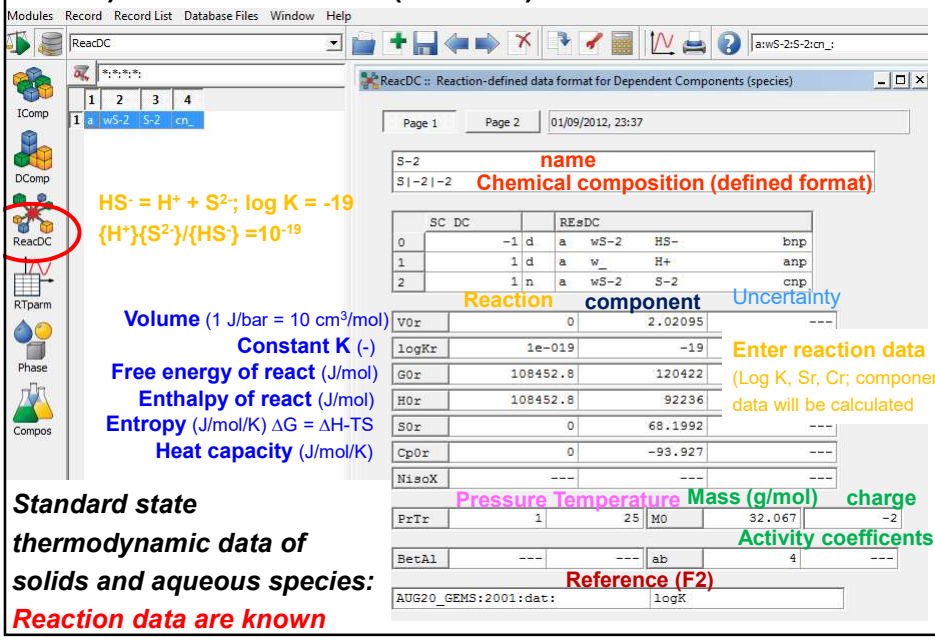
22

GEMS: dependent components (DComp)



23

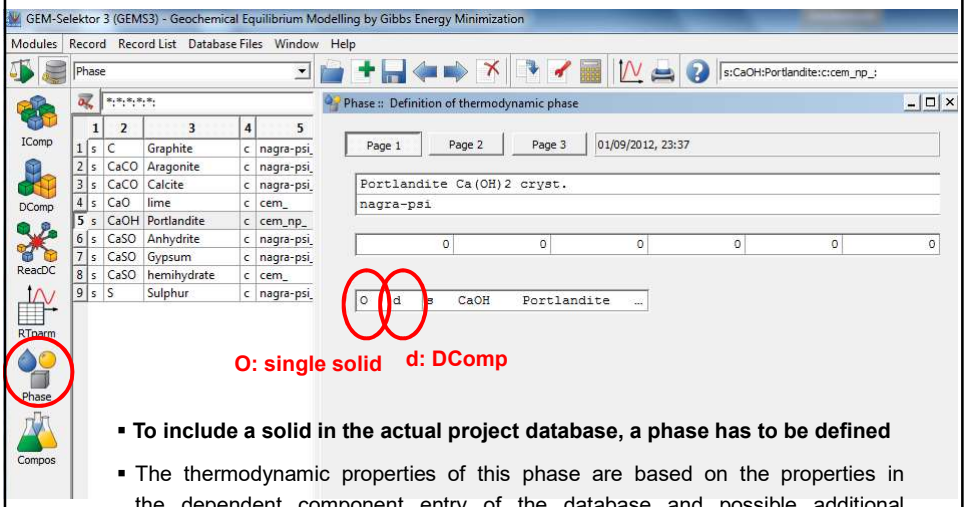
3) GEMS: reactions (ReacDC)



Standard state thermodynamic data of solids and aqueous species:
Reaction data are known

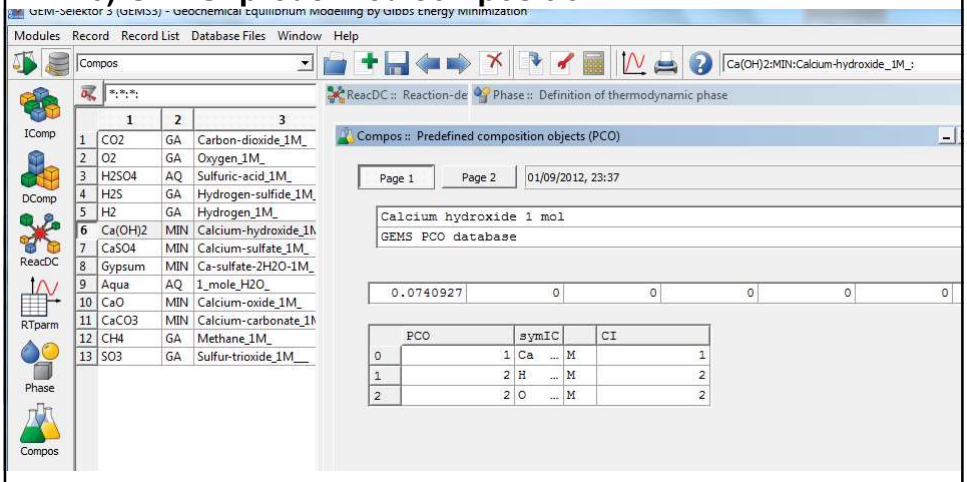
24

5.) Thermodynamic Phases



- **To include a solid in the actual project database, a phase has to be defined**
- The thermodynamic properties of this phase are based on the properties in the dependent component entry of the database and possible additional data e.g. mixing parameters for solid solutions

6) GEMS: predefined composition



Contains chemical compositions of input (e.g. PC, slag, Ca(OH)2, HCl, …)

Alternative way of input, no thermodynamic properties needed

Thermodynamic data

1. Databases
2. **Portlandite solubility and speciation**
   a. **effect of temperature**
   b. **pH**
3. Saturation indices
4. Hydrates in cement
5. Details on how to manage thermodynamic data in GEMS
   => Self study

27

Thermodynamic data portlandite

- $Ca(OH)_2$
  - $K_{s0,H+} = \frac{\{H^+\}^2\{Ca(OH)_2\}}{\{Ca^{2+}\}\{H_2O^0\}} = \frac{\{H^+\}^2\ 1}{\{Ca^{2+}\}\{H_2O^0\}} = 10^{-22.8}$
  - $K_{s0,OH-} = \frac{\{Ca(OH)_2\}}{\{Ca^{2+}\}\{OH^-\}^2} = \frac{1}{\{Ca^{2+}\}\{OH^-\}^2} = 10^{5.2}$

Δ = 1 / K_w^2

Δ = 1 / $(10^{-14})^2$

Δ = 10^{28}

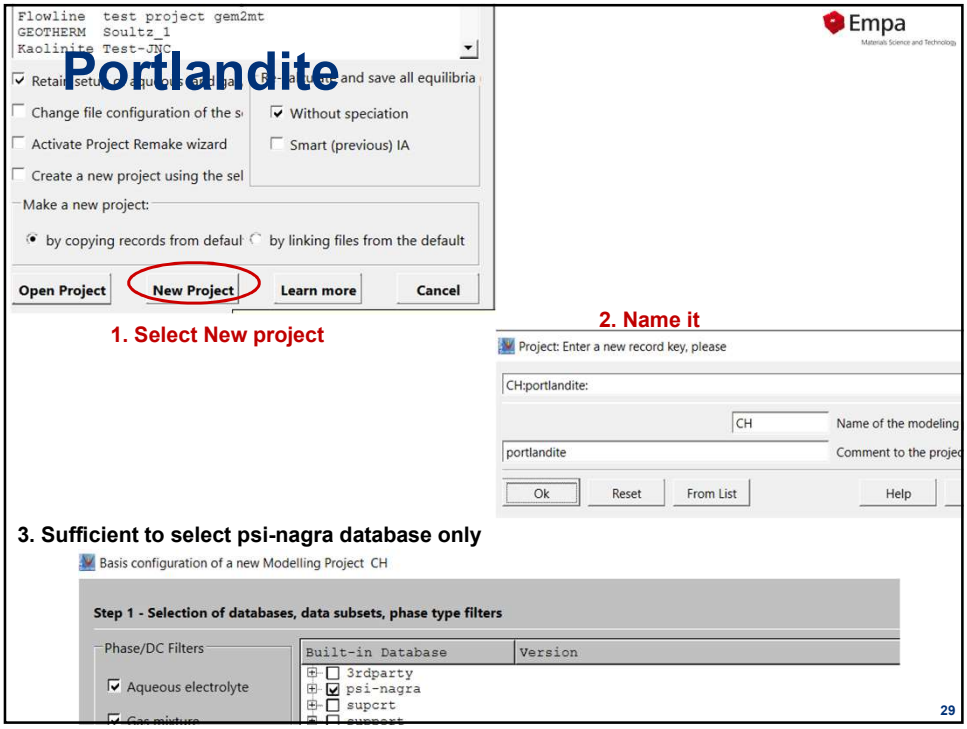
$$K = e^{-\frac{\Delta G_r^\circ}{RT}}$$

$$\Delta G_r^\circ = \sum_i \nu_i \Delta G_f^\circ$$

Portlandite					
Ca(OH)2					
M0	74.0927	Zz	0	ab	---
V0d	3.306	0			
G0d	ΔG_f° -897013	---			
H0d	ΔH_f° -984675	---			
S0d	83.4	---			
Cp0d	87.5053	0			
PrTr	1	25			
LamST	---	---			
BetAlp	---	---			

0	Robie_Hem:1995:pap:	All
1	AUG20_GEMS:2001:dat:	G0 from logK = -22.8

Portlandite

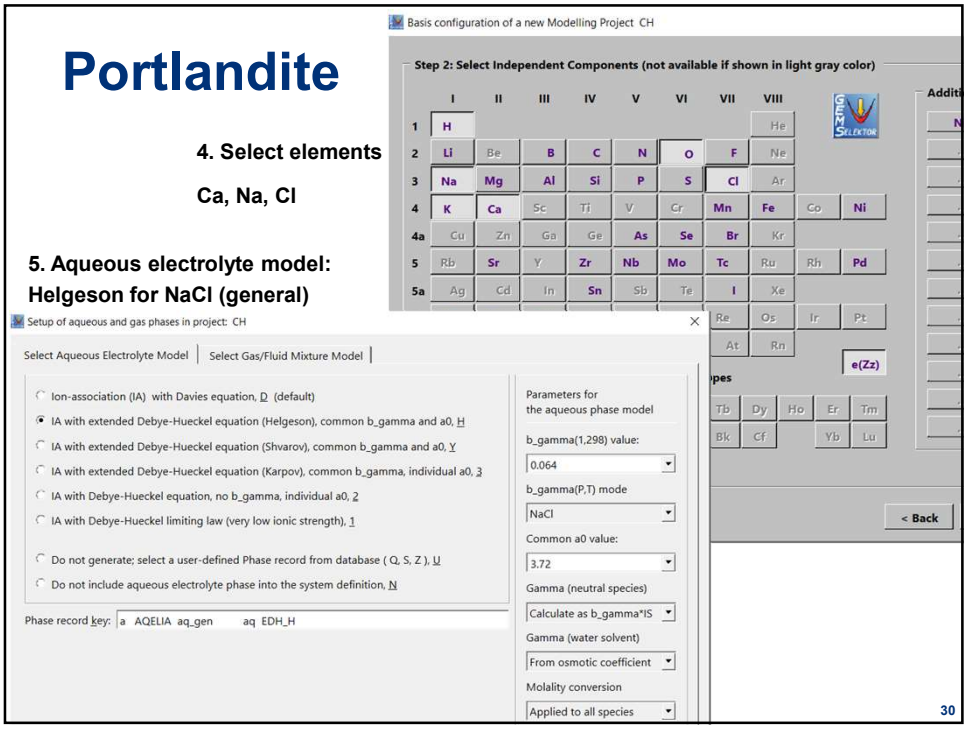


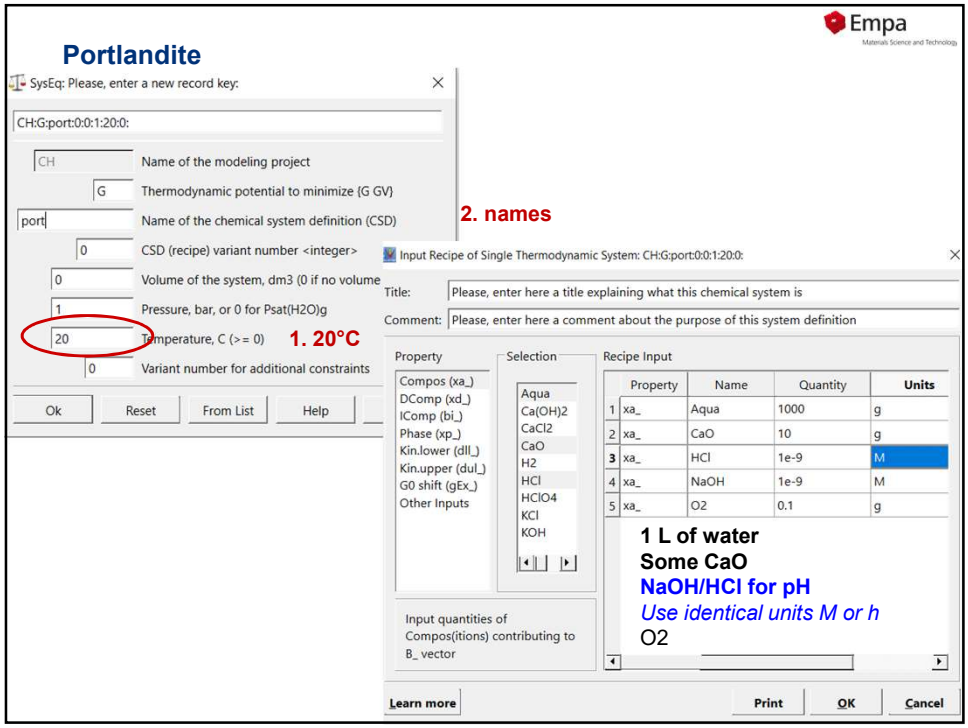
Portlandite

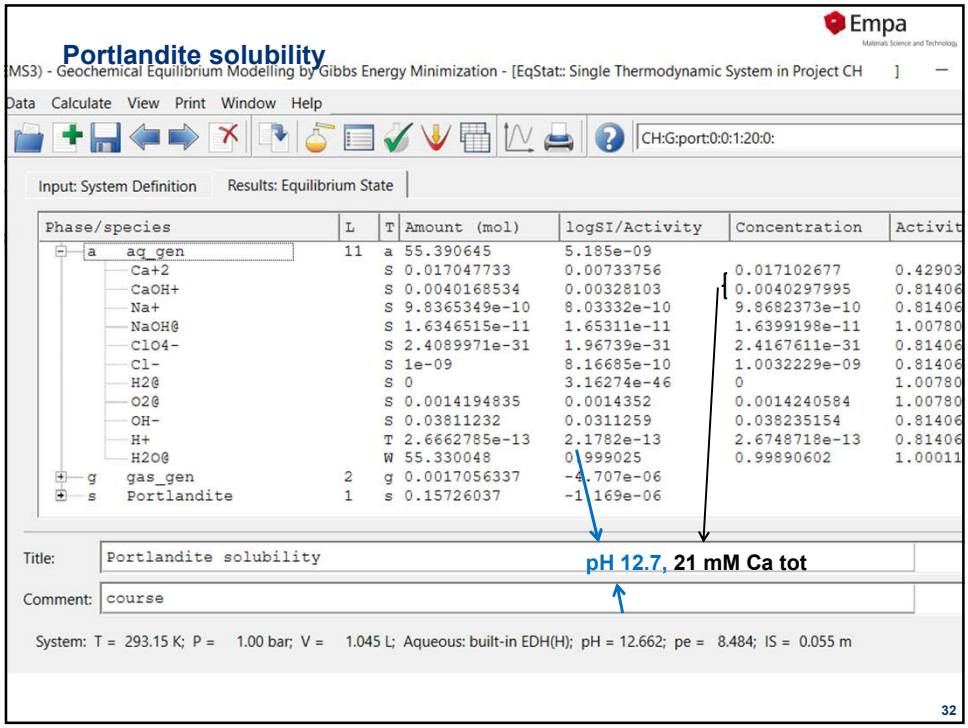
4. Select elements

Ca, Na, Cl

5. Aqueous electrolyte model: Helgeson for NaCl (general)

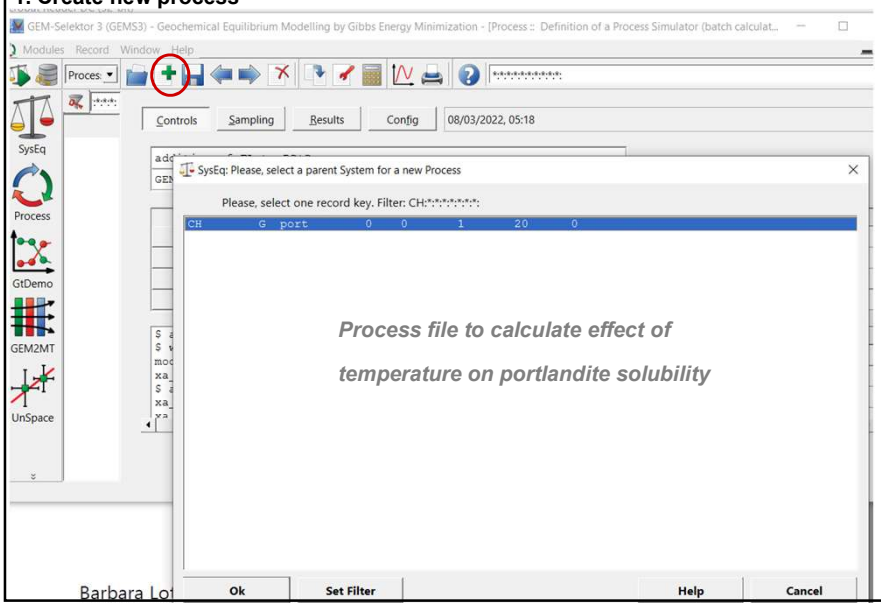



Empa
Portlandite
SysEq: Please, enter a new record key:
CH:G:port:0:0:1:20:0:
CH
Name of the modeling project
G
Thermodynamic potential to minimize {G GV}
port
Name of the chemical system definition (CSD)
0
CSD (recipe) variant number <integer>
0
Volume of the system, dm3 (0 if no volume
1
Pressure, bar, or 0 for Psat(H2O)g
20
Temperature, C (>= 0)
1. 20°C
0
Variant number for additional constraints
Ok
Reset
From List
Help
2. names
Input Recipe of Single Thermodynamic System: CH:G:port:0:0:1:20:0:
Title:
Please, enter here a title explaining what this chemical system is
Comment:
Please, enter here a comment about the purpose of this system definition
Property
Compos (xa_)
DComp (xd_)
IComp (bi_)
Phase (xp_)
Kin.lower (dll_)
Kin.upper (dul_)
G0 shift (gEx_)
Other Inputs
Selection
Aqua
Ca(OH)2
CaCl2
CaO
H2
HCl
HClO4
KCl
KOH
Recipe Input
Property
Name
Quantity
Units
1 xa_ Aqua 1000 g
2 xa_ CaO 10 g
3 xa_ HCl 1e-9 M
4 xa_ NaOH 1e-9 M
5 xa_ O2 0.1 g
1 L of water
Some CaO
NaOH/HCl for pH
Use identical units M or h
O2
Input quantities of Compos(itions) contributing to B_ vector
Learn more
Print
OK
Cancel


Empa
Portlandite solubility
(MS3) - Geochemical Equilibrium Modelling by Gibbs Energy Minimization - [EqStat:: Single Thermodynamic System in Project CH]
Data Calculate View Print Window Help
CH:G:port:0:0:1:20:0:
Input: System Definition
Results: Equilibrium State
Phase/species L T Amount (mol) logSI/Activity Concentration Activit
a ag_gen 11 a 55.390645 5.185e-09
Ca+2 s 0.017047733 0.00733756 0.017102677 0.42903
CaOH+ s 0.0040168534 0.00328103 0.0040297995 0.81406
Na+ s 9.8365349e-10 8.03332e-10 9.8682373e-10 0.81406
NaOH@ s 1.6346515e-11 1.65311e-11 1.6399198e-11 1.00780
ClO4- s 2.4089971e-31 1.96739e-31 2.4167611e-31 0.81406
Cl- s 1e-09 8.16685e-10 1.0032229e-09 0.81406
H2@ s 0 3.16274e-46 0 1.00780
O2@ s 0.0014194835 0.0014352 0.0014240584 1.00780
OH- s 0.03811232 0.0311259 0.038235154 0.81406
H+ T 2.6662785e-13 2.1782e-13 2.6748718e-13 0.81406
H2O@ W 55.330048 0.999025 0.99890602 1.00011
g gas_gen 2 g 0.0017056337 -4.707e-06
s Portlandite 1 s 0.15726037 -1.169e-06
Title: Portlandite solubility
pH 12.7, 21 mM Ca tot
Comment: course
System: T = 293.15 K; P = 1.00 bar; V = 1.045 L; Aqueous: built-in EDH(H); pH = 12.662; pe = 8.484; IS = 0.055 m
32

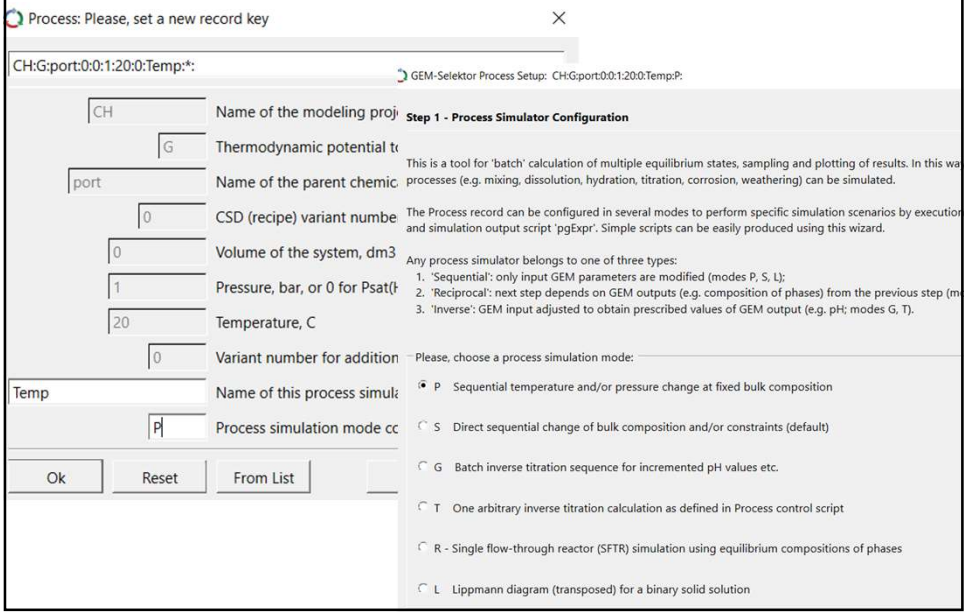
Portlandite: effect of temperature

1. Create new process



Portlandite

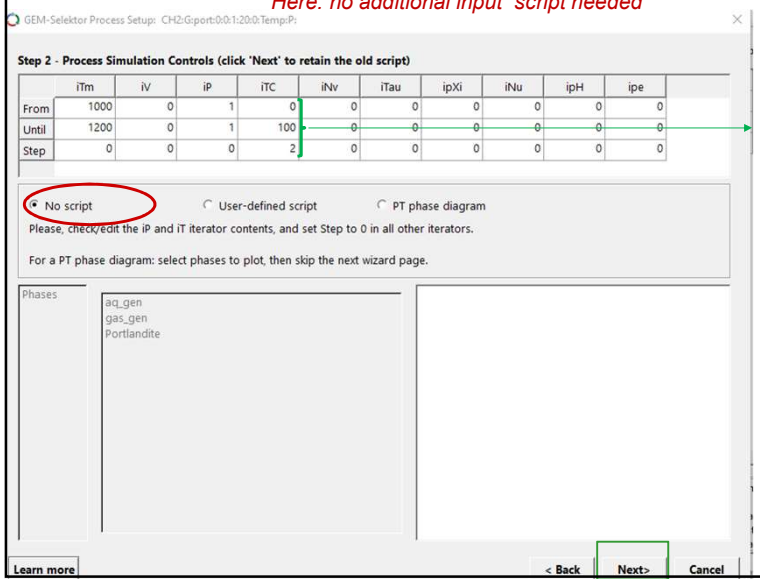
P: sequential change of temperature



Portlandite

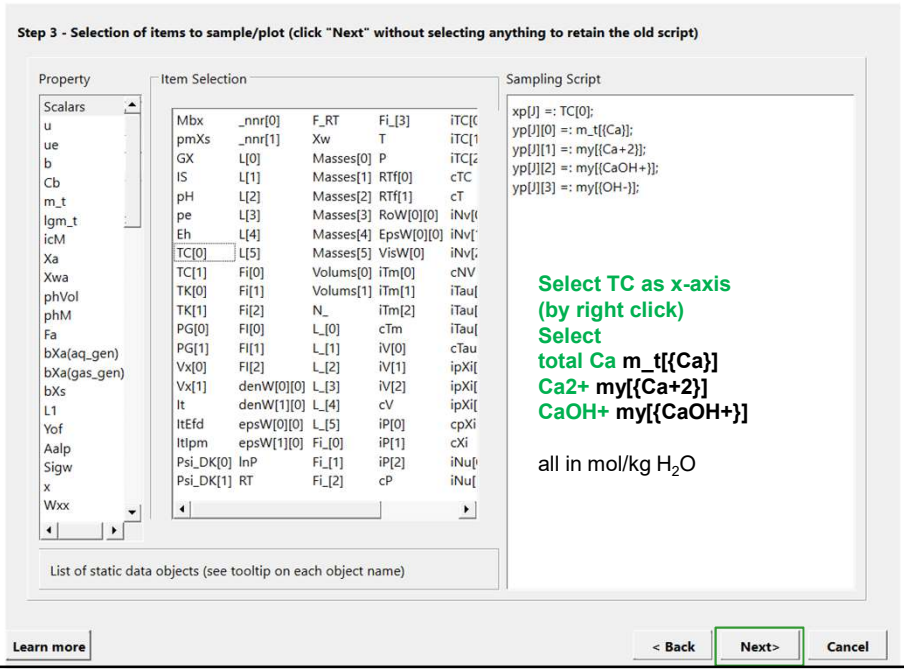
P: sequential change of temperature

Here: no additional input script needed



Start temp
End temp
step

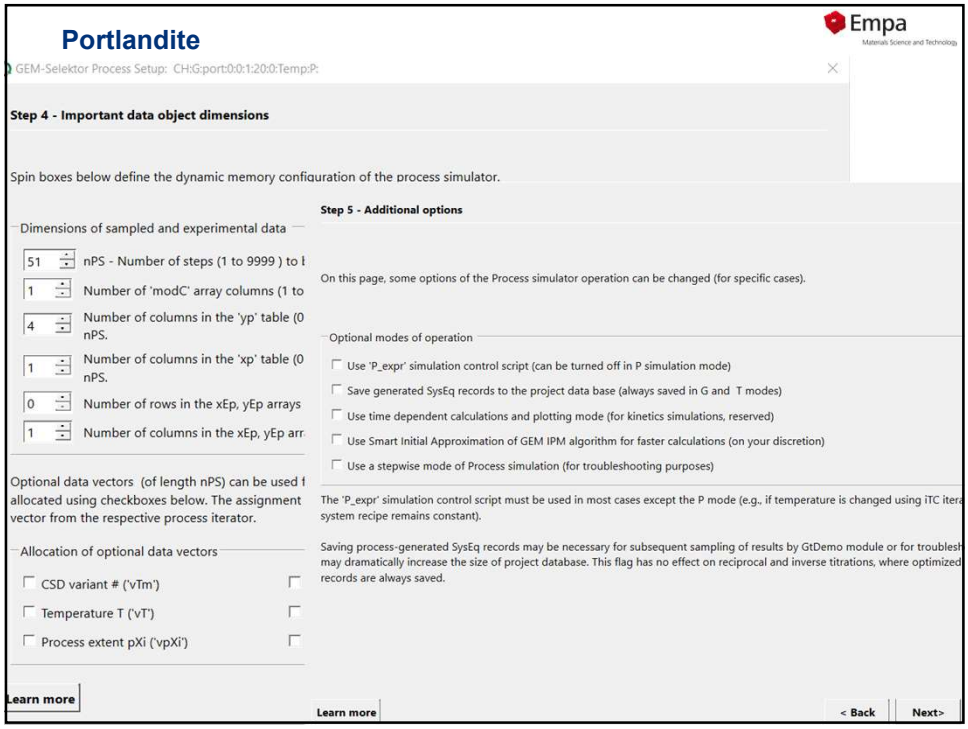
Portlandite



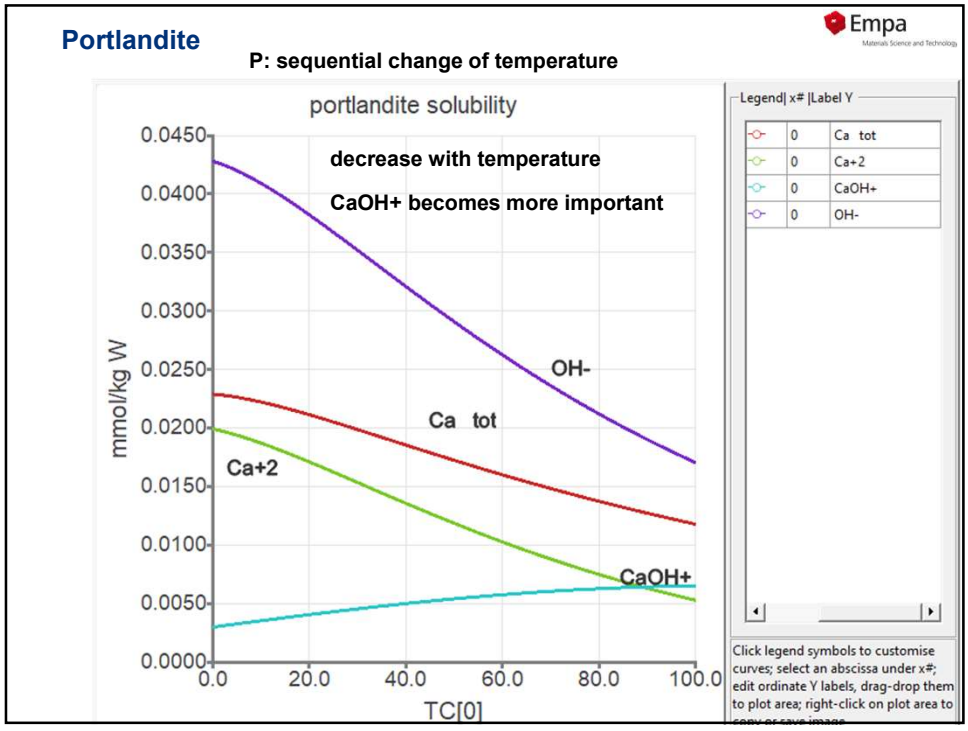
Select TC as x-axis
(by right click)
Select
total Ca **m_t[{Ca}]**
Ca2+ **my[{Ca+2}]**
CaOH+ **my[{CaOH+}]**

all in mol/kg H_2O

Portlandite



Portlandite



Portlandite

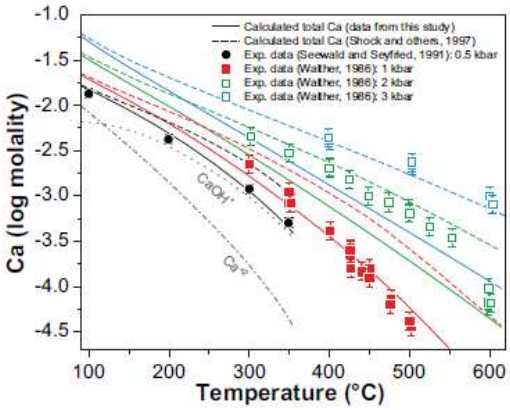


Fig. 16. Comparison between calculated and experimentally determined portlandite solubility in water (Walther, 1986; Seewald and Seyfried, 1991), expressed as total dissolved Ca as function of temperature at pressures of 0.5, 1.0, 2.0 and 3.0 kbar. Solid symbols represent experimental data points which were used to refine the properties of the $CaOH^+$ complex, while open symbols represent experimental data points which were not used.

Portlandite solubility decreases with temperature

Agrees well with experimental trends

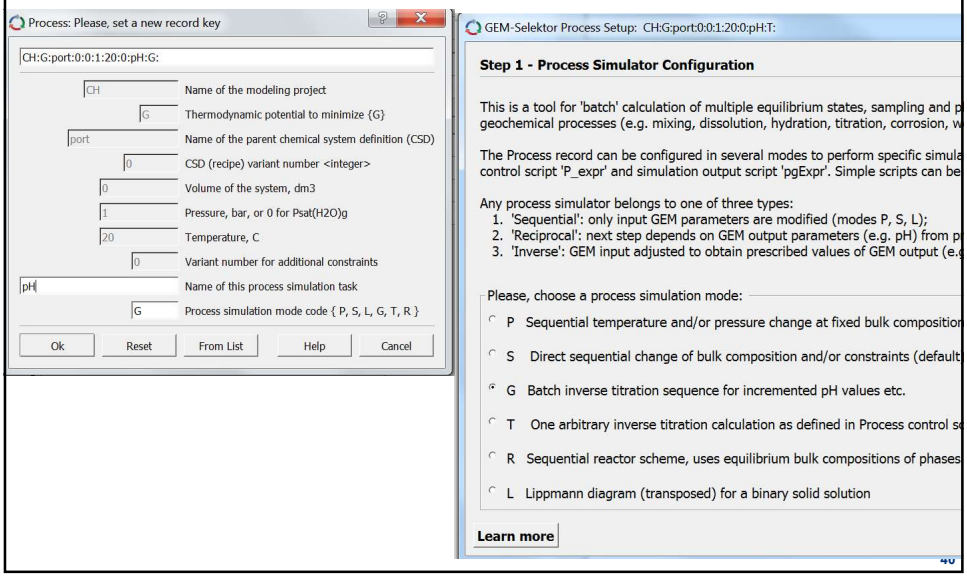
High pressures (kbar!) increases solubility
=> see group work

Miron ea (2017) *American Journal of Science*, 317(7), 755-806

39

Portlandite: effect of pH

1. Create new process

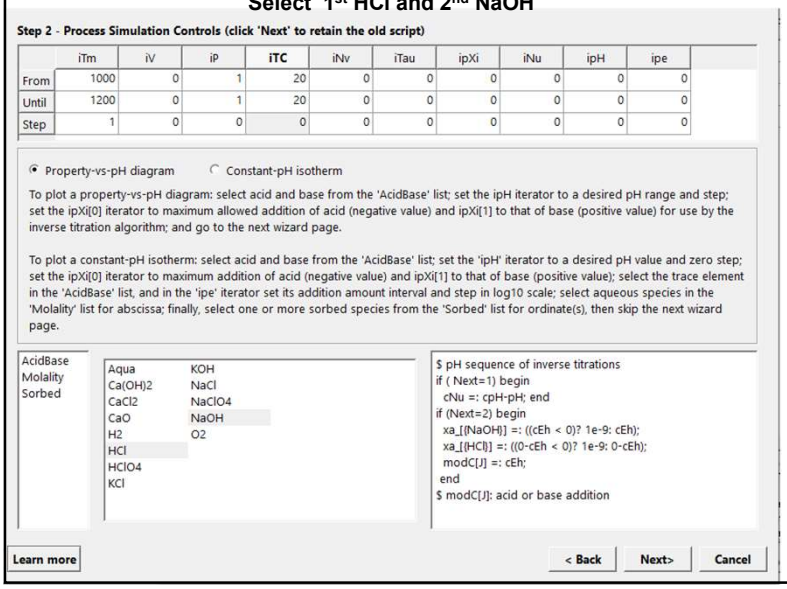


Portlandite

Empa
Materials Science and Technology

G: Batch inverse titration (Variation of pH)

Select 1st HCl and 2nd NaOH



41

Portlandite

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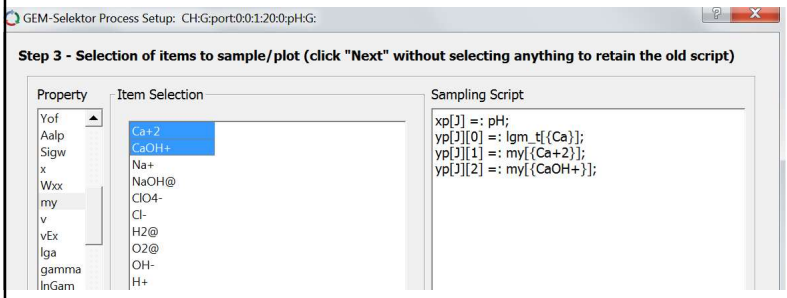
Materials Science and Technology

Output
pH as x-axis (right hand click)
log(Ca tot), Ca2+ and CaOH+

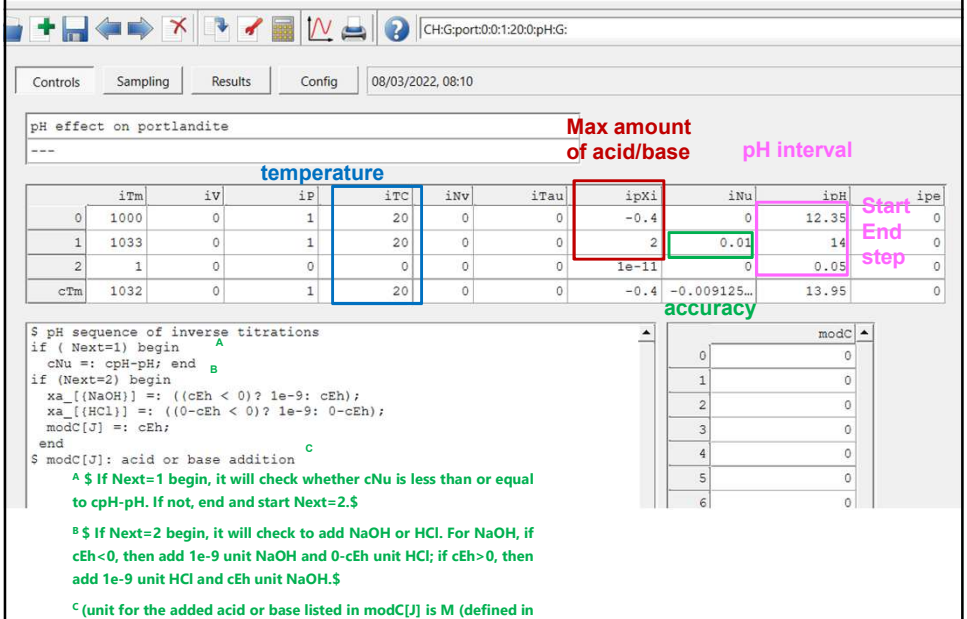


my[{Ca+2}] = Ca^{2+} concentration (in mol/kg H_2O)
m_t[{Ca}] = total concentration (in mol/kg H_2O) = Ca^{2+} + $CaOH^+$ + …

lgm_t[{Ca}] = log(10) of total concentration (in mol/kg H_2O) = Ca^{2+} + $CaOH^+$ + …)
lg(my[{Ca+2}]) = log(10) of Ca^{2+} concentration (in mol/kg H_2O)
(lg(…) has to be adapted afterwards)

42

Adapt input: Temperature, pH interval, max. amount of acid and base



	iTm	iV	iP	iTC	iNv	iTau	ipXi	iNu	ipH	ipe
0	1000	0	1	20	0	0	-0.4	0	12.35	0
1	1033	0	1	20	0	0	2	0.01	14	0
2	1	0	0	0	0	0	1e-11	0	0.05	0
cTm	1032	0	1	20	0	0	-0.4	-0.009125…	13.95	0

	modC
0	0
1	0
2	0
3	0
4	0
5	0
6	0

[A] $ If Next=1 begin, it will check whether cNu is less than or equal to cpH-pH. If not, end and start Next=2.$

[B] $ If Next=2 begin, it will check to add NaOH or HCl. For NaOH, if cEh<0, then add 1e-9 unit NaOH and 0-cEh unit HCl; if cEh>0, then add 1e-9 unit HCl and cEh unit NaOH.$

[C] (unit for the added acid or base listed in modC[J] is M (defined in single calculation (SysEq))

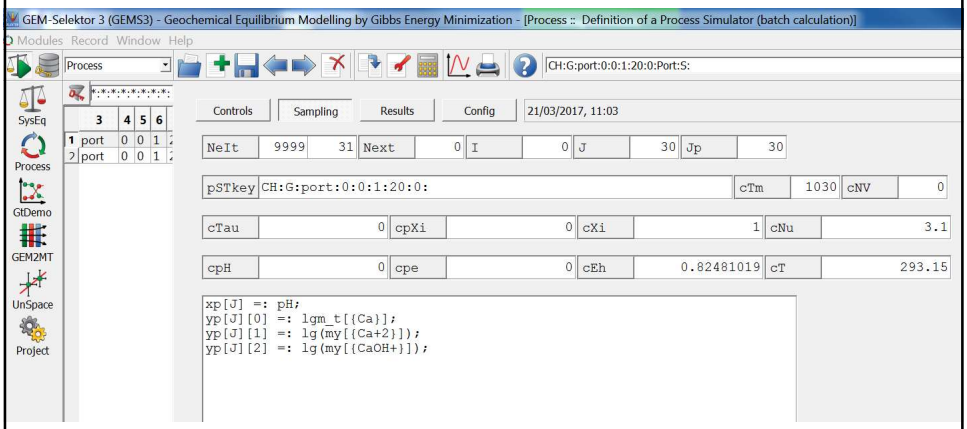
43

Collection of data

pH, total concentrations

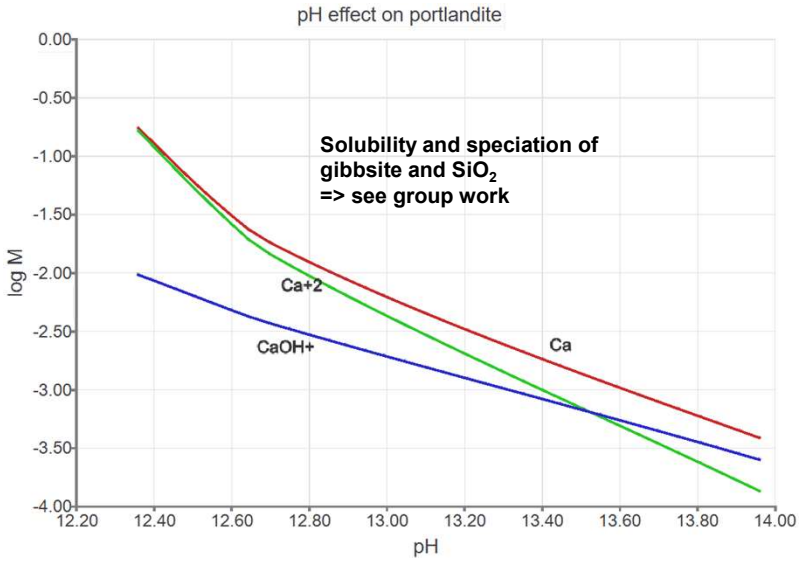
concentrations of species

(use lg() = $\log_{10}$ for better readability)



44

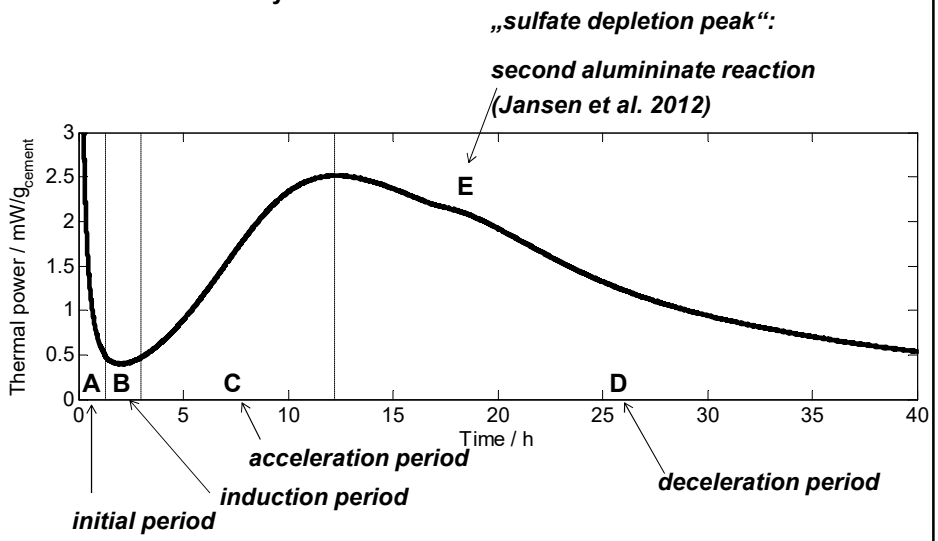
- Lower Ca concentrations at high pH
  - $K_{S0} = \{Ca^{2+}\}\cdot\{OH^-\}^2$: pH↑ = OH^-↑ => Ca^{2+}↓
  - pH increase: more $CaOH^+$



45

Cement hydration: calorimetry ⇔ enthalpy

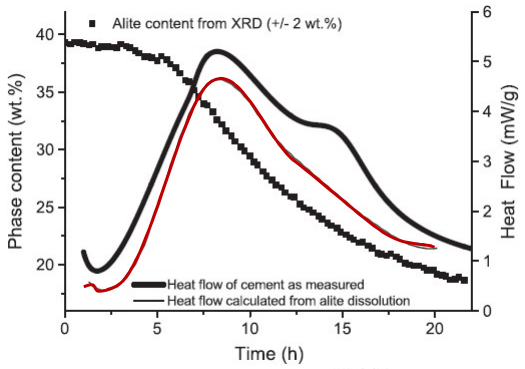
Isothermal calorimetry



46

Heat of hydration (I)

Main early reaction: **C_3S(alite) + 3.9 water → $C_{1.7}SH_{2.6}$ + 1.3 portlandite**



	ΔH_f [kJ/Mol]	Mol weight [g/Mol]
Alite	-2929	228.2
H_2O	-286	18
C-S-H	-2890	201.9
Portlandite	-986	73.97

Enthalpy of alite reaction

=-(-2929-3.9*286)+(-2890-1.3*986)

= -127 kJ/mol

=> -558 J/g Alite

23°C, w/c = 0.50

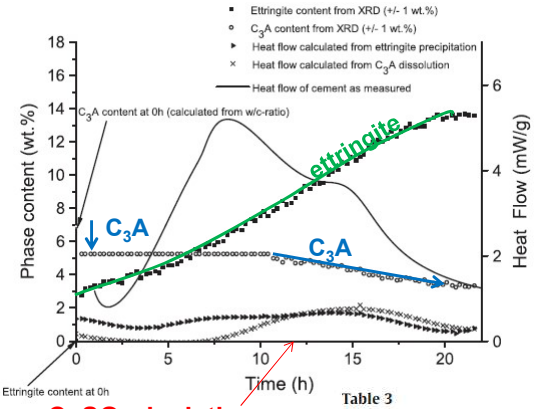
Jansen et al. 2012, CCR

Table 3
Enthalpies of reaction for the assumed reactions.

Reaction	Enthalpy
Eq. (1) (Silicate reaction)	−561 J/g_{Alite}
Eq. (3) (Dissolution C_3A)	−868 J/g_{C3A}
Eq. (4) (Dissolution anhydrite)	−50 J/$g_{Anhydrite}$
Eq. (5) (Dissolution gypsum)	59 J/g_{Gypsum}
Eq. (6) (Precipitation ettringite)	−214 J/$g_{Ettringite}$

Heat of hydration (III)

Main early reaction: **C_3A(aluminate) + $CaSO_4$ +H2O → ettringite**



$CaSO_4$ depletion

C_3A + 3Cs + 32H → $C_6As_3H_{32}$

two C_3A dissolution events

- **1st minutes**
- **Depletion of $CaSO_4$**

Ettringite forms continously

23°C, w/c = 0.50

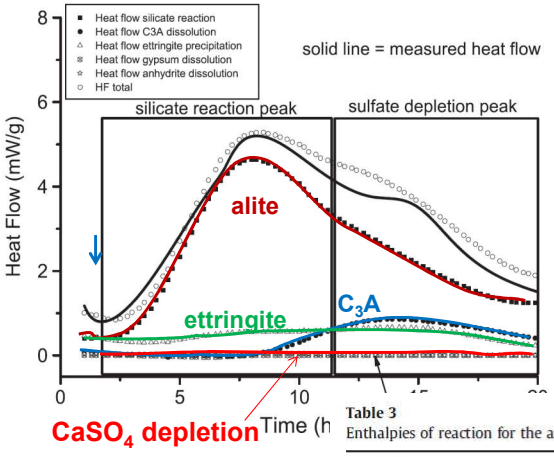
Jansen et al. 2012, CCR

Table 3
Enthalpies of reaction for the assumed reactions.

Reaction	Enthalpy
Eq. (1) (Silicate reaction)	−561 J/g_{Alite}
Eq. (3) (Dissolution C_3A)	−868 J/g_{C3A}
Eq. (4) (Dissolution anhydrite)	−50 J/$g_{Anhydrite}$
Eq. (5) (Dissolution gypsum)	59 J/g_{Gypsum}
Eq. (6) (Precipitation ettringite)	−214 J/$g_{Ettringite}$

Heat of hydration (II)

Main early reaction: C_3A(aluminate) + $CaSO_4$ +H2O → ettringite



C_3A + 3Cs + 32H → $C_6As_3H_{32}$

two C_3A dissolution events

- 1st minutes
- Depletion of $CaSO_4$

Ettringite forms continously

Little effect of $CaSO_4$ dissolution

23°C, w/c = 0.50

Jansen et al. 2012, CCR

Table 3
Enthalpies of reaction for the assumed reactions.

Reaction	Enthalpy
Eq. (1) (Silicate reaction)	−561 J/g_{Alite}
Eq. (3) (Dissolution C_3A)	−868 J/g_{C3A}
Eq. (4) (Dissolution anhydrite)	−50 J/$g_{Anhydrite}$
Eq. (5) (Dissolution gypsum)	59 J/g_{Gypsum}
Eq. (6) (Precipitation ettringite)	−214 J/$g_{Ettringite}$

How to calculate heat

	log K_{S0}	$\Delta_f G°$ [kJ/mol]	$\Delta_f H°$ [kJ/mol]	$S°$ [J/K/mol]	a_0 [J/K/mol]	a_1	a_2	a_3	$V°$ [cm^3/mol]	Ref
(Al-)ettringite[a,b,q]	-44.9	-15205.94	-17535	1900	1939	0.789			707	[1,2]
$C_4As_3H_{30}$[q]		**-14728.1**	**-16950.2**	**1792.4**	**1452**	**2.156**			**708**	**[24]**
$C_4As_3H_{13}$		**-10540.6**	**-11530.3**	**1960.4**	**970.7**	**1.483**			**411**	**[24]**
$C_4As_3H_9$		**-9540.4**	**-10643.7**	**646.6**	**764.3**	**1.638**			**361**	**[24]**
tricarboaluminate[a]	-46.5	-14565.64	-16792	1858	2042	0.559	-7.78e6		650	[2,1]
Fe-ettringite[b]	-44.0	-14282.36	-16600	1937	1922	0.855	2.02e6		717	[3,1]
Thaumasite	-24.75	-7564.52	-8700	897.1	1031	0.263	-3.40e6		330	[9]
C_3AH_6[c]	-20.50	-5008.2	-5537.3	422	290	0.644	-3.25e6		150	[10]
*$C_3AS_{0.41}H_{5.18}$[*c]*	*-25.35*	*-5192.9*	*-5699*	*399*	*310*	*0.566*	*-4.37e6*		*146*	*[11]*
*$C_3AS_{0.84}H_{4.32}$[*d]*	*-26.70*	*-5365.2*	*-5847*	*375*	*331*	*0.484*	*-5.55e6*		*142*	*[11]*
C_3FH_6[e++]	*-26.30*	*-4122.8*	*-4518*	*870*	*330*	*1.237*	*-4.74e6*		*155*	*[11]*
$C_3FS_{0.84}H_{4.32}$[d,e]	-32.50	-4479.9	-4823	840	371	0.478	-7.03e6		149	[11]
$C_3(A,F)S_{0.84}H_{4.32}$[d]	**-30.10**	**-4925.4**	**-5335**	**617**	**367**	**0.471**	**-8.10e6**		**146**	**[11]**
$C_3FS_{1.34}H_{3.32}$	-34.20	-4681.1	-4994	820	395	0.383	-8.39e6		145	[11]
C_4AH_{19}[f]	-25.45	-8749.9	-10017.9	1120	1163	1.047		-1600	**369**	[10,23]
C_4AH_{13}		**-7325.7**	**-8262.4**	**831.5**	**208.3**	**3.13**			**274**	**[23]**
C_4AH_{11}		**-6841.4**	**-7656.6**	**772.6**	**0.0119**	**3.56**	**1.34e-7**		**257**	**[23]**

- Measured heat is due to enthalpy changes
- ! Water very important, involved in most reactions !
  $\Delta_f H°$ (H_2O) = -285.88 kJ/mol

50

How to calculate heat

	log K_{S0}	$\Delta_f G°$ [kJ/mol]	$\Delta_f H°$ [kJ/mol]	S° [J/K/mol]	a_0 [J/K/mol]	a_1	a_2	a_3	V° [cm^3/mol]	Ref
Cs (anhydrite)	-4.357	-1322.12	-1434.60	106.7	70.2	-0.099			46	[6,7]
CsH_2 (gypsum)	-4.581	-1797.76	-2023.36	193.8	91.4	-0.318			75	[6,7]
β-$CsH_{0.5}$(hemihyd)	-3.59[v]	-1436.34[v]	-1575.3[v]	134.3	124.1				62	[19]

Example: hydration of anhydrite to gypsum

1) 1M $CaSO_4$ (= 136.14 g) + 2 M H_2O (36.03 g) => 1M $CaSO_4$ $2H_2O$
   -2'023'361 -(-1'434'601 +2*(-285'881)) = -16'998 J/mol = **-17.0 kJ/mol**
   => -125 J/g anhydrite or -98.7 J/g gypsum

$$\Delta_r H° = \Delta_f H°_{\text{gypsum}} - \Delta_f H°_{\text{anhydrite}} - 2\,\Delta_f H°_{\text{water}}$$
$$= -2022.63 - (-1434.11) - 2\,(-285.830)$$
$$= -16.86\ \text{kJ mol}^{-1}$$

from which we see that the reaction between anhydrite and water to form gypsum is exothermic; that is, 16.86 kJ of heat would be released for every mole of anhydrite reacted.

Anderson (2017): Thermodynamics of Natural Systems

51

How to calculate heat

	log K_{S0}	$\Delta_f G°$ [kJ/mol]	$\Delta_f H°$ [kJ/mol]	S° [J/K/mol]	a_0 [J/K/mol]	a_1	a_2	a_3	V° [cm^3/mol]	Ref
Cs (anhydrite)	-4.357	-1322.12	-1434.60	106.7	70.2	-0.099			46	[6,7]
CsH_2 (gypsum)	-4.581	-1797.76	-2023.36	193.8	91.4	-0.318			75	[6,7]
β-$CsH_{0.5}$(hemihyd)	-3.59[v]	-1436.34[v]	-1575.3[v]	134.3	124.1				62	[19]

Example: hydration of anhydrite to gypsum

1) 1M $CaSO_4$ (= 136.14 g) + 2 M H_2O (36.03 g) => 1M $CaSO_4$ $2H_2O$
   -2'023'361 -(-1'434'601 +2*(-285'881)) = -16'998 J/mol **= -17.0 kJ/mol**
   => -125 J/g anhydrite or -98.7 J/g gypsum

2) Dissolution of CaSO4 in water: 1 g anhydrite (in 1 L H2O)

Input	M	g/mol	H (J/mol)	g/L	J/g CaSO4
CaSO4	0.0073	136	-1434601	1	-10537
output					
Ca2+	0.0055	40	-543069	0.22105834	-2995
SO4-2	0.0055	96	-909697	0.5298638	-5018
CaSO4 aq	0.0018	136	-1448430	0.2490777	-2650
Dissolution					**-126**

52

Thermodynamic data

1. Databases
2. Portlandite solubility and speciation
3. **Saturation indices**
   a) **Pore solution**
   b) **Calculation of SI**

4. Hydrates in cement
5. Details on how to manage thermodynamic data in GEMS
   => Self study

Poresolution PC

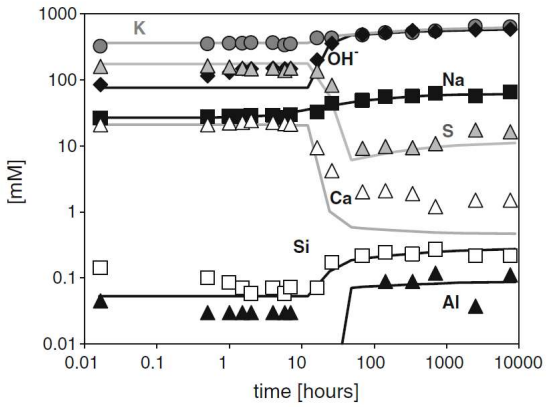


Fig. 1 Evolution of the pore solution during the hydration of OPC. *Symbols* refer to measured concentrations, *lines* to modeled concentrations. Adapted from [17]

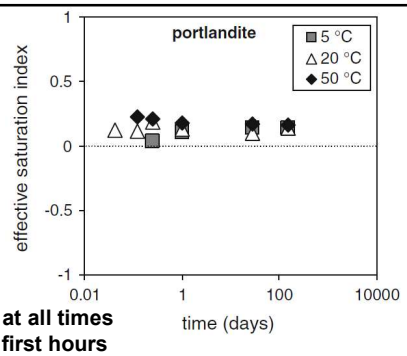
Lothenbach (2010) Materials and Structures 43, 1413-1433

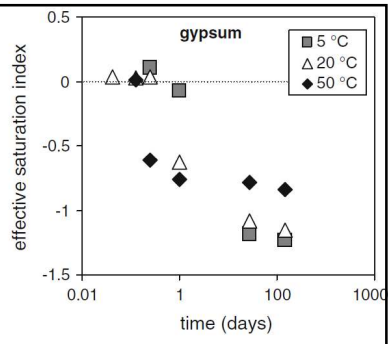
Composition changes during cement reaction

In particular for calcium and sulfate:

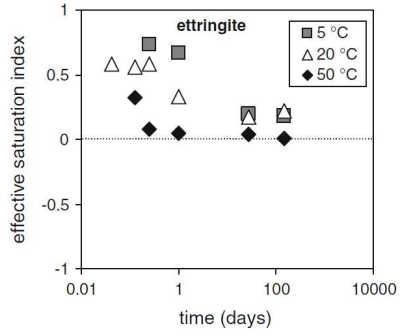
Calculation of saturation indices
=> indicate changes in solid phases

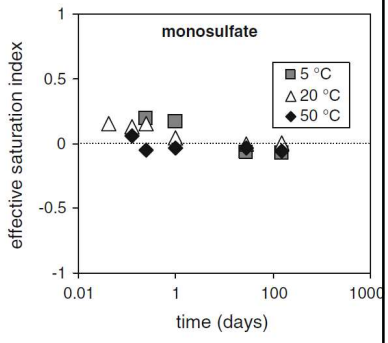
PC





CH, AFt, AFm at all times
Gypsum only first hours

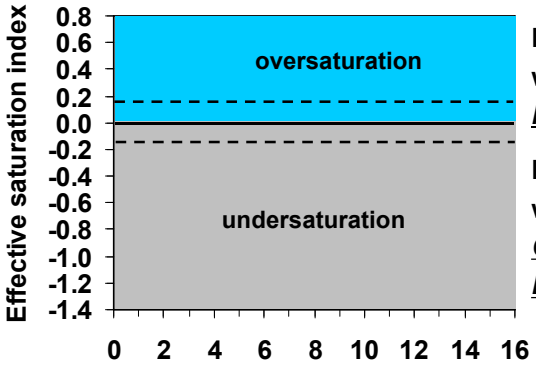




Lothenbach (2010) Materials and Structures 43, 1413-1433

Empa

Calculation of saturation indices



Phase in equilibrium with pore solution *Might* form

Phase not in equilibrium with pore solution *Cannot* form *Dissolves*

Derived from measured data e.g. pH, Ca_{tot}

$$SI = \log\left(\frac{IAP}{K_{S0}}\right) = \log\left(\frac{\{Ca^{2+}\}\{OH^-\}^2}{K_{S0\,portlandite}}\right)$$

theoretical solubility

GEMS used to calculalate $\{Ca^{2+}\}$ from Ca_{tot}

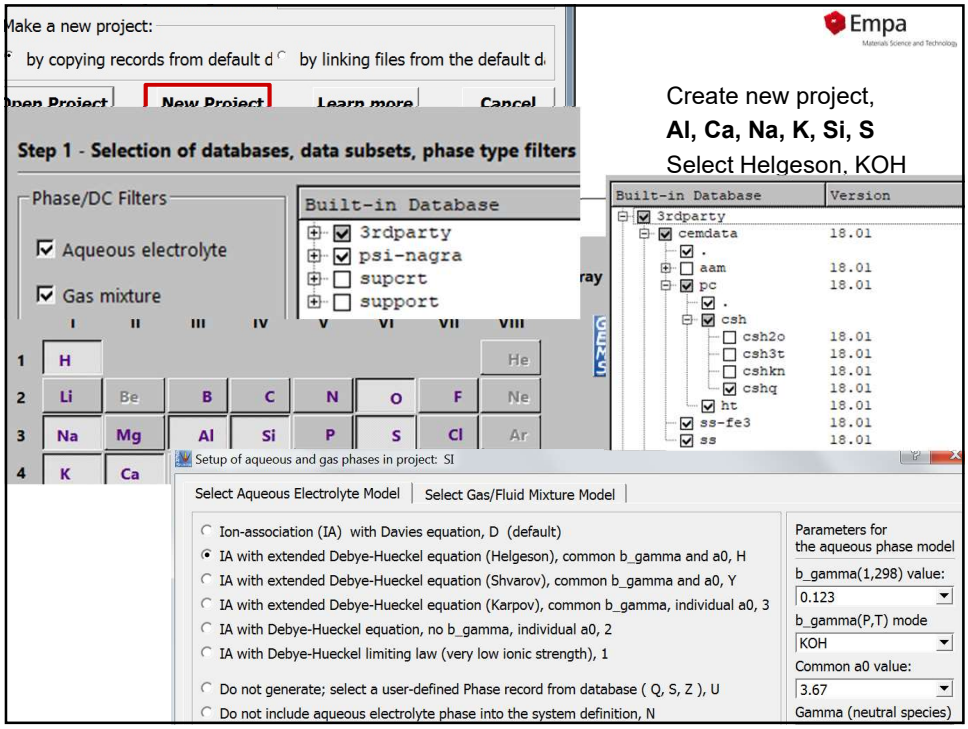
$IAP = ion\ activity\ product = measured\ concentrations$

56

Saturation indices: measured conc.

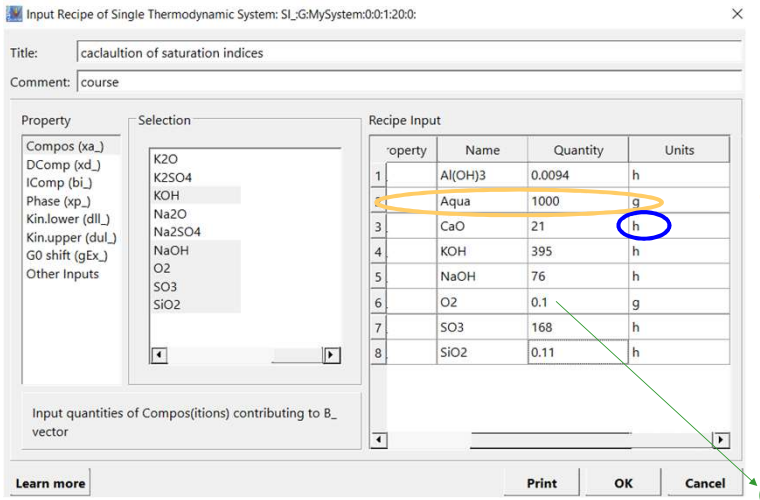
time days	Al	Ca	S	K	Na	Si	OH-	pH
	mmol/l	mmol/l	mmol/l	mmol/l	mmol/l	mmol/l	mmol/l	
0.04	0.0094	21	168	395	76	0.11	170	13.2
0.08	0.0043	21	175	404	77	0.13	164	13.2
0.17	0.0074	21	176	401	78	0.13	164	13.2
0.25	0.032	18	180	408	83	0.17	164	13.2
1	0.216	2.5	2.6	447	106	0.31	472	13.6
7	0.621	1.5	3.4	556	173	0.31	587	13.7
28	0.384	1.4	10	595	189	0.33	650	13.8
197	0.372	1.3	21	645	333	0.20	675	13.8
400	0.326	1.2	22	665	396	0.43	725	13.8

57



Create new project,
Al, Ca, Na, K, Si, S
Select Helgeson, KOH

Calculation of saturation inidices



1 kg of water

h: mmol

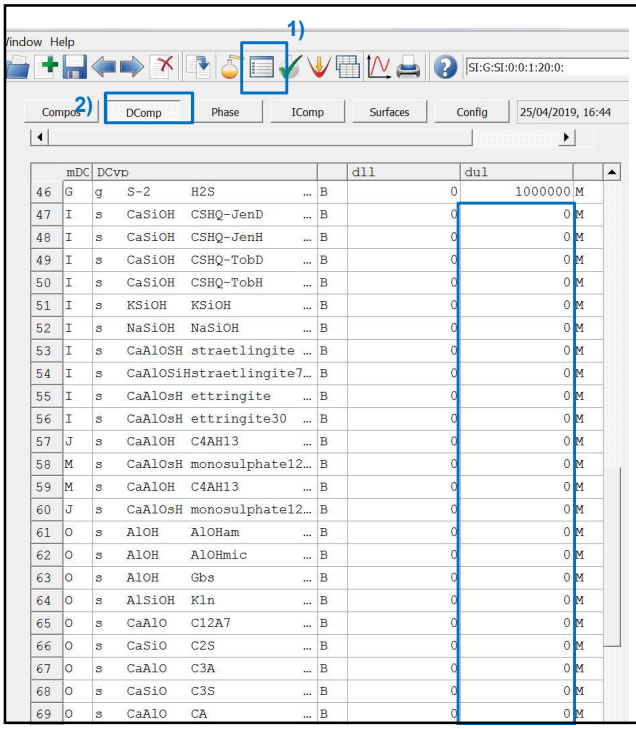
=> mmol/l

O_2 => oxidising cond.

Al(OH)3, CaO, KOH, NaOH, SO3, SiO2 used as proxy for measured total Ca, Al, …concentrations [mmol/l]

=> Input of uncharged species

59



3) Scroll down to 2nd table

4) Select all dul of solids

5) Press F8, 0, Ok-do it

dul = upper limit

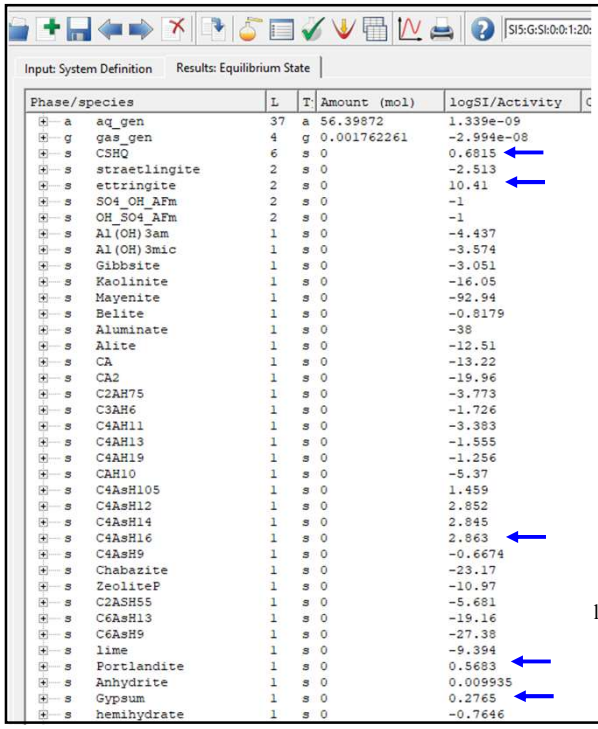
dul = 0

Solid cannot form

But saturation is calculated

dll = lower limit

60



Input: System Definition | Results: Equilibrium State

Phase/species	L	T	Amount (mol)	logSI/Activity
aq_gen	37	a	56.39872	1.339e-09
gas_gen	4	g	0.001762261	-2.994e-08
CSHQ	6	s	0	0.6815
straetlingite	2	s	0	-2.513
ettringite	2	s	0	10.41
SO4_OH_AFm	2	s	0	-1
OH_SO4_AFm	2	s	0	-1
Al(OH)3am	1	s	0	-4.437
Al(OH)3mic	1	s	0	-3.574
Gibbsite	1	s	0	-3.051
Kaolinite	1	s	0	-16.05
Mayenite	1	s	0	-92.94
Belite	1	s	0	-0.8179
Aluminate	1	s	0	-38
Alite	1	s	0	-12.51
CA	1	s	0	-13.22
CA2	1	s	0	-19.96
C2AH75	1	s	0	-3.773
C3AH6	1	s	0	-1.726
C4AH11	1	s	0	-3.383
C4AH13	1	s	0	-1.555
C4AH19	1	s	0	-1.256
CAH10	1	s	0	-5.37
C4AsH105	1	s	0	1.459
C4AsH12	1	s	0	2.852
C4AsH14	1	s	0	2.845
C4AsH16	1	s	0	2.863
C4AsH9	1	s	0	-0.6674
Chabazite	1	s	0	-23.17
ZeoliteP	1	s	0	-10.97
C2ASH55	1	s	0	-5.681
C6AsH13	1	s	0	-19.16
C6AsH9	1	s	0	-27.38
lime	1	s	0	-9.394
Portlandite	1	s	0	0.5683
Anhydrite	1	s	0	0.009935
Gypsum	1	s	0	0.2765
hemihydrate	1	s	0	-0.7646

Empa

PC pore solution after 1 hour
Oversaturated: logSI > 0
with respect to
- **C-S-H**
- **Ettringite**
- **Monosulfate**
- **Portlandite**
- **Gypsum**

$$\log SI = \log\left(\frac{IAP}{K_{S0}}\right) = \log\left(\frac{\{Ca^{2+}\}\{OH^-\}^2}{K_{S0\,portlandite}}\right)$$

61

Empa

Thermodynamic data

1. Databases
2. Solubility and speciation
3. Saturation indices

4. **Hydrates in cements**

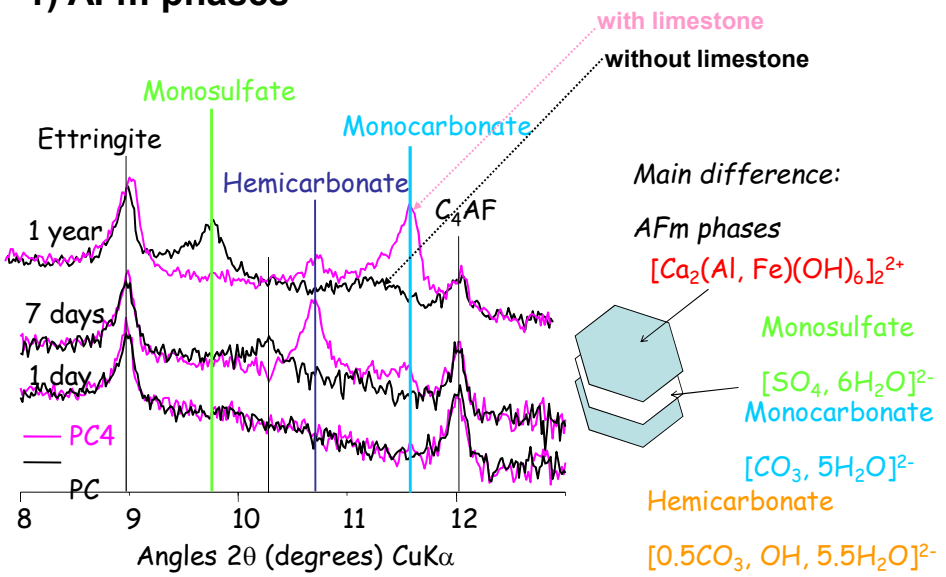
5. Details on how to manage thermodynamic data in GEMS
   => Self study

62

Main hydrates

Empa

1) AFm phases



Main difference:

AFm phases

$[Ca_2(Al, Fe)(OH)_6]_2^{2+}$

Monosulfate

$[SO_4, 6H_2O]^{2-}$

Monocarbonate

$[CO_3, 5H_2O]^{2-}$

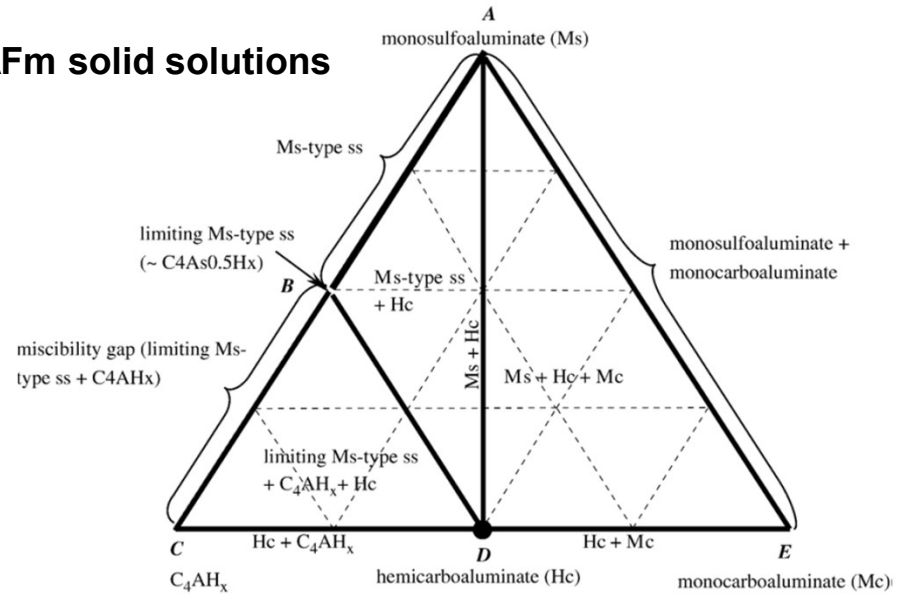
Hemicarbonate

$[0.5CO_3, OH, 5.5H_2O]^{2-}$

63

Empa

AFm solid solutions



Matschei ea 2007

64

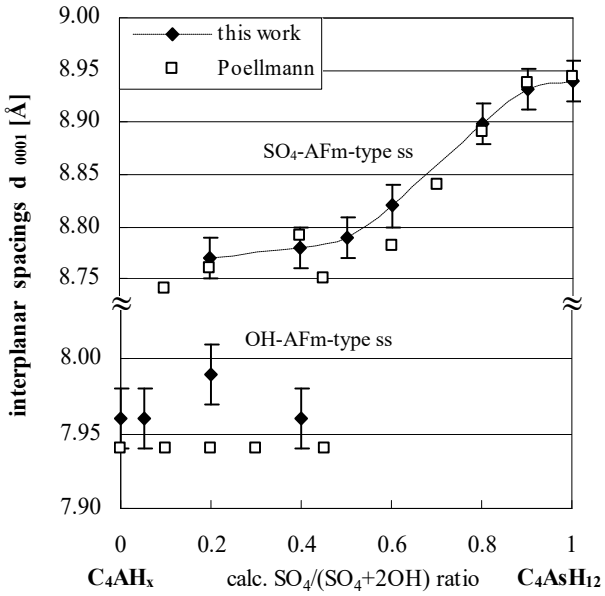
1) AFm phases

Empa

Characteristics solid solutions:

- XRD peak shift

- change of concentrations



C_4AH_{13} – monosulfate: solid solution

Matschei et al (2007) CCR 37, 118-130

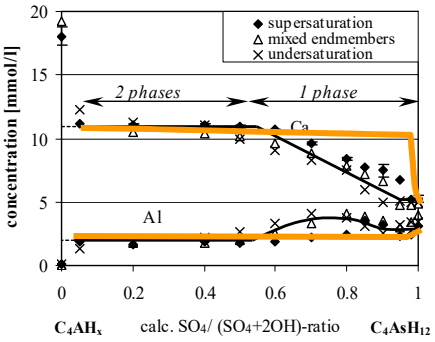
65

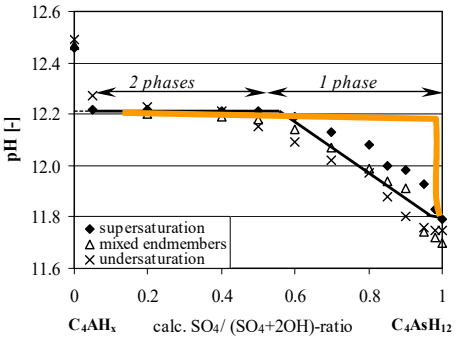
1) AFm phases

Empa

Characteristics of solid solution:
- peak shift in XRD
- continuous change of concentrations

Matschei et al (2007)





Effects of solid solution:
- stabilizes solids
- lowers aqueous concentrations

- miscibility gap 0.03-0.5
- no solid solution

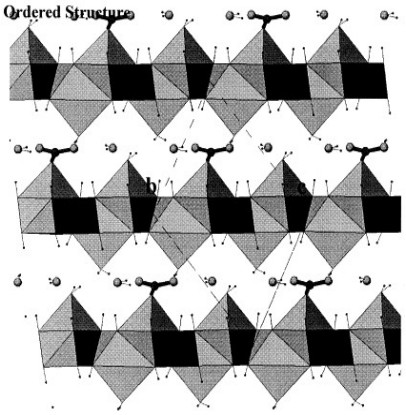
66

Solid solutions probable

- Similar charge
- Similar structure
- Similar size

AFm: $4CaO \cdot Al_2O_3 \cdot CaX \cdot nH_2O$

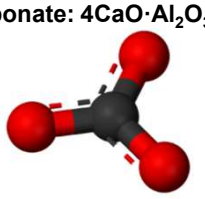
CO_3^{2-} H_2O



$[Ca_4Al_2(OH)_{12}]^{2+}$ Renaudin 1999

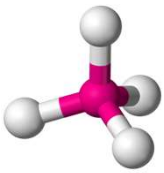
Monocarbonate: $4CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 11H_2O$

CO_3^{2-}

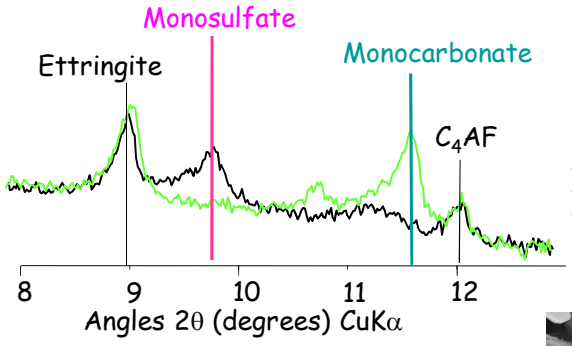


Monosulfate: $4CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O$

SO_4^{2-}

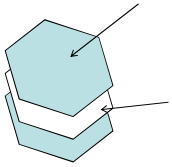


Solid solution CO_3-AFm – SO_4-AFm?

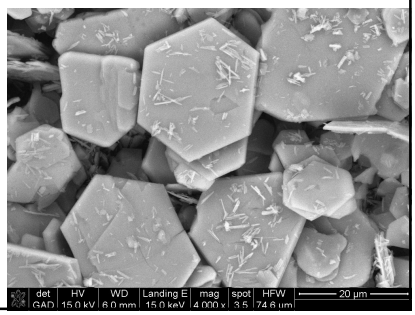


Main difference:
AFm phases

$[Ca_2(Al, Fe)(OH)_6]_2^{2+}$



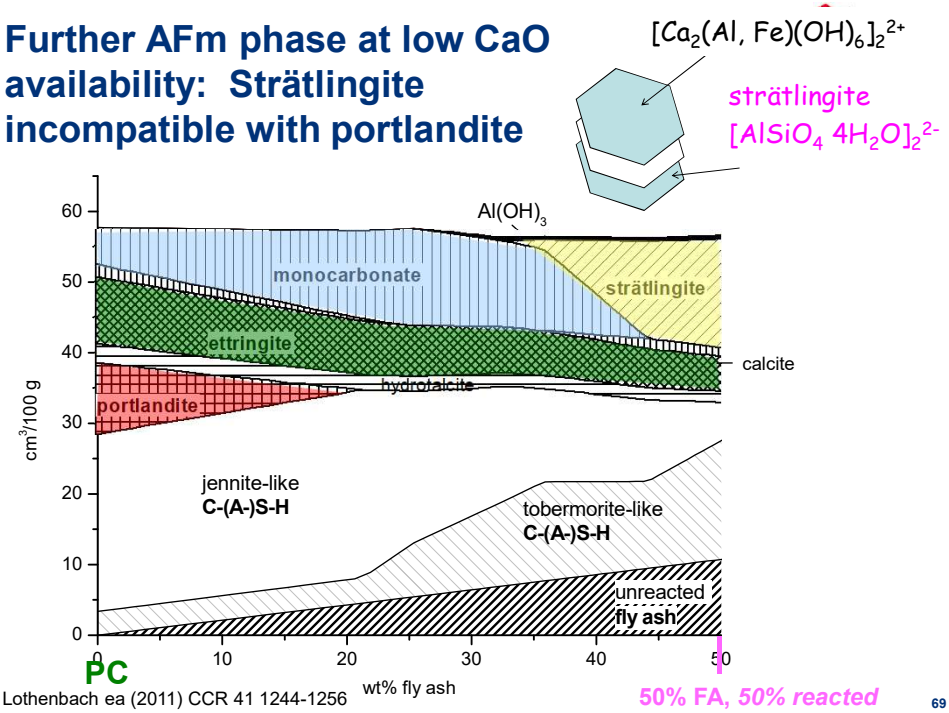
Monosulfate
$[SO_4, 6H_2O]^{2-}$
Monocarbonate
$[CO_3, 5H_2O]^{2-}$



Solid solution not probable:

- Similar charge ✓
- Similar structure -
- Similar size -

Further AFm phase at low CaO availability: Strätlingite incompatible with portlandite



Lothenbach ea (2011) CCR 41 1244-1256

69

Ettringite:

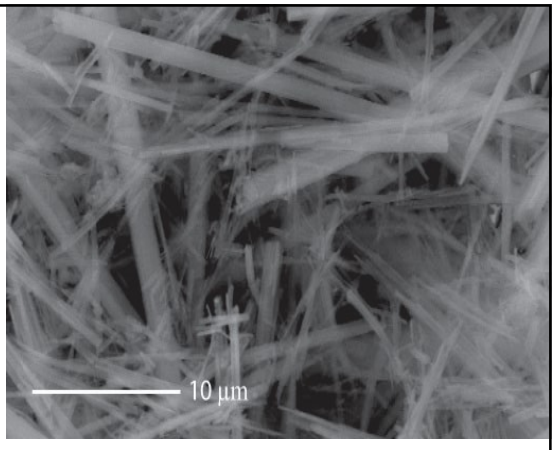
$C_6As_3H_{32}$

high water content

-> voluminous

-> low density 1.8 kg/dm^3

-> good space filling



Takes up other ions
(solid solutions)

-> Al ↔ Fe

-> SO_4^{2-} ↔ CO_3^{2-}, CrO_4^{2-}, …

solid solution with thaumasite

$C_6As_3H_{32} \leftrightarrow C_6S_2s_2c_2H_{30}$

70

Ettringite:

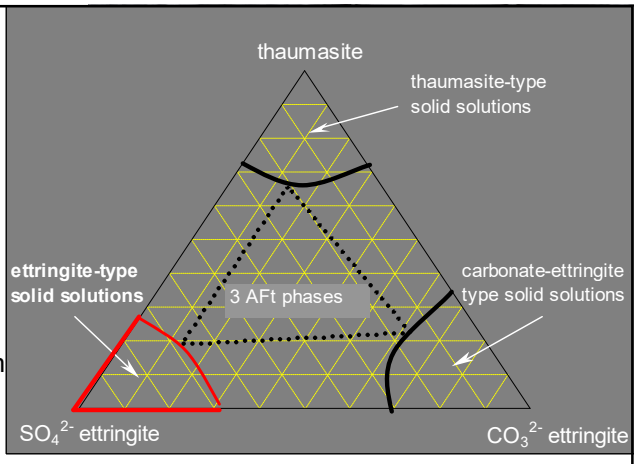
$C_6As_3H_{32}$

high water content

-> voluminous

-> low density 1.8 kg/dm

-> good space filling



Takes up other ions
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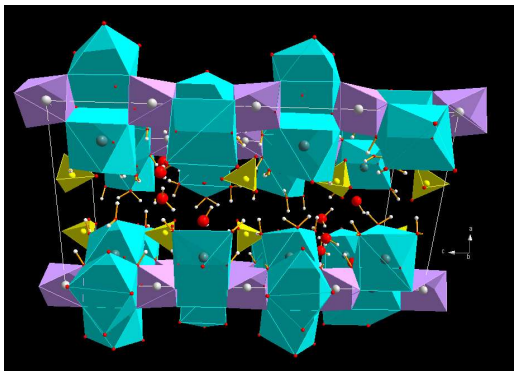
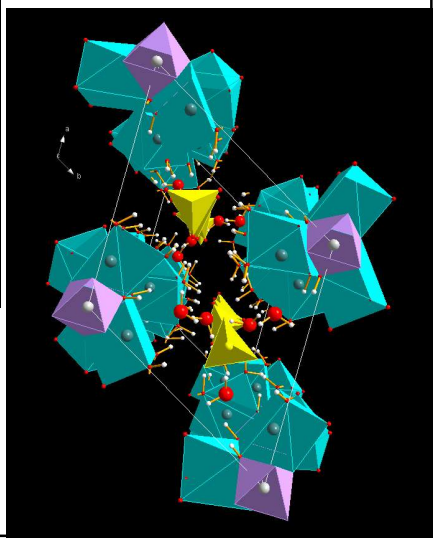
solid solution with thaumasite

$C_6As_3H_{32} \leftrightarrow C_6S_2s_2c_2H_{30}$

71

Empa
Materials Science and Technology





ettringite
crystal system: hexagonal
a=1.12 nm
c=2.14 nm

* F. Goetz- Neunuhoeffer et al. Powder diffraction 21 (2006) 4-11

Hydrogarnets:

$C_3AS_xH_{6-2x}$

Solid solutions

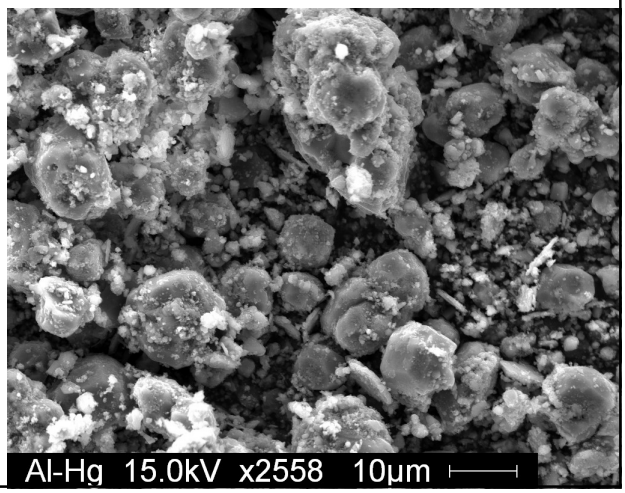
-> Al ↔ Fe

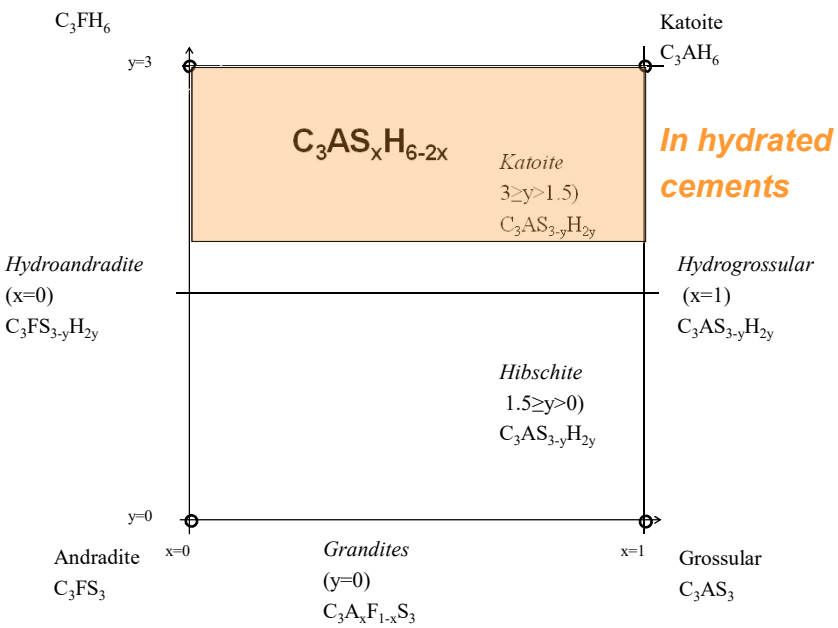
-> SiO_2^0↔ $2H_2O$

low water content

-> higher density

> 2.5 kg/dm^3

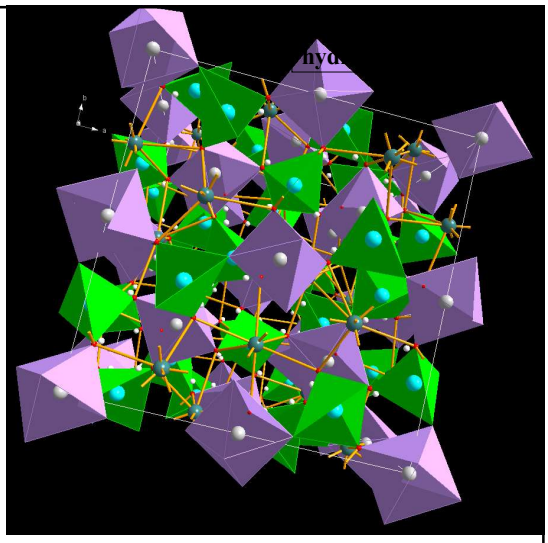




74

Hydrogarnets:

$C_3AS_xH_{6-2x}$



$Ca_3 Al_2 Si_{1.092} O_{12} H_{7.632}$

Katoite (y=1.9):

crystal system: cubic

a=1.22 nm

* Ferro et al. European J. Min. 15 (2003) 419- 426

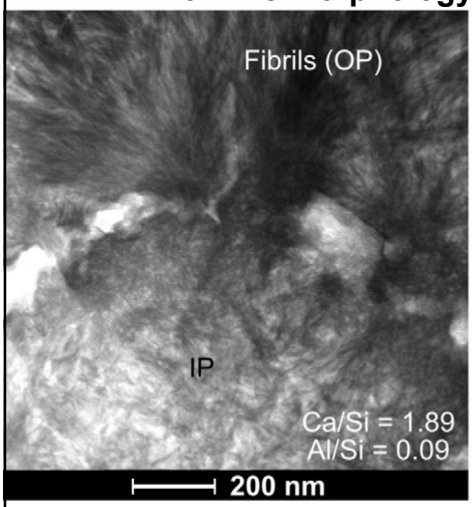
75

Empa

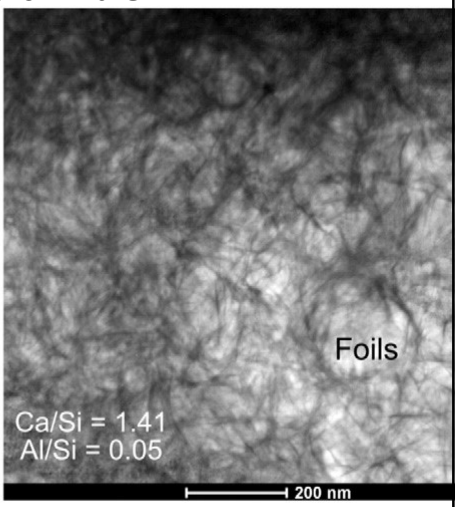
Materials Science and Technology

C-S-H in cements

Foil like morphology at low Ca/Si



a) Plain cement (PC), 90 days, 20°C



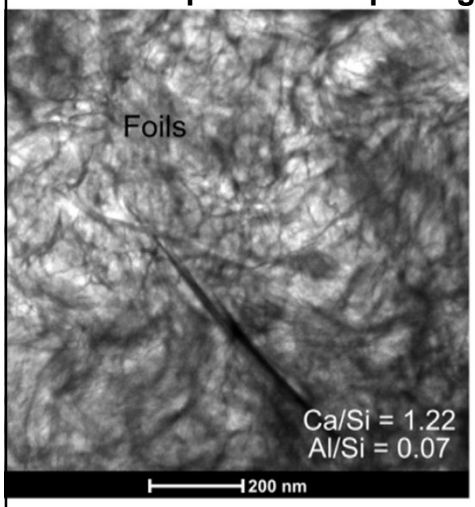
(b) PC 10SF, 90 days, 20°C

Rossen ea (2015) CCR 75

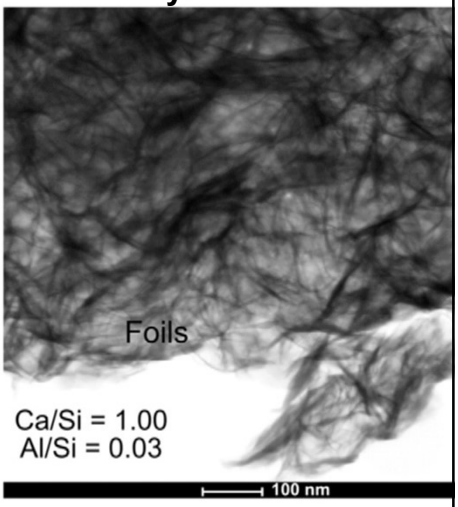
76

C-S-H in cements and synthetic C-SH

Comparable morphology in PC and synthetic C-S-H



(c) PC(Q) 20SF, 90 days, 20°C

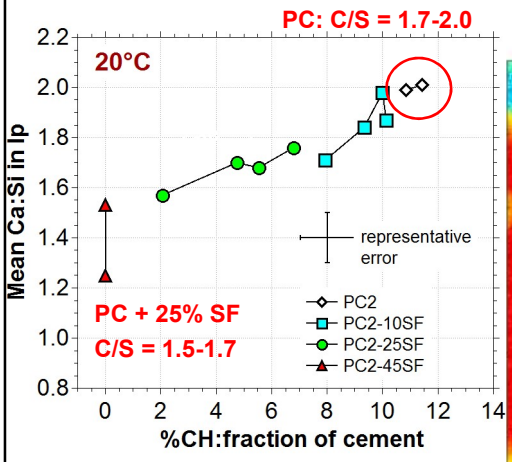


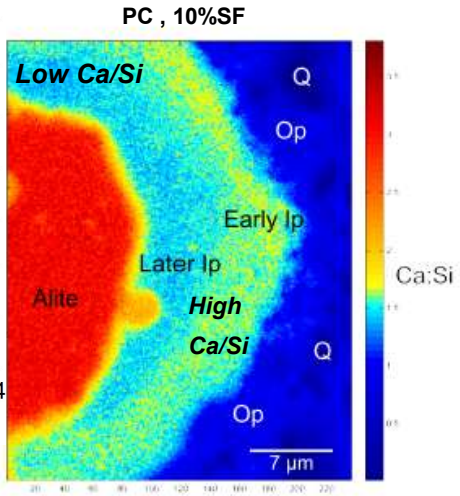
(d) Synthetic C-S-H, 20°C

Rossen ea (2015) CCR 75

77

C-S-H in Pastes





PC + SCM's:

C-S-H composition changes with time as CH is consumed

Rossen ea (2015) CCR

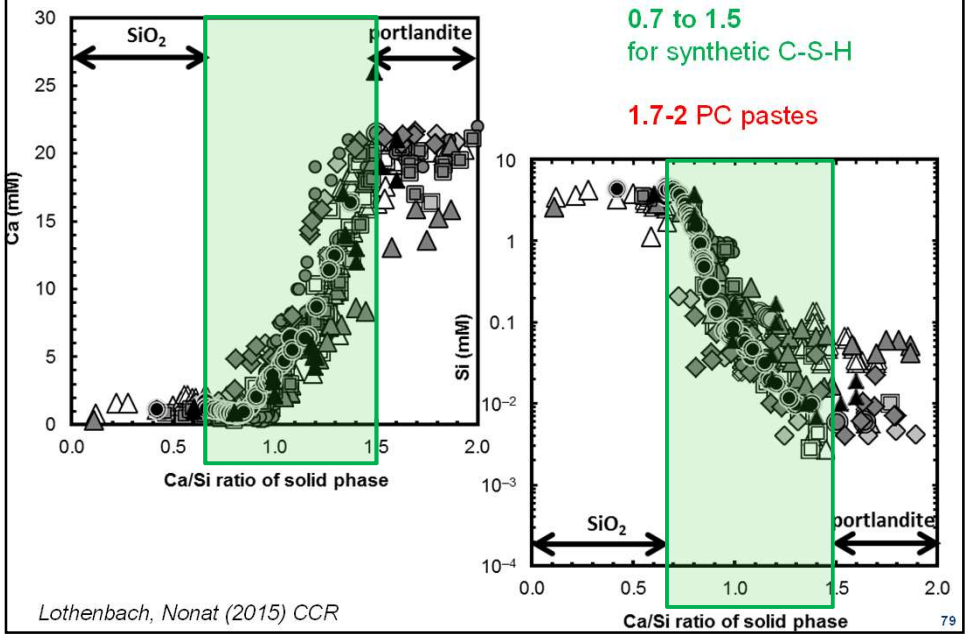
78

C-S-H: range of compositions

Empa

Ca/Si =
0.7 to 1.5
for synthetic C-S-H

1.7-2 PC pastes

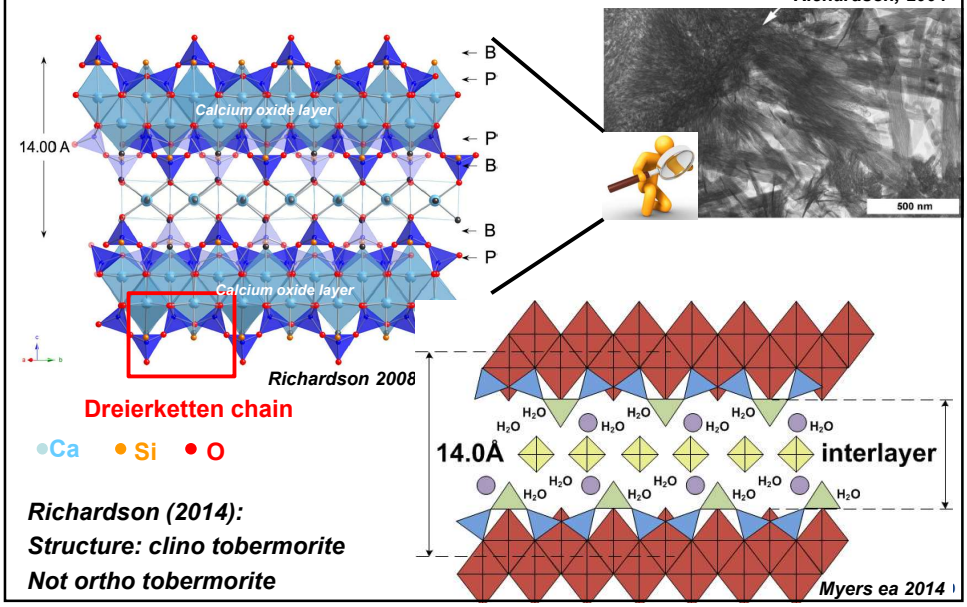


Lothenbach, Nonat (2015) CCR

79

C-S-H
=> structurally imperfect tobermorite

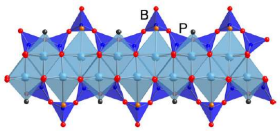
Richardson, 2004



Richardson (2014):
Structure: clino tobermorite
Not ortho tobermorite

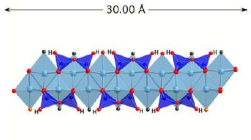
C-S-H structure: Variation of Ca/Si ratio

Richardson 2008



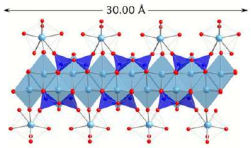
Ca/Si=0.67

- Infinite chain



Ca/Si=1.0

- Dimer, pentamer, …



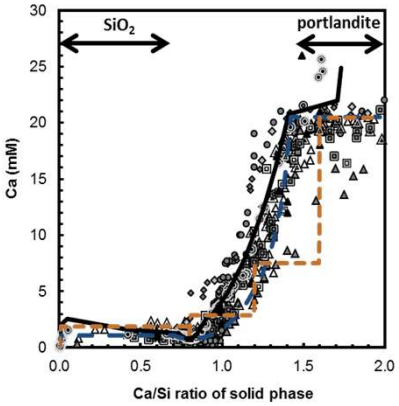
Ca/Si=1.50

- Mainly dimer
- Ca in the interlayer
- Intergrowth with CH possible

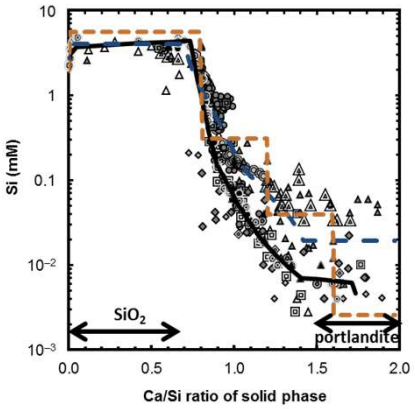
81

Different types of thermodynamic (geochemcial) models for C-S-H

[Ca]



[Si]



3 different CSH

$C_{0.8}SH_{1.5}$
$C_{1.2}SH_{2.1}$
$C_{1.6}SH_{2.6}$

Blanc et al. (2010) CCR 40, 851-866

Solid solution

infinite $C_{0.67}SH_{1.8}$
pentamer $CSH_{2.0}$
dimer $C_{1.5}SH_{2.5}$

Kulik (2011) CCR 41, 477-495

Surface reaction model

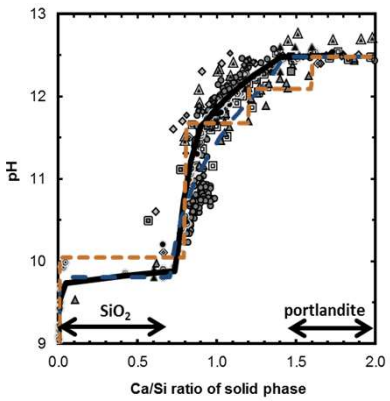
Pentamer $C_{0.8}SH_{1.6}$
dimer CSH_2
dimer $C_{1.5}SH_{2.5}$

Haas, Nonat (2015) CCR 68, 124-138

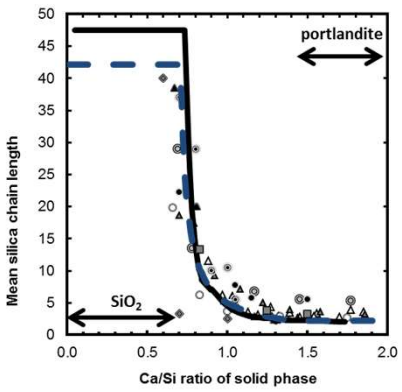
82

Different types of thermodynamic (geochemcial) models for C-S-H

pH



Mean Chain Length



3 different CSH

$C_{0.8}SH_{1.5}$
$C_{1.2}SH_{2.1}$
$C_{1.6}SH_{2.6}$

Solid solution

infinite	$C_{0.67}SH_{1.8}$
pentamer	$CSH_{2.0}$
dimer	$C_{1.5}SH_{2.5}$

Surface reaction model

Pentamer	$C_{0.8}SH_{1.6}$
dimer	CSH_2
dimer	$C_{1.5}SH_{2.5}$

Haas, Nonat (2015) CCR 68, 124-138

Blanc et al. (2010) CCR 40, 851-866 *Kulik (2011) CCR 41, 477-495*

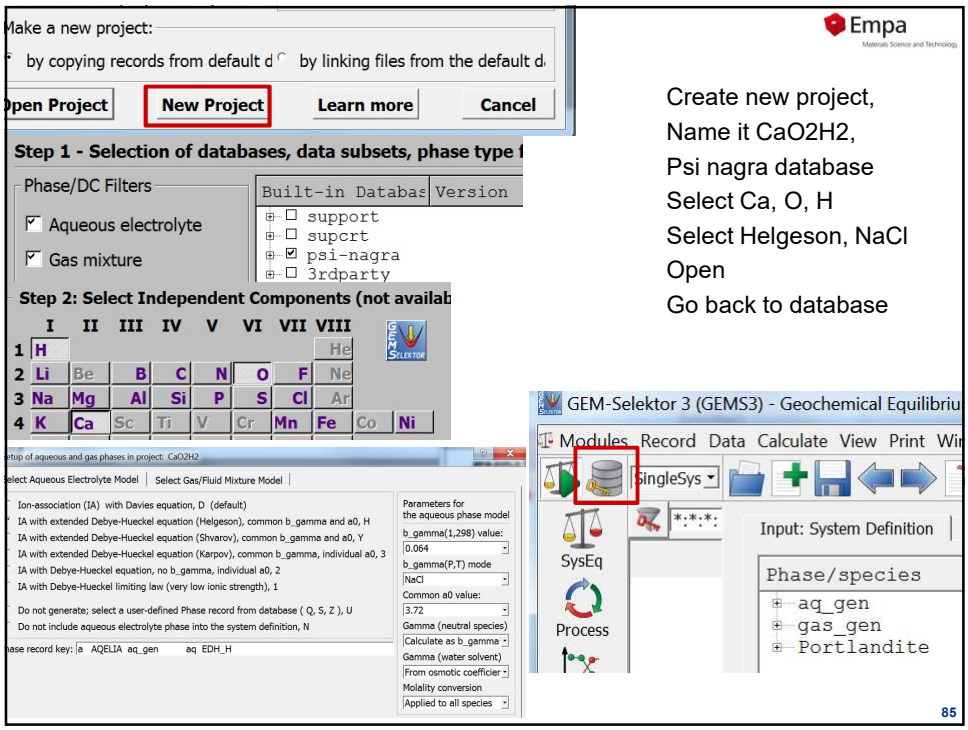
83

Thermodynamic data

1. Databases
2. Portlandite solubility and speciation
3. Saturation indices
4. Hydrates
5. **How to create new entries for thermodynamic data in GEMS:**
   - a) **Dcomp**
   - b) **ReacDC**
   - c) **Temperature and pressure plots**
   - d) **Thermodynamic phases**

=> Self study

84



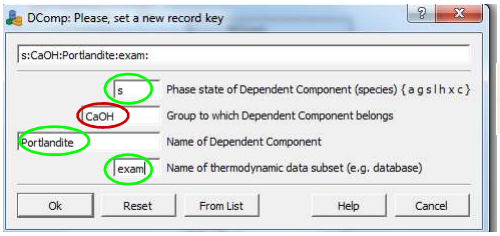
Empa

Create new project,
Name it CaO2H2,
Psi nagra database
Select Ca, O, H
Select Helgeson, NaCl
Open
Go back to database

DComp– creation of new entries

Empa

1) Make a new entry: Record: Create(New)



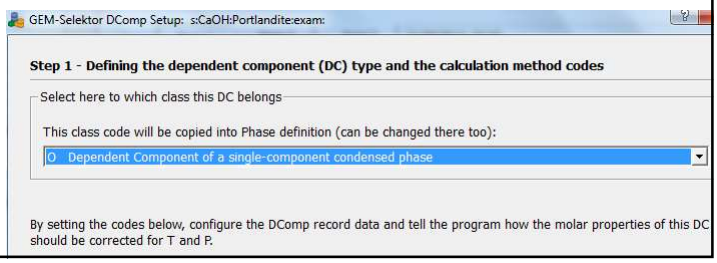
Phase state (s … solid; a … aqueous; g … gaseou
Group id (e.g. elements of chem composition
name
Comment (e.g. cem … cement; Exam: Example)

Leave default values if including a single phase or an ideal solid solution
<u>Optional:</u> Choice of mixing model if a non ideal solid solution is included

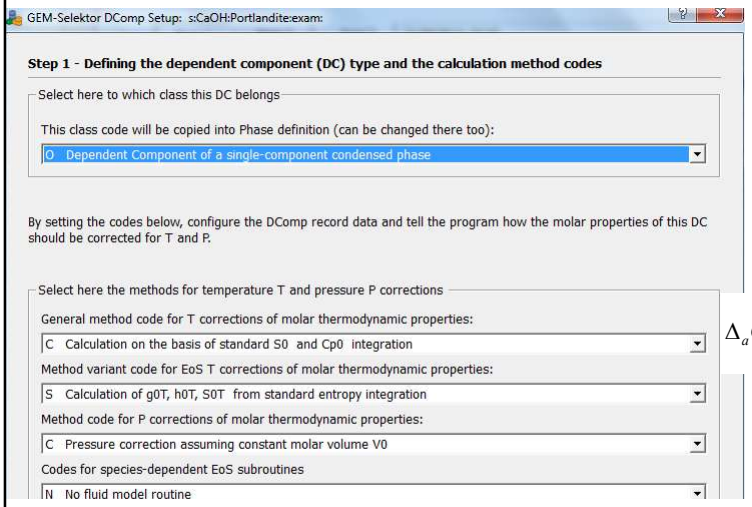
O: solid phase

S: Aqueous species

M: Major end-member *(solvent)*
J: Junior end-member *(solute)*



DComp– creation of new entries



Optional parameters for experienced users, else leave default values

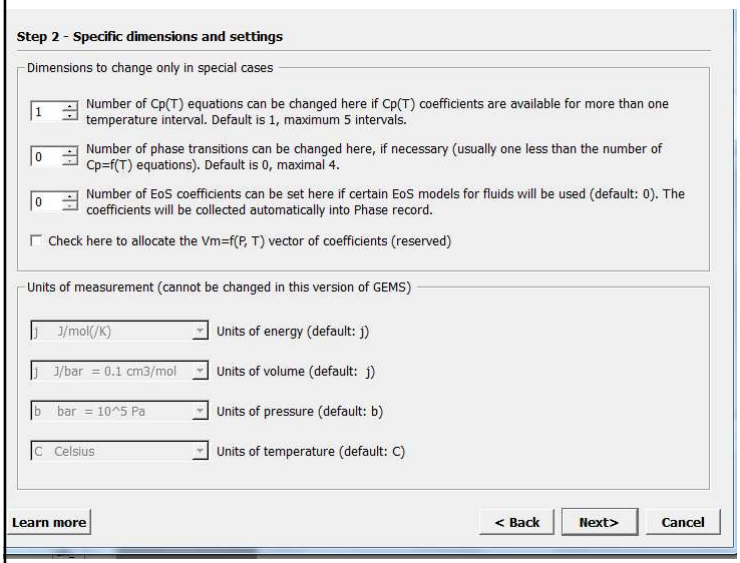
Default: "CS"

$$\Delta_a G^o_T = \Delta_f G^o_{T_0} - \int_{T_0}^{T} S^o_T dT$$

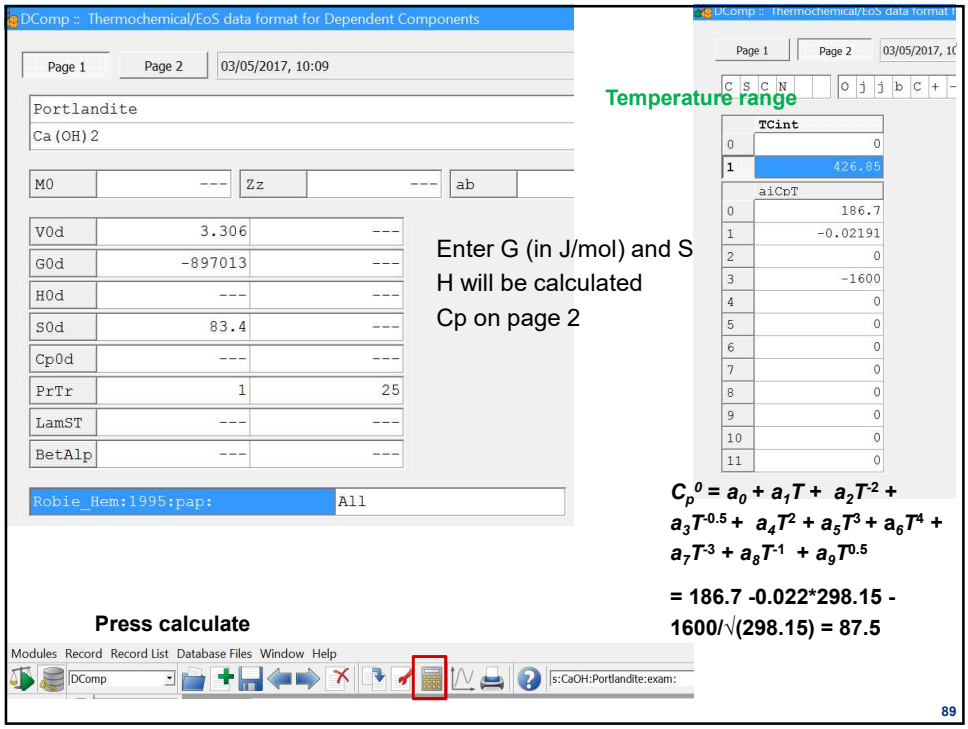
and "C"

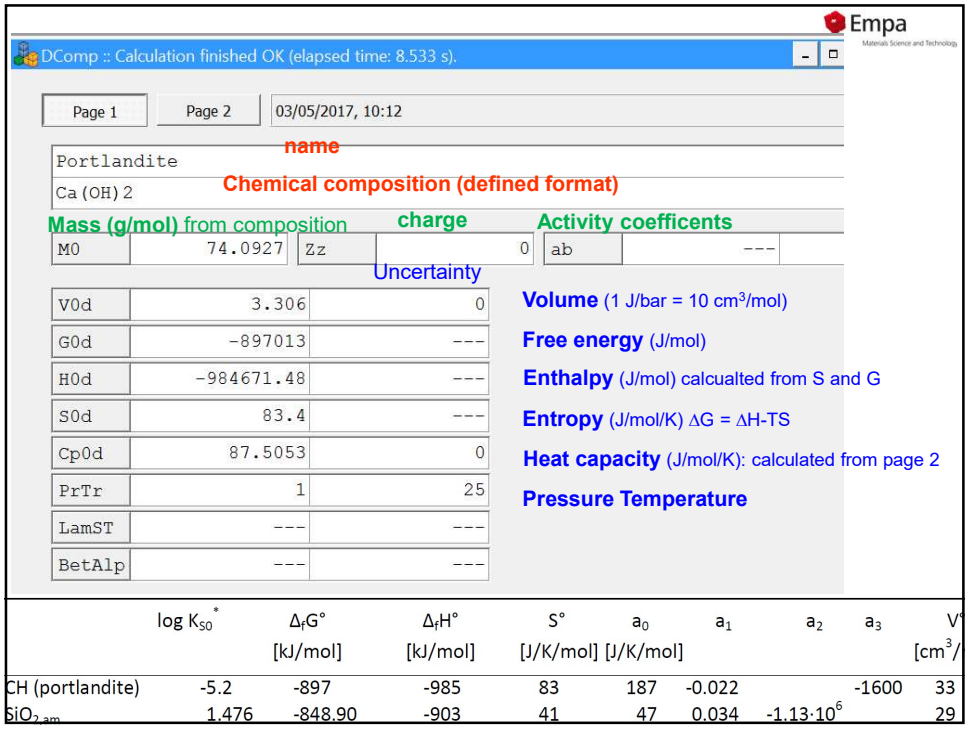
Alternatively, the "HKF" is used for aqueous species. *This optional vector contains empirical parameters of revised Helgeson- Kirkham- Flowers equation of state for calculation of standard partial molal properties of aqueous species up to 1000 oC and 5000 bar [1981HEL/KIR; 1997SHO/SAS]. The coefficients were imported from SPRONS92.DAT file [1992JOH/OEL] and its latest extension, SLOP98.DAT [1997SHO/SAS;*

DComp– creation of new entries



Optional parameters for experienced users, else leave default values





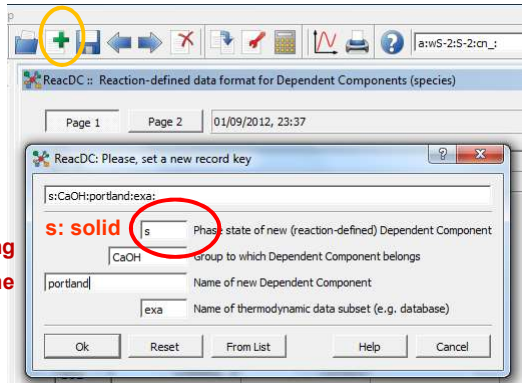
	log K_{s0}^*	$\Delta_f G°$ [kJ/mol]	$\Delta_f H°$ [kJ/mol]	S° [J/K/mol]	a_0 [J/K/mol]	a_1	a_2	a_3	V° [cm^3/
CH (portlandite)	-5.2	-897	-985	83	187	-0.022		-1600	33
$SiO_{2,am}$	1.476	-848.90	-903	41	47	0.034	$-1.13 \cdot 10^6$		29

3) GEMS: reactions (ReacDC): new

Portlandite solubility:

$Ca(OH)_2 = Ca^{2+} + 2OH^-$; log K = -5.2

$\{Ca^{2+}\}\{OH^-\}/\{Ca(OH)_2\} = 10^{-5.2}$

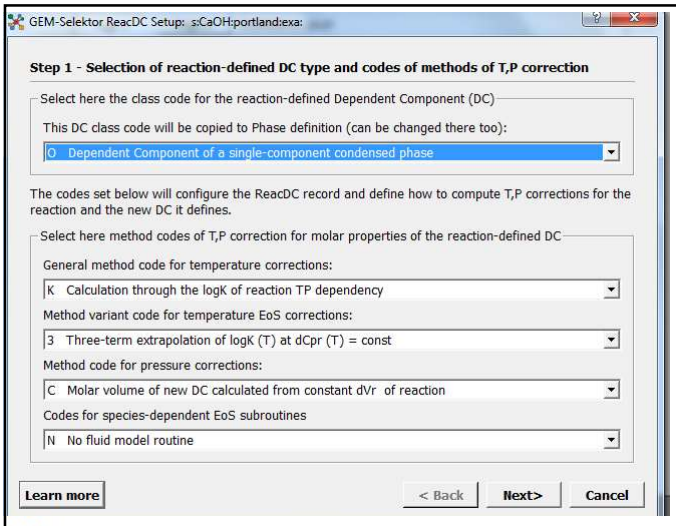


Elements:ordering

Component name

Data base: «example»

91



$$\log K_T = A_0 + A_2 T^{-1} + A_3 \ln T$$

(K) 3

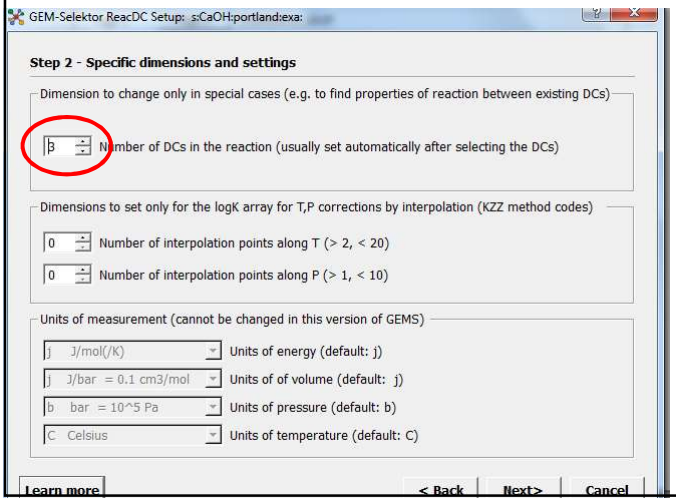
Three-term extrapolation of log*K (T)* at *dCpr(T)* = const (preferable). Enter non-[empty] values into the Cp0r[0,0] cell, and into either H0r[0,0] or S0r[0,0] cells (another must contain [empty]); enter a non-empty value in either logKr[0,0], logKr[0,1] or G0r[0,0] cells (the other two cells and G0r[0,1] must contain [empty]). Then re-calculate and save the record. Use this code combination also for the PRONSPREP calculation.

C

Molar volume of species V^o (in DComp) or dVr of reaction (in ReacDC) is assumed to be constant, independent of P and T (may be used for minerals up to a 1-2 kbar pressures at low-to-moderate temperatures).

3) GEMS: reactions (ReacDC): new

Portlandite solubility:
$Ca(OH)_2 = Ca^{2+} + 2OH^-$; log K = -5.2
$\{Ca^{2+}\}\{OH^-\}^2/\{Ca(OH)_2\} = 10^{-5.2}$

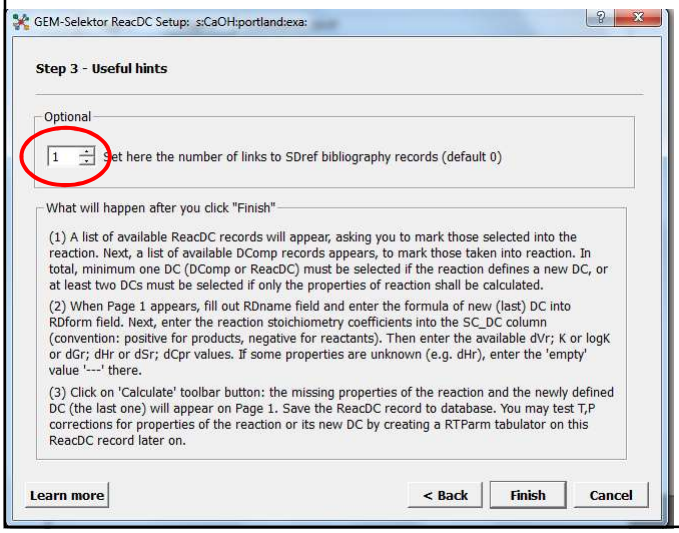


Ca^{2+}, OH^-, $Ca(OH)_2$

93

3) GEMS: reactions (ReacDC)

Portlandite solubility:
$Ca(OH)_2 = Ca^{2+} + 2OH^-$; log K = -5.2
$\{Ca^{2+}\}\{OH^-\}^2/\{Ca(OH)_2\} = 10^{-5.2}$

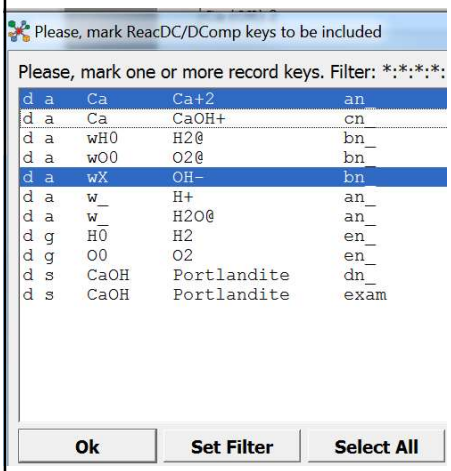


Literature reference

94

3) GEMS: reactions (ReacDC)

Portlandite solubility:
$Ca(OH)_2 = Ca^{2+} + 2OH^-$; log K = -5.2
$\{Ca^{2+}\}\{OH^-\}^2/\{Ca(OH)_2\} = 10^{-5.2}$



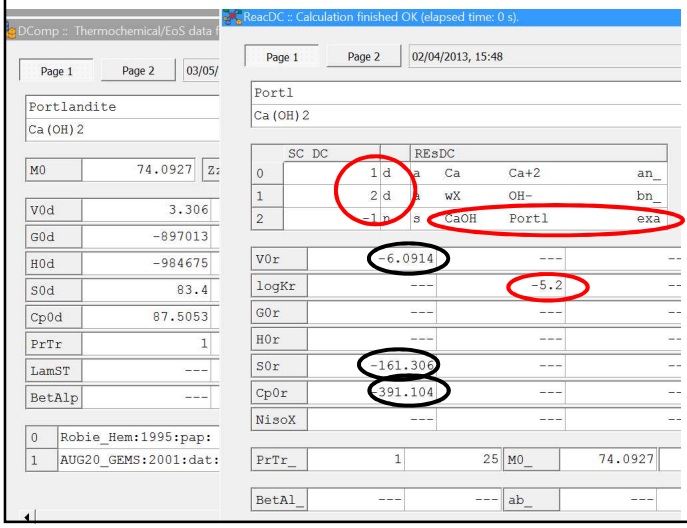
Chose existing compounds;

New compound «$Ca(OH)_2$» will be made by the programme

95

3) GEMS: reactions (ReacDC)

Portlandite solubility:
$Ca(OH)_2 = Ca^{2+} + 2OH^-$; log K = -5.2
$\{Ca^{2+}\}\{OH^-\}^2/\{Ca(OH)_2\} = 10^{-5.2}$



Reaction coefficients

New component

Volume changes

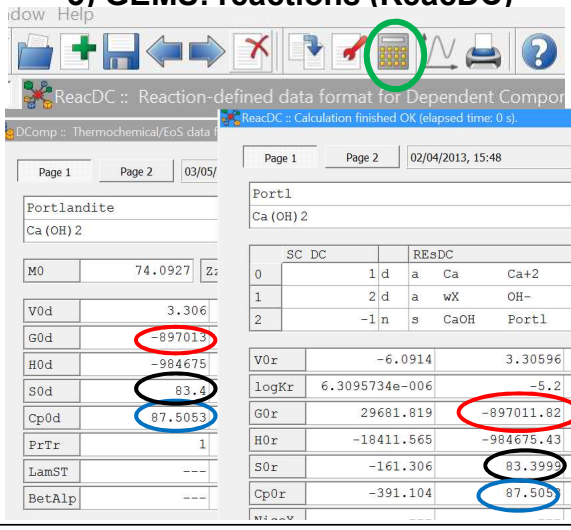
Log K

S reaction

Cp reaction

96

3) GEMS: reactions (ReacDC)



Portlandite solubility:

$Ca(OH)_2 = Ca^{2+} + 2OH^-$; log K = -5.2

$\{Ca^{2+}\}\{OH^-\}^2/\{Ca(OH)_2\} = 10^{-5.2}$

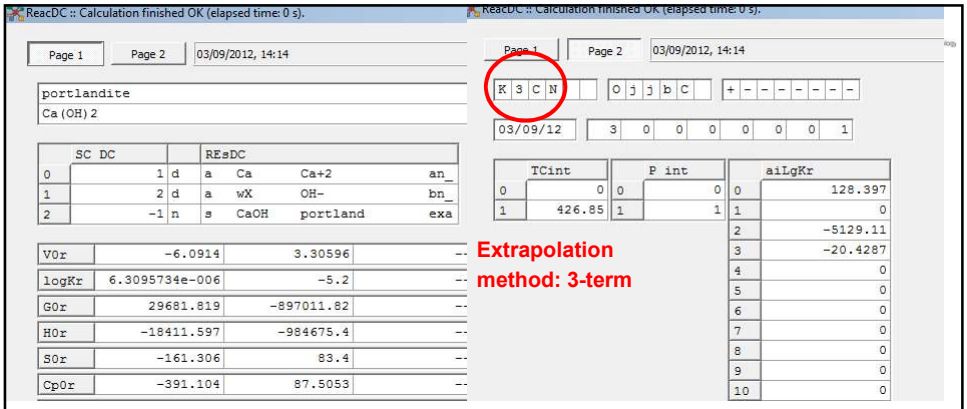
Volume

Gf

S

Cp

	log K_{S0}^*	$\Delta_f G°$ [kJ/mol]	$\Delta_f H°$ [kJ/mol]	S° [J/K/mol]	a_0 [J/K/mol]	a_1	a_2	a_3	V° [cm^3/
CH (portlandite)	-5.2	-897	-985	83	187	-0.022		-1600	33
SiO_2 (quartz)	1.476	-848.90	-903	41	47	0.034	$-1.13 \cdot 10^6$		29



Extrapolation method: 3-term

Calculates automatically temperature dependent function of the solubility product, depending on the initial data input

see C:\GEMS337\Gems3-app\Resources\doc\pdf\T-corrections-Reac.pdf

3-term extrapolation $\Delta Cp_T = \Delta Cp_{T_0} = const$

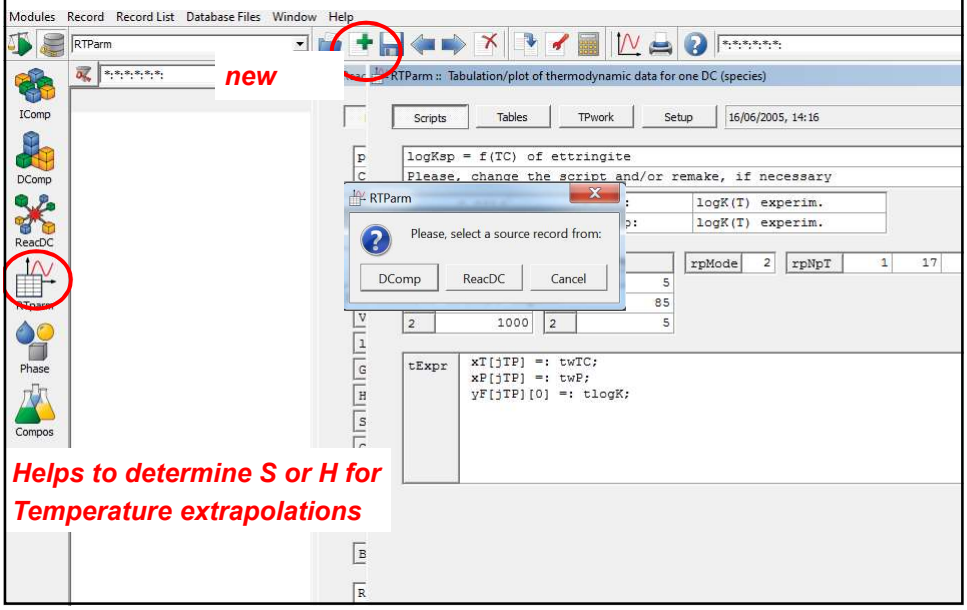
$$\log K_T = A_0 + A_2 T^{-1} + A_3 \ln T$$

$$A_0 = \frac{0.4343}{R} \cdot \left[\Delta_r S^0_{T_0} - \Delta_r Cp_{T_0} (\ln T_0 + 1)\right]$$

$$A_2 = -\frac{0.4343}{R} \cdot (\Delta_r H^0_{T_0} - \Delta_r Cp_{T_0} T_0)$$

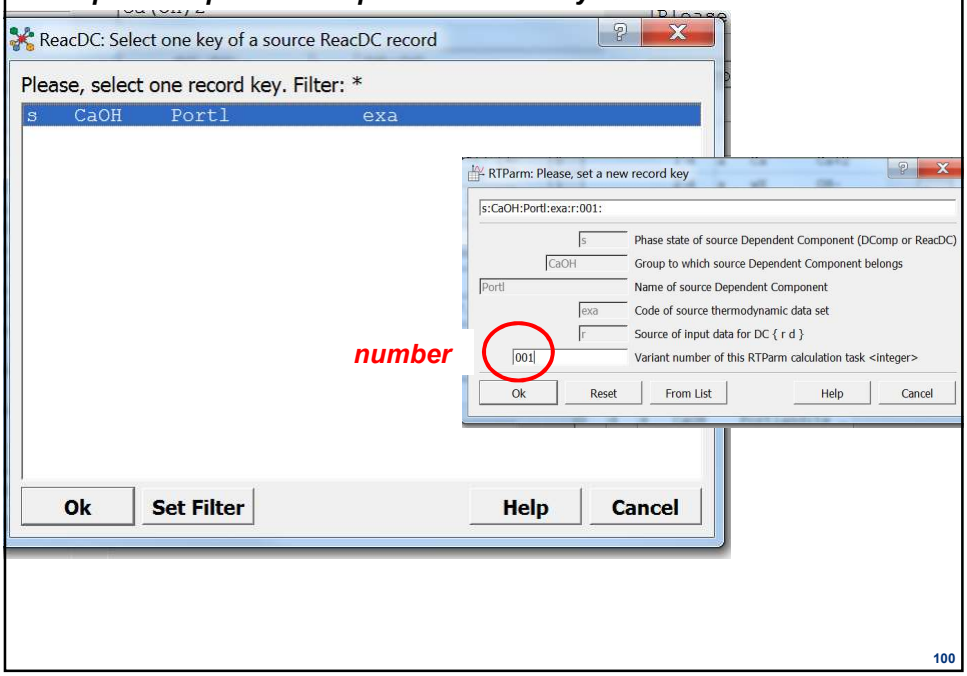
$$A_3 = \frac{0.4343}{R} \cdot \Delta_r Cp_{T_0} = \frac{0.4343}{8.3145} \cdot -391.1 = -20.43$$

4.) Plot of temperature/pressure dependent thermodynamic data



Helps to determine S or H for Temperature extrapolations

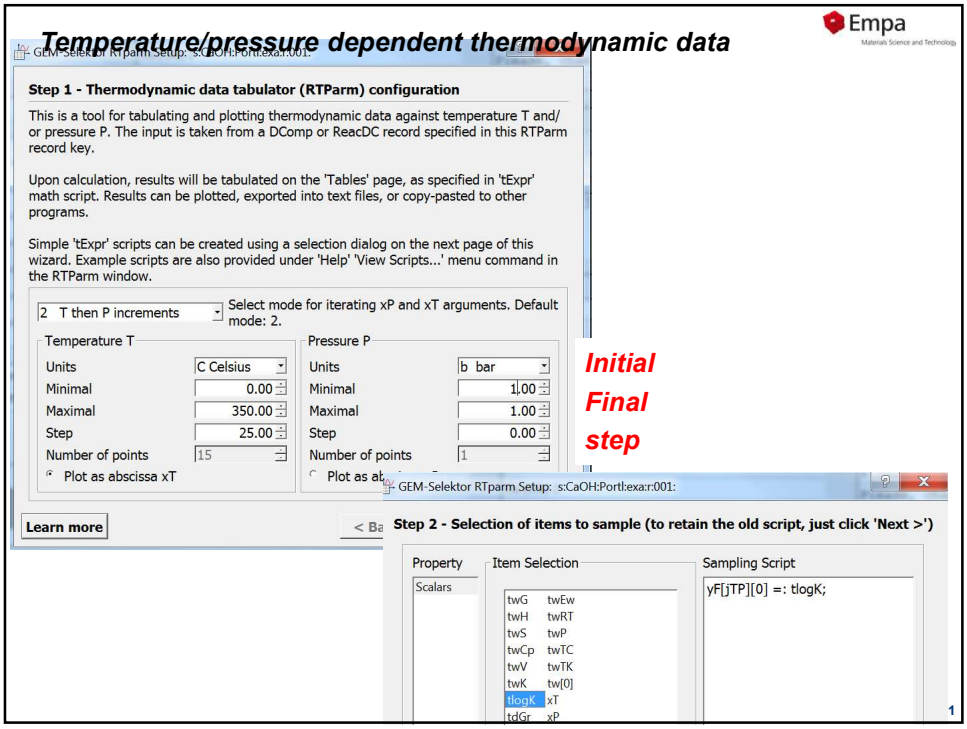
Temperature/pressure dependent thermodynamic data



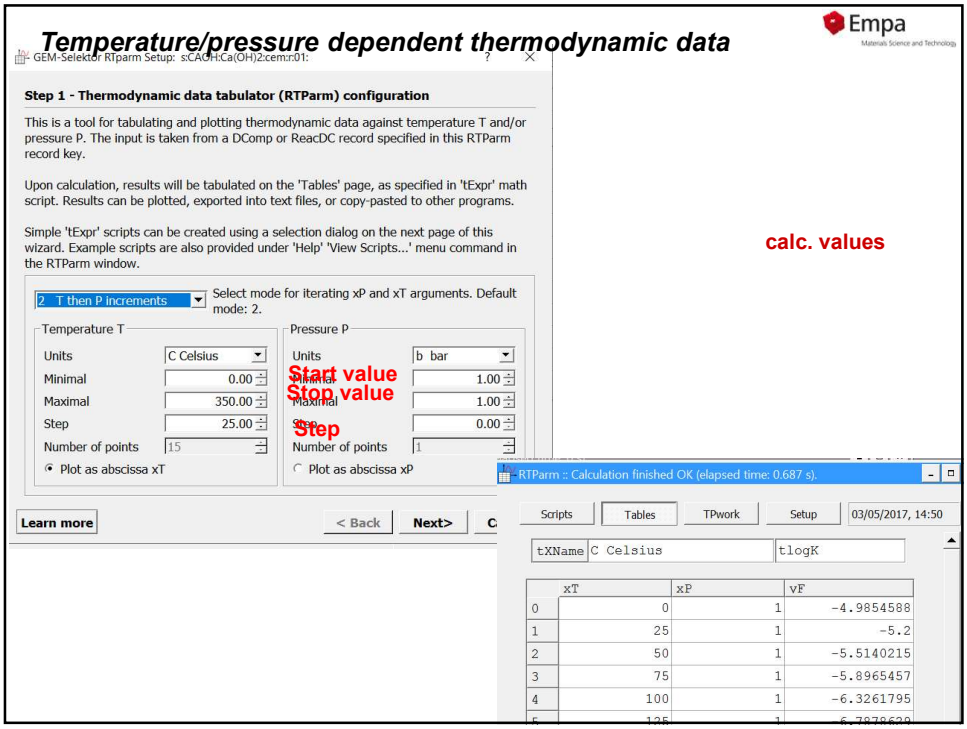
number

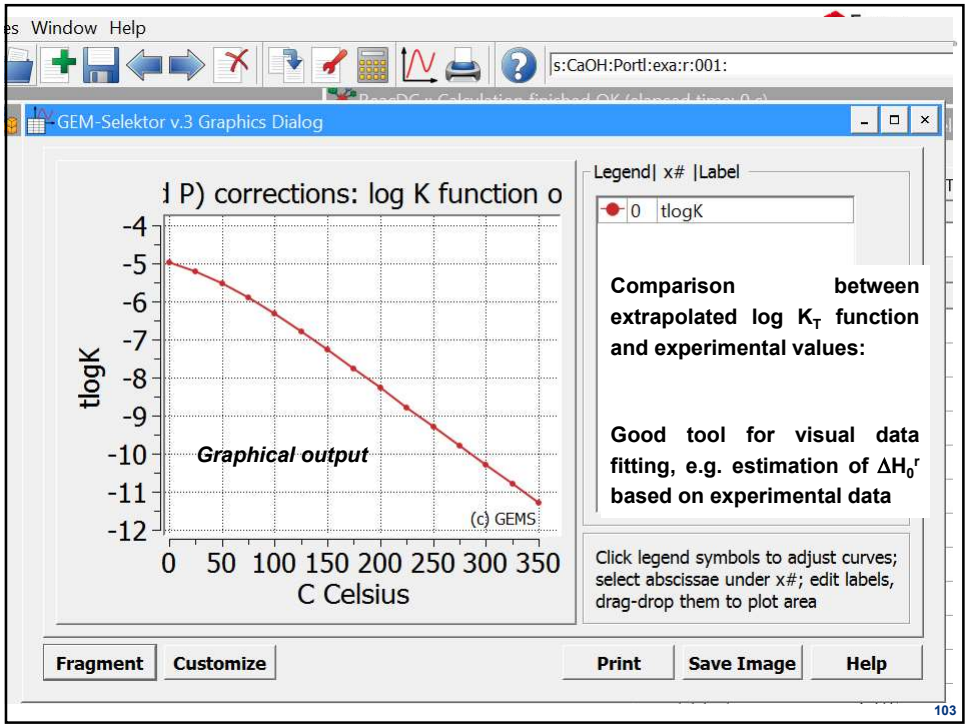
100

Temperature/pressure dependent thermodynamic data



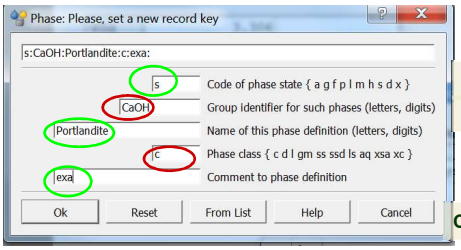
Temperature/pressure dependent thermodynamic data





5.) Thermodynamic Phases – creation of entries

Empa



Phase state (s … solid; a … aqueous; g … gaseous)

Group id (e.g. elements of chem composition name

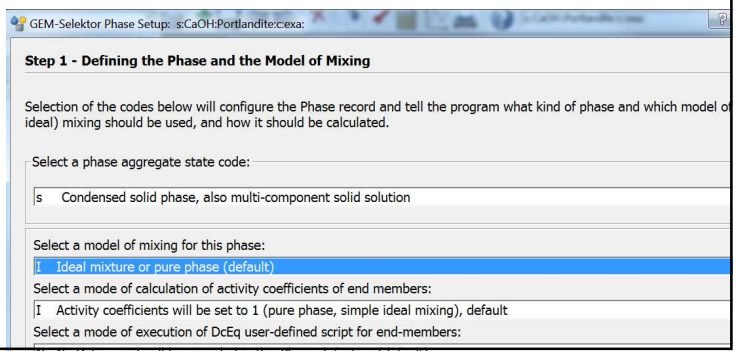
c: condensed solid (single compound); ss: solid solution; aq: Aqueous

Comment (e.g. cem: cement; exa: example)

Leave default values if including a single phase or an ideal solid solution

Optional: Choice of mixing model if a non ideal solid solution is included

I for Single phase or ideal solid solution:



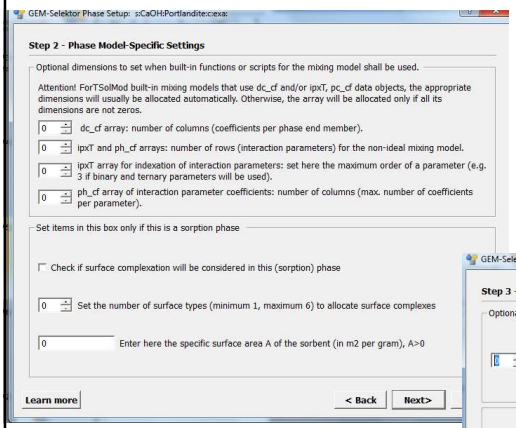
5.) Thermodynamic Phases – creation of entries

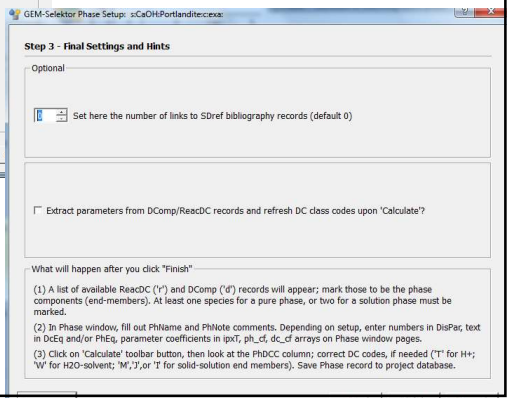
I	Ideal mixture (also multi-site) or pure phase, default
M	Binary subregular Margules solid-solution model
G	Binary Redlich-Kister solid-solution model
T	Ternary regular Margules solid-solution model
R	Regular multicomponent solid- or liquid solution model
V	Van Laar multicomponent solid- or liquid solution model
K	Redlich-Kister multicomponent solid- or liquid solution model
B	Microscopic a(symmetric) multicomponent solid-solution model (reserved)
L	NRTL multicomponent liquid solution model
W	Wilson multicomponent liquid solution (or ion exchange) model

Optional parameters only for experienced users, otherwise leave default value "I" !

105

5.) Thermodynamic Phases – creation of entries



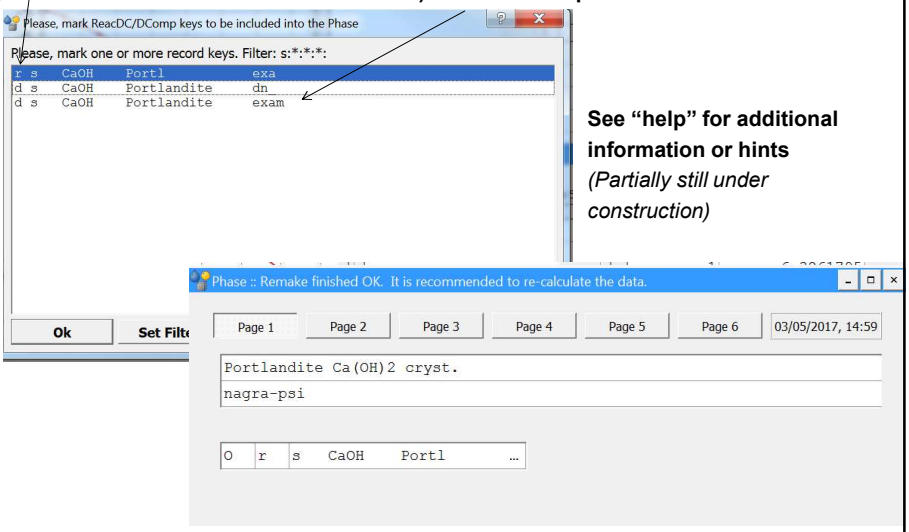


Optional parameters only for experienced users, otherwise leave default values

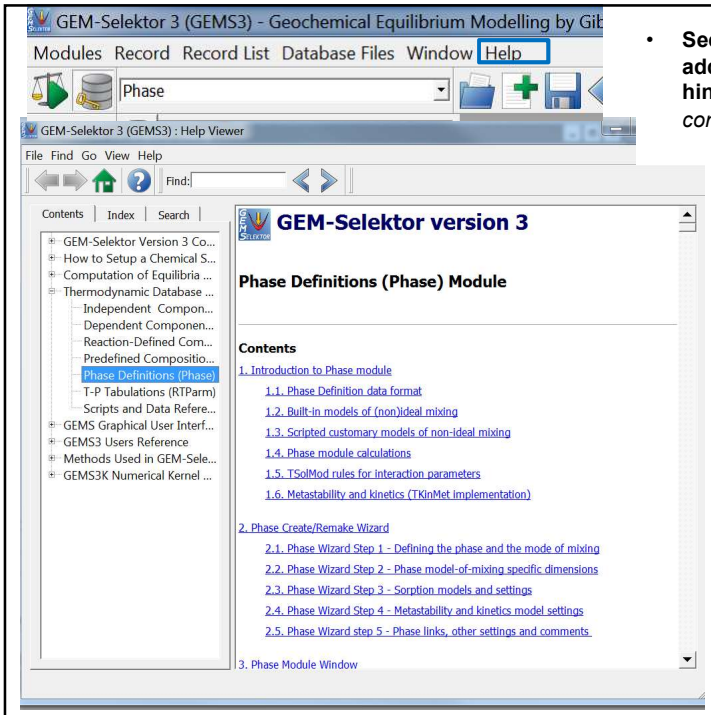
5.) Thermodynamic Phases – creation of entries

Mark dependent component to be included in the project database

a) either from ReacDC **b) or from DComp**



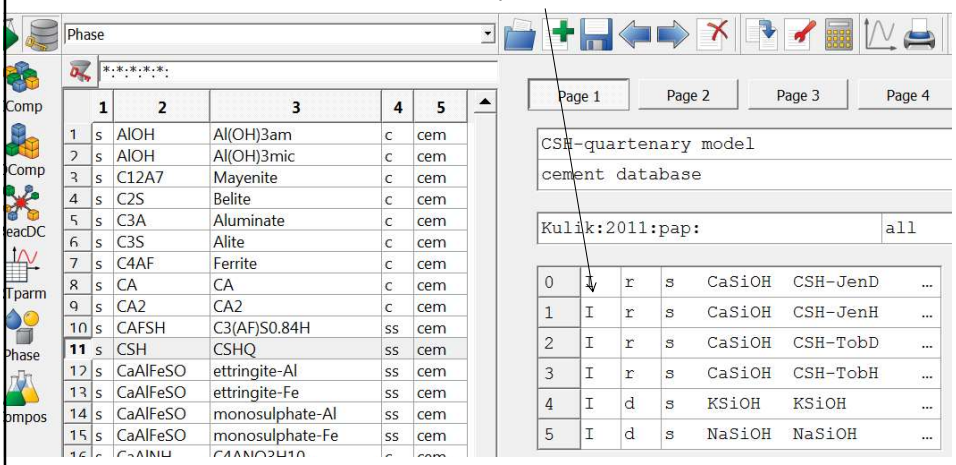
See "help" for additional information or hints *(Partially still under construction)*



- **See** "Help:Help" **for additional information or hints** *(Partially still under construction)*

5.) Thermodynamic Phases – creation of entries

b) Solid solution



	1	2	3	4	5
1	s	AlOH	Al(OH)3am	c	cem
2	s	AlOH	Al(OH)3mic	c	cem
3	s	C12A7	Mayenite	c	cem
4	s	C2S	Belite	c	cem
5	s	C3A	Aluminate	c	cem
6	s	C3S	Alite	c	cem
7	s	C4AF	Ferrite	c	cem
8	s	CA	CA	c	cem
9	s	CA2	CA2	c	cem
10	s	CAFSH	C3(AF)S0.84H	ss	cem
11	s	CSH	CSHQ	ss	cem
12	s	CaAlFeSO	ettringite-Al	ss	cem
13	s	CaAlFeSO	ettringite-Fe	ss	cem
14	s	CaAlFeSO	monosulphate-Al	ss	cem
15	s	CaAlFeSO	monosulphate-Fe	ss	cem

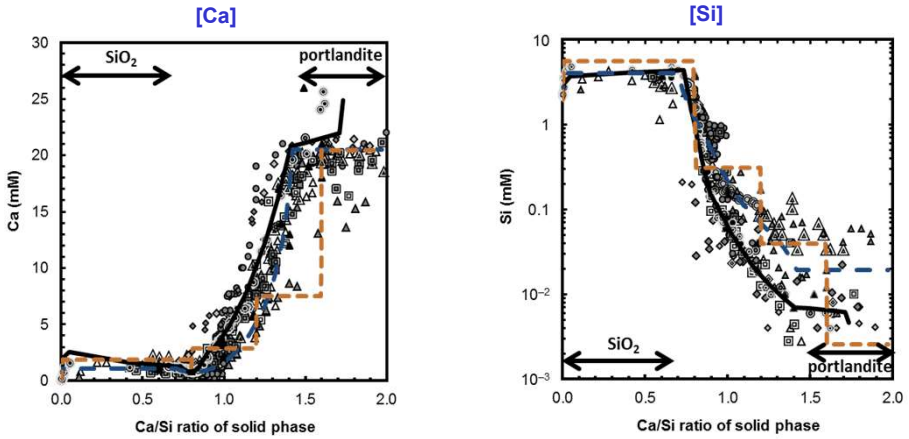
0	I	r	s	CaSiOH	CSH-JenD	...
1	I	r	s	CaSiOH	CSH-JenH	...
2	I	r	s	CaSiOH	CSH-TobD	...
3	I	r	s	CaSiOH	CSH-TobH	...
4	I	d	s	KSiOH	KSiOH	...
5	I	d	s	NaSiOH	NaSiOH	...

CSHQ (Kulik): Ca/Si 0.67 – 2.2 (portlandite limits Ca/Si to ≤ 1.6)

Plus $(KOH)_{2.5}SiO_2H_2O$) and $(NaOH)_{2.5}SiO_2H_2O$) to **estimate** alkali uptake

109

Other thermodynamic models for C-S-H



3 different CSH

$C_{0.8}SH_{1.5}$
$C_{1.2}SH_{2.1}$
$C_{1.6}SH_{2.6}$

Blanc et al. (2010) CCR 40, 851-866

Solid solution: CSHT

infinite $C_{0.67}SH_{1.8}$
pentamer $CSH_{2.0}$
dimer $C_{1.5}SH_{2.5}$

Kulik (2011) CCR 41, 477-495

Surface reaction model

Pentamer $C_{0.8}SH_{1.6}$
dimer CSH_2
dimer $C_{1.5}SH_{2.5}$

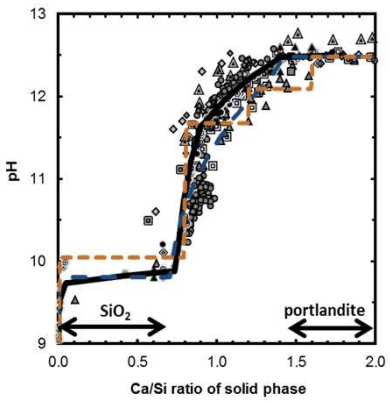
Haas Nonat (2015) CCR 68, 124-138

110

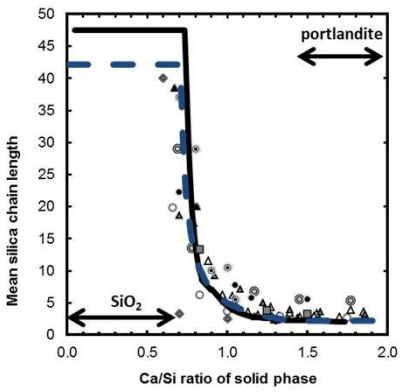
Thermodynamic models for C-S-H

Empa

pH



Mean Chain Length



3 different CSH

~~$C_{0.8}SH_{1.5}$~~
~~$C_{1.2}SH_{2.1}$~~
~~$C_{1.6}SH_{2.6}$~~

Blanc et al. (2010) CCR 40, 851-866

Solid solution

infinite	$C_{0.67}SH_{1.8}$
pentamer	$CSH_{2.0}$
dimer	$C_{1.5}SH_{2.5}$

Kulik (2011) CCR 41, 477-495

Surface reaction model

Pentamer	$C_{0.8}SH_{1.6}$
dimer	CSH_2
dimer	$C_{1.5}SH_{2.5}$

Haas Nonat (2015) CCR 68, 124-138

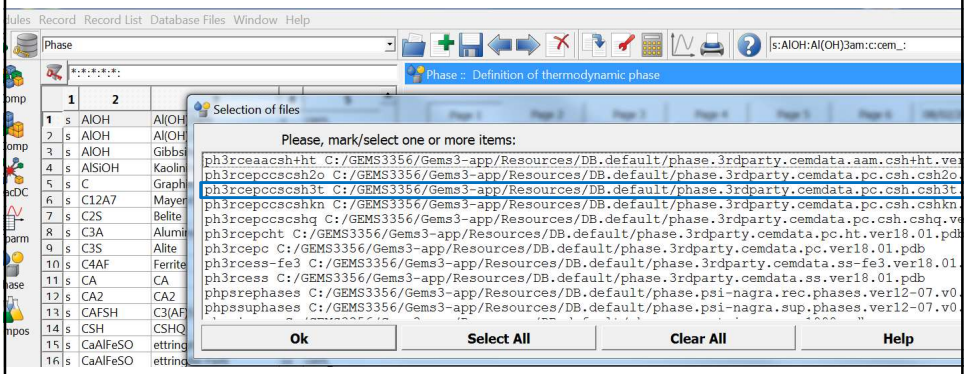
111

Selection of CSH model

Empa

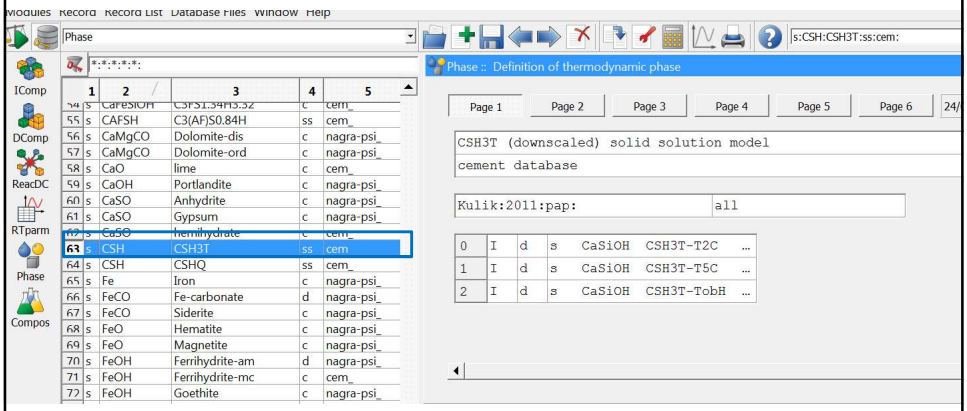
1) **When defining the project OR**

2) **Add later in database *Phase : Record List : Database***
   => select any of the available CSH models
   => store them in your database using
   "Record: save as"



112

Selection of CSH models

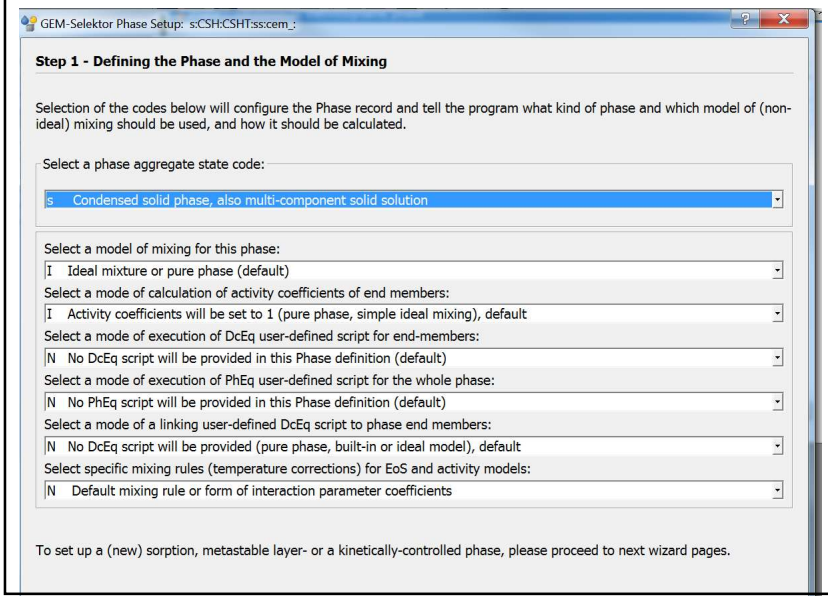


CSH T (Kulik 2011): Ca/Si = 0.67 to 1.5
further information

113

5.) Thermodynamic Phases – Treatment of solid solutions

a) Ideal solid solutions, e.g. C-S-H

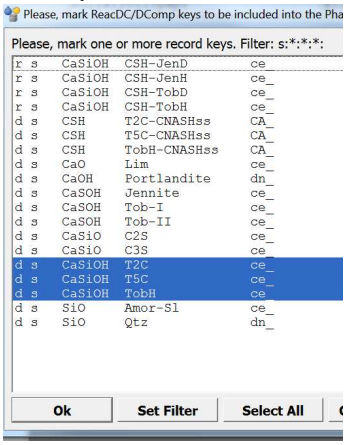


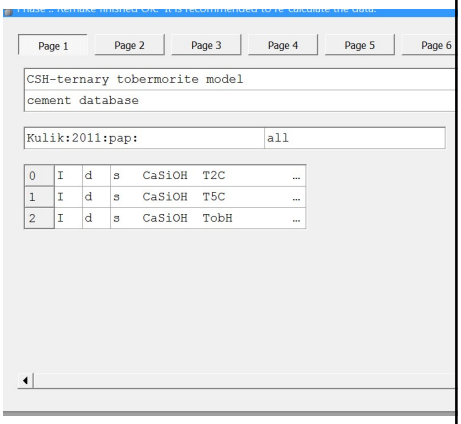
114

GEMS – Database management

5.) Thermodynamic Phases – Treatment of solid solutions

a) Ideal solid solutions, e.g. C-S-H





Includes the data of the end members of the solid solution series

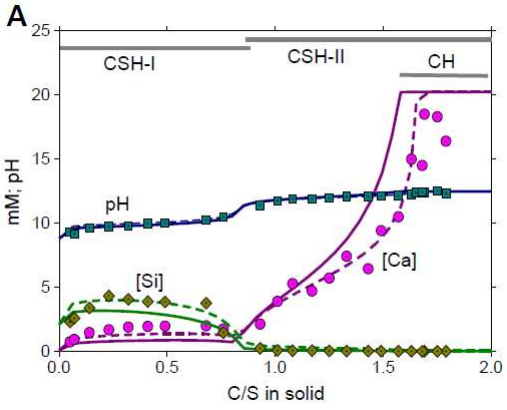
Ideal solid solution phase

CSH «Tob-Jennite»: used in Cemdata07

CSHII: Ca/Si 0.83 to 1.67

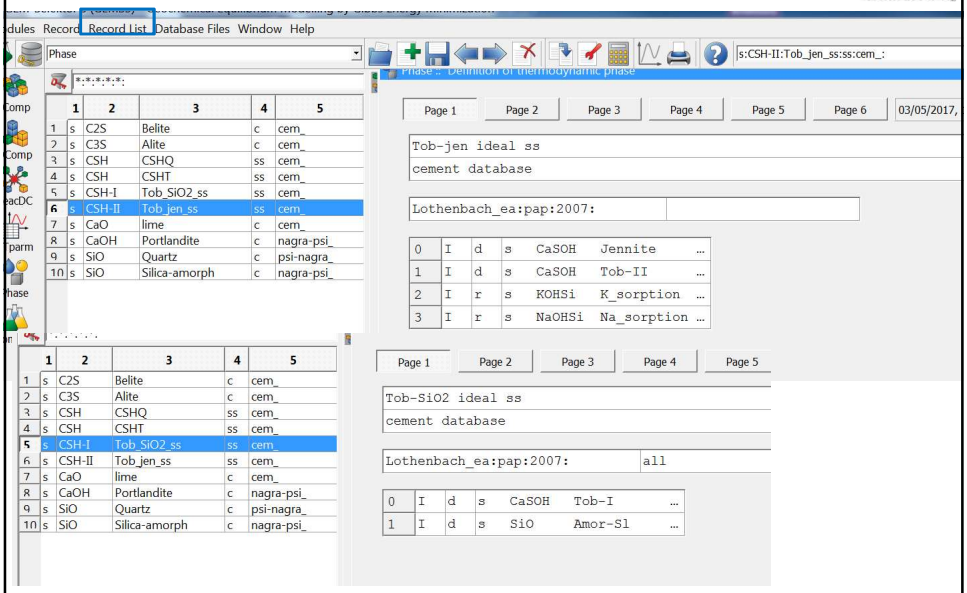
i) CSH-I solid solution system with the end-members SiO_2 (am) and tobermorite (Tob-I: $(CaO)_2(SiO_2)_{2.4}\cdot(H_2O)_{3.2}$) and

ii) CSH-II solid solution system with the end-members jennite $(CaO)_{1.67}(SiO_2)_1\cdot(H_2O)_{2.1}$ and tobermorite (Tob-II: $(CaO)_{0.83}(SiO_2)_1\cdot(H_2O)_{1.3}$).



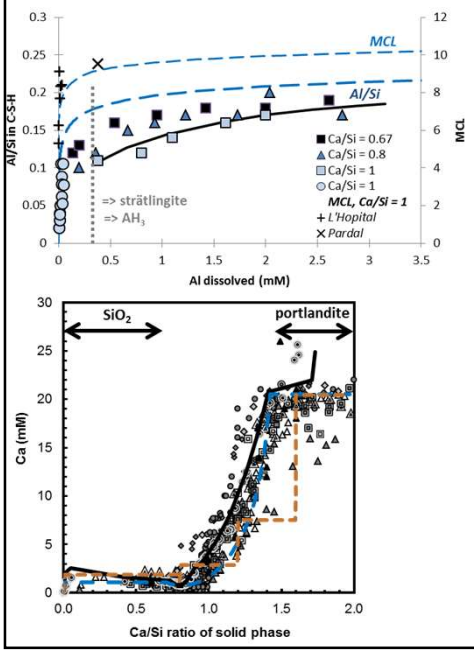
***Details in* (Kulik and Kersten 2001, Lothenbach et al. 2008)**

CSH «Tob-Jennite»: used in Cemdata07



Details in **(Kulik and Kersten 2001, Lothenbach ea 2008)**

Al-uptake in CSH

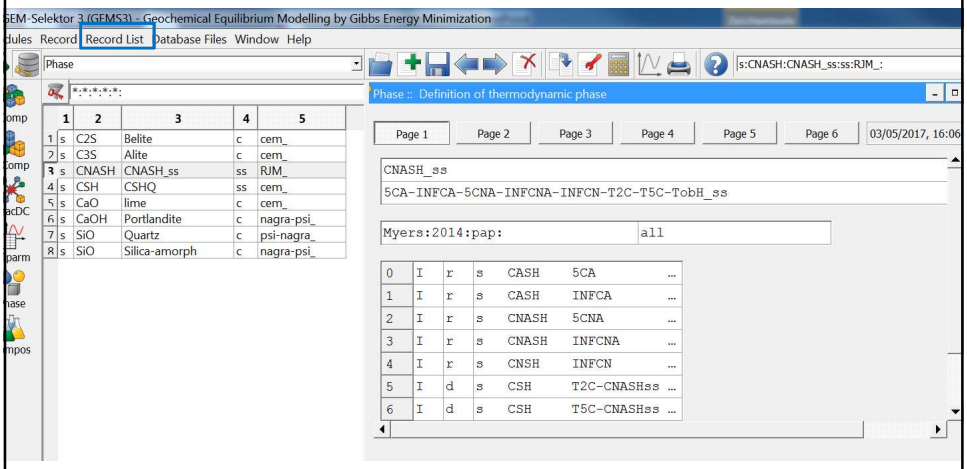


Sorption (Haas & Nonat) and solid solution (Kulik ea, Myers ea) Models:

- **relate to structure: dimer, pentamer, infinite**
- **calculate MCL**
- **Al and alkali binding**
- **New models under construction**
- **Need for more systematic experimental data for different Al sorption sites**

CNASH (Myers ea 2014): Ca/Si = 0.67 to 1.5

Based on CSHT (Kulik 2011)



Activate by: Phase : Record List : Restore : select "CNASH_ss Phase.txt"
Details in Myers ea 2104

C-S-H

Different models available

The user has to decide for 1 model
Do not use several at the same time

For PC
- CSHQ (incl. MCL)
- Or Tob-JEN

For alkali activated
- CSHT (incl. MCL)
- Or CNASH

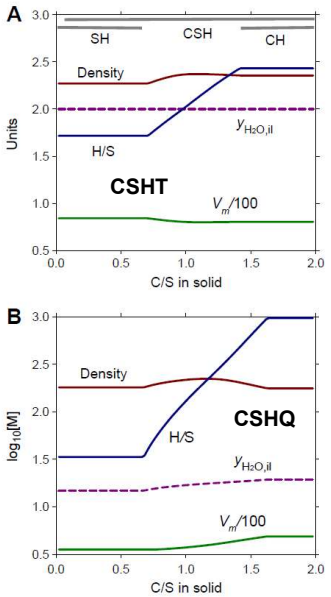


Fig. 8. Variations of density (in g cm^{-3}), volume V_m (in cm^3 mol^{-1}), interlayer H_2O mole fraction $y_{H2O,il}$, and H_2O/SiO_2 mole ratio H/S of the C-S-H phase, as predicted by the downscaled CSH3T simple ideal model Table 5 (A) and by the downscaled CSHQ simple ideal model Table 6 (B).

120