

## Lecture 06 Database, solubility,



## saturation indices

Barbara Lothenbach

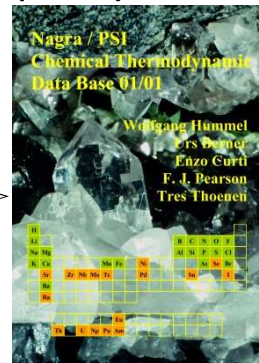
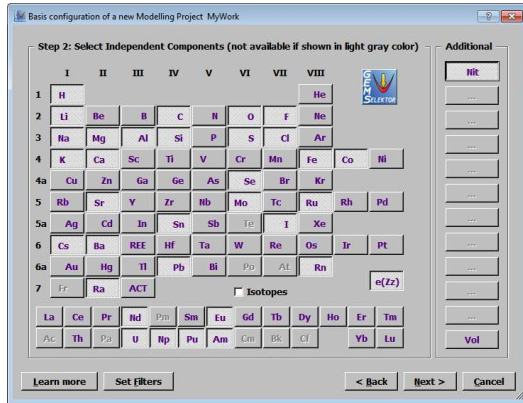
## Thermodynamic data

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

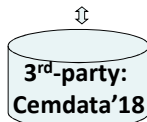
## Default ThermoDynamic Databases

New modeling projects can easily be created using default TDBs.

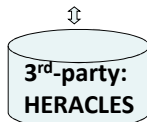
PSI/Nagra 12/07 TDB  
[Thoenen et al.]



logK at 1 bar 25 C, enhanced with  
T,P corrections from SUPCRT



[www.empa.ch/cemdata](http://www.empa.ch/cemdata)



[www.psi.ch/heracles/heracles](http://www.psi.ch/heracles/heracles)



[www.asu.edu/geopig](http://www.asu.edu/geopig)



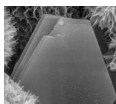
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## Thermodynamic databases

Generic data

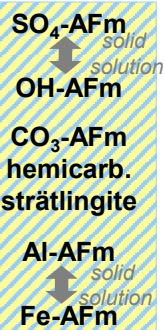
### general-TDB

- Aqueous phase ( $\text{Ca}^{2+}$ ,  $\text{Ca}(\text{OH})^+$ , ...)
- Gaseous phase (e.g.  $\text{CO}_2$  (g), ...)
- Minerals (calcite, gypsum, portlandite, ...)



### Cemdata 18

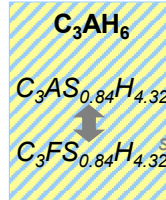
#### AFm



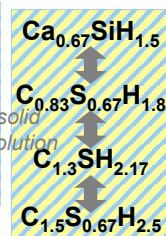
#### AFt



#### hydrogarnet



#### C-S-HQ



**Cemdata18 additions:**  
 $\text{Cl}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2\text{-AFm}$ ,  
 relative humidity,  $\text{M-S-H}$ ,  
 zeolites,  $\text{C-N-A-S-H}$ , ...

Data based on solubility measurements at different  
temperatures + solid phase characterisation

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# Database 1

- **Geochemical database** (generally integrated in software)
  - Complex formation:  $\text{CaOH}^+$ ,  $\text{CaHCO}_3^+$ , ...
  - 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
    - **$\text{NO}_2^-$  and  $\text{NO}_3^-$ -AFm**: Balonis ea (2011) Adv Cem Res, 23 (2011) 129-143
    - **$\text{CO}_3$ -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

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## 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].

	$\log K_{50}^*$	$\Delta_f G^\circ$ [kJ/mol]	$\Delta_f H^\circ$ [kJ/mol]	$S^\circ$ [J/K/mol]	$a_0$ [J/K/mol]	$a_1$	$a_2$	$a_3$	$V^\circ$ [cm <sup>3</sup> /mol]	Ref
[Al]-jettringite <sup>a,b,c</sup>	-44.9	-15205.94	-17535	1900	1939	0.789			707	[3, 4]
$\text{C}_6\text{As}_3\text{H}_{30}^c$		-14728.1	-16950.2	1792.4	1452	2.156			708	[8]
$\text{C}_6\text{As}_3\text{H}_{13}$		-10540.6	-11530.3	1960.4	970.7	1.483			411	[8]
$\text{C}_6\text{As}_3\text{H}_9$		-9540.4	-10643.7	646.6	764.3	1.638			361	[8]
tricarboaluminate <sup>a</sup>	-46.5	-14565.64	-16792	1858	2042	0.559	-7.78·10 <sup>6</sup>		650	[3, 4]
Fe-ettringite <sup>b</sup>	-44.0	-14282.36	-16600	1937	1922	0.855	2.02·10 <sup>6</sup>		717	[3, 9]
Thaumasite	-24.75	-7564.52	-8700	897.1	1031	0.263	-3.40·10 <sup>6</sup>		330	[10]
$\text{C}_3\text{AH}_6^d$	-20.50	-5008.2	-5537.3	422	290	0.644	-3.25·10 <sup>6</sup>		150	[11, 12]
$\text{C}_3\text{AS}_{0.41}\text{H}_{5.18}^{**d}$	-25.35	-5192.9	-5699	399	310	0.566	-4.37·10 <sup>6</sup>		146	[12]
$\text{C}_3\text{AS}_{0.84}\text{H}_{4.32}^{**e}$	-26.70	-5365.2	-5847	375	331	0.484	-5.55·10 <sup>6</sup>		142	[12]
$\text{C}_3\text{FH}_6^{***}$	-26.30	-4122.8	-4518	870	330	1.237	-4.74·10 <sup>6</sup>		155	[12]
$\text{C}_3\text{FS}_{0.84}\text{H}_{4.32}^{e,f}$	-32.50	-4479.9	-4823	840	371	0.478	-7.03·10 <sup>6</sup>		149	[12]
$\text{C}_3\text{A}_{0.5}\text{F}_{0.5}\text{S}_{0.84}\text{H}_{4.32}^e$	-30.20	-4926.0	-5335	619	367	0.471	-8.10·10 <sup>6</sup>		146	[12]
$\text{C}_3\text{FS}_{1.34}\text{H}_{3.32}$	-34.20	-4681.1	-4994	820	395	0.383	-8.39·10 <sup>6</sup>		145	[12]
$\text{C}_6\text{AH}_{19}^g$	-25.45	-8749.9	-10017.9	1120	1163	1.047		-1600	369	[11, 13]
$\text{C}_6\text{AH}_{13}$		-7325.7	-8262.4	831.5	208.3	3.13			274	[13]
$\text{C}_6\text{AH}_{11}$		-6841.4	-7656.6	772.7	0.0119	3.56	1.34·10 <sup>-7</sup>		257	[13]
$\text{C}_6\text{AH}_{7.5}$	-13.80	-4695.5	-5277.5	450	323	0.728			180	[11]
$\text{CAH}_{10}$	-7.60	-4623.0	-5288.2	610	151	1.113		3200	193	[11]
$\text{C}_6\text{ASH}_{16}$		-8726.8	-9930.5	975.0	636	1.606			351	[13, 14]
$\text{C}_6\text{ASH}_{14}^g$		-8252.9	-9321.8	960.9	1028.5				332	[13, 14]
$\text{C}_6\text{ASH}_{12}^h$		-7778.4	-8758.6	791.6	175	2.594			310	[13, 14]
$\text{C}_6\text{ASH}_{10.5}$		-7414.9	-8311.9	721	172	2.402			282	[13, 14]
$\text{C}_6\text{ASH}_9$		-7047.6	-7845.5	703.6	169	2.211			275	[13, 14]
$\text{C}_6\text{ACH}_{11}$	-31.47	-7337.46	-8250	657	618	0.982	-2.59·10 <sup>6</sup>		262	[3, 4]
$\text{C}_6\text{ACH}_9$		-6840.3	-7618.6	640.6	192.4	2.042			234	[13]
$\text{C}_6\text{AC}_{0.5}\text{H}_{12}$	-29.13	-7335.97	-8270	713	664	1.014	-1.30·10 <sup>6</sup>	-800	285	[3, 4]
$\text{C}_6\text{AC}_{0.5}\text{H}_{10.5}$		-6970.3	-7813.3	668.3	0.0095	2.836	1.07·10 <sup>-7</sup>		261	[13]
$\text{C}_6\text{AC}_{0.5}\text{H}_9$		-6597.4	-7349.7	622.5	0.0088	2.635	9.94·10 <sup>-8</sup>		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  $\approx$  1.6)
- $(\text{KOH})_{2.5}\text{SiO}_2\text{H}_2\text{O}$  and  $(\text{NaOH})_{2.5}\text{SiO}_2\text{H}_2\text{O}$  to **estimate** alkali uptake
- Very stable hydrotalcite from Atkins:  $\text{Mg}_4\text{Al}_2\text{O}_{10} \cdot 10\text{H}_2\text{O}$

- **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)  
 $\text{Mg}_4\text{Al}_2\text{O}_{10} \cdot 10\text{H}_2\text{O}$ ,  $\text{Mg}_6\text{Al}_2\text{O}_{12} \cdot 12\text{H}_2\text{O}$ ,  $\text{Mg}_8\text{Al}_2\text{O}_{14} \cdot 14\text{H}_2\text{O}$

**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*

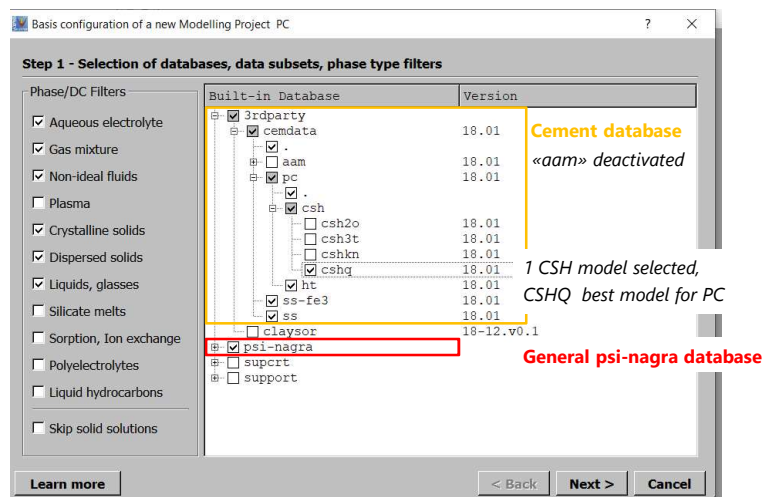
*New CSH model with alkali and earth alkali uptake in preparation:*

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

*Al and sulfate in preparation*

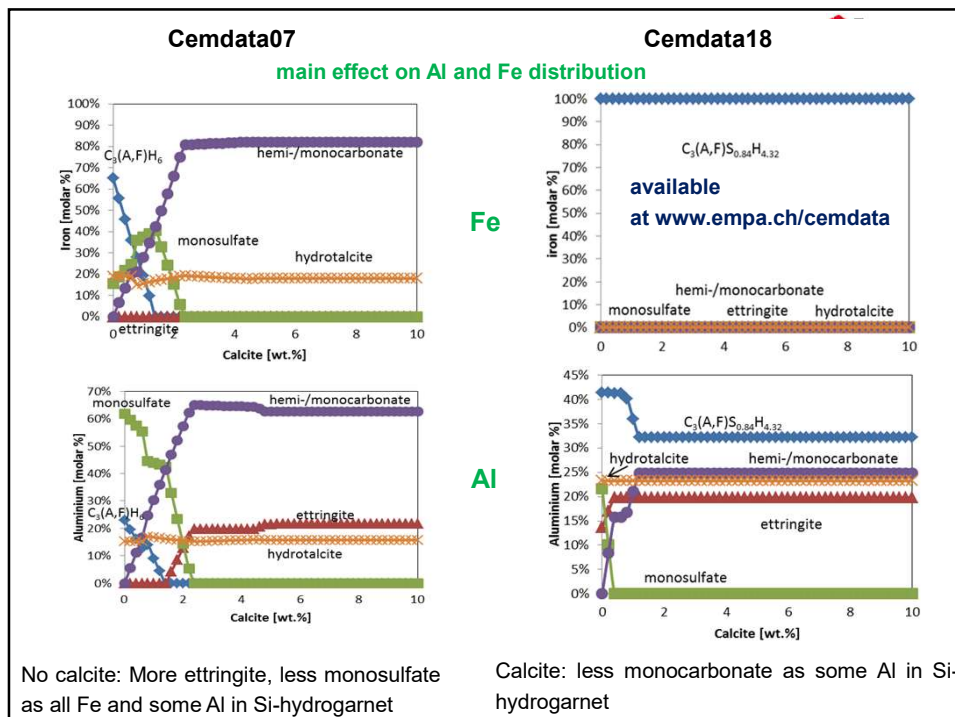
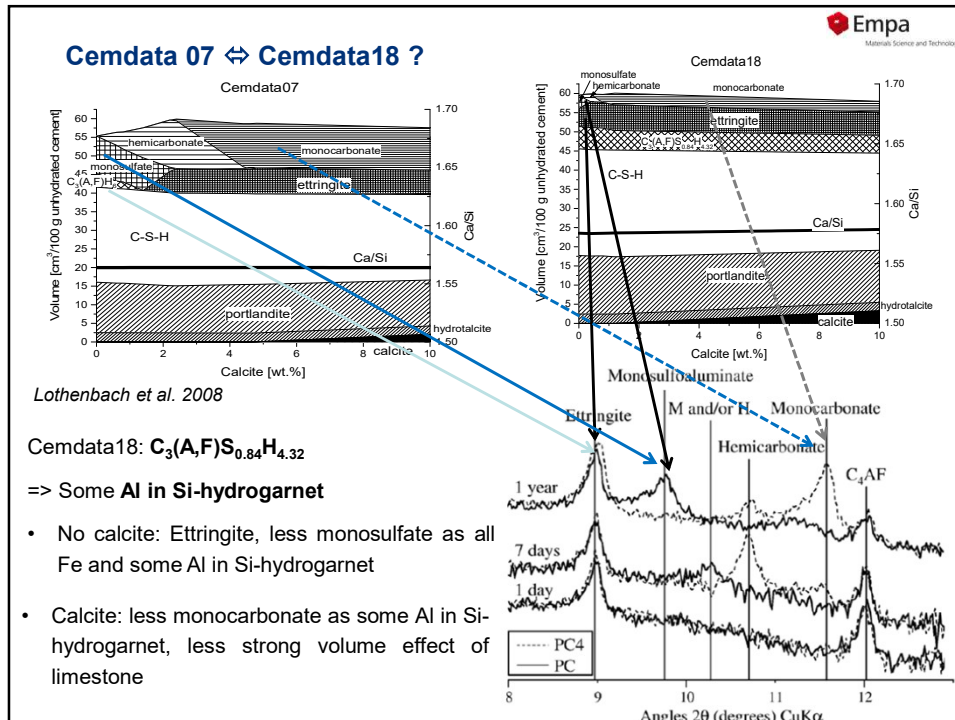
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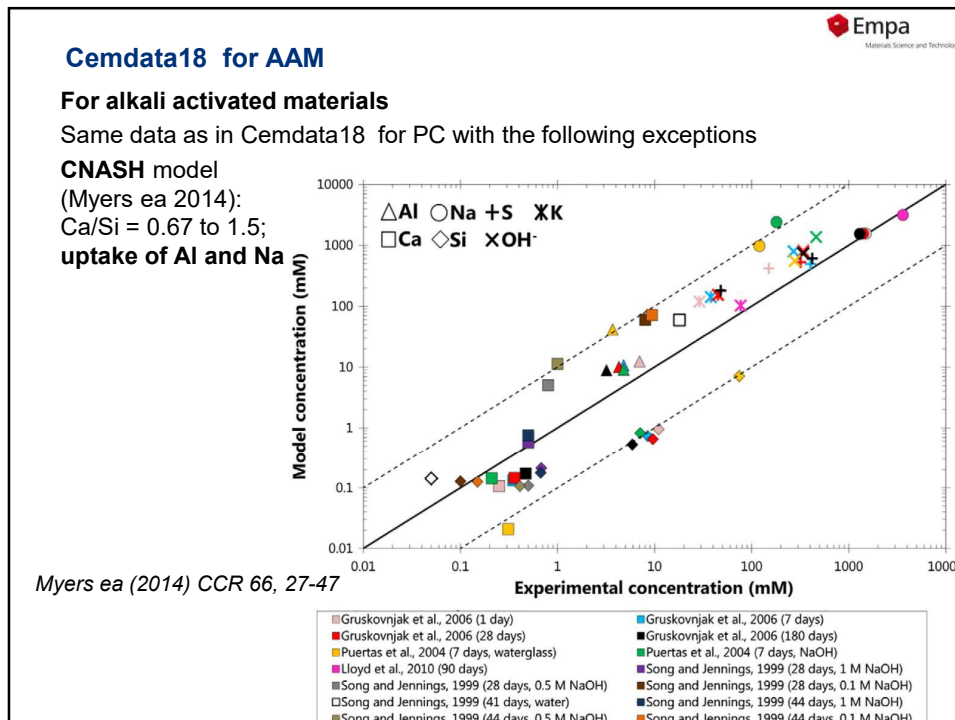
## Recommended selection for PC and blended cements



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### Recommended selection for alkali activated materials

Basis configuration of a new Modelling Project AAS

**Step 1 - Selection of databases, data subsets, phase type filters**

**Phase/DC Filters**

- ☒ Aqueous electrolyte
- ☒ Gas mixture
- ☒ Non-ideal fluids
- ☐ Plasma
- ☒ Crystalline solids
- ☒ Dispersed solids
- ☒ Liquids, glasses
- ☐ Silicate melts
- ☐ Sorption, Ion exchange
- ☐ Polyelectrolytes
- ☐ Liquid hydrocarbons
- ☐ Skip solid solutions

Built-in Database	Version
<input checked="" type="checkbox"/> 3rdparty	
<input checked="" type="checkbox"/> cemdata	18.01
<input checked="" type="checkbox"/> .	
<input checked="" type="checkbox"/> aam	18.01
<input checked="" type="checkbox"/> csh+ht	18.01
<input type="checkbox"/> pc	18.01
<input checked="" type="checkbox"/> ss-fe3	18.01
<input checked="" type="checkbox"/> ss	18.01
<input type="checkbox"/> claysor	18-12.v0.1
<input checked="" type="checkbox"/> psi-nagra	
<input type="checkbox"/> supcrt	
<input type="checkbox"/> support	

**Cement database**

**«aam» database**

**«pc» deactivated**

**General psi-nagra database**

[Learn more](#)

[< Back](#) [Next >](#) [Cancel](#)

## GEMS versus PHREEQC

Cemdata18 also available in PHREEQC format (uses  $\log K$  instead of  $G^\circ$ ):

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 added 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!**

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## GEMS versus PHREEQC

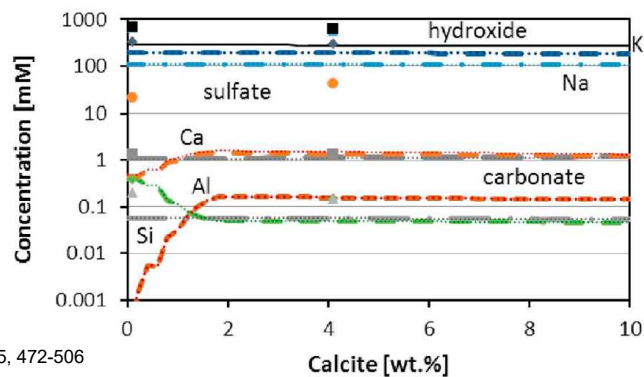
Cemdata18 also available in PHREEQC format (uses  $\log K$  instead of  $G^\circ$ ):

C3AH6  
 $\text{Ca}_3\text{Al}_2\text{O}_6(\text{H}_2\text{O})_6 + 4\text{H}^+ = 3\text{Ca}^{2+} + 2\text{AlO}_2^- + 8\text{H}_2\text{O}$   
 -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, ...)
  - $\Delta G_f^\circ$  (Gibbs free energy of formation) (GEMS, MTDATA, ...)

– convertible:

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

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

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## 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), ...

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## 1) GEMS: independent components

GEM-Selektor 3 (GEMS3) - Geochemical Equilibrium Modelling by Gibbs Energy Minimization

Modules Record Record List Database Files Window Help

IComp

1	2	3
1	Al	e Aluminum_
2	C	e Carbon_
3	Ca	e Calcium_
4	Fe	e Iron_
5	H	h Hydrogen_
6	K	e Potassium_
7	Mg	e Magnesium_
8	Na	e Sodium_
9	O	o Oxygen_
10	S	e Sulfur_
11	Si	e Silicon_
12	Zz	z Electric_charge_

IComp - Data for Independent Components

07/03/2022, 13:05

ICname Calcium NEA (CODATA)  
ICform Ca  
StdSt s IC\_DC ---

M0i 40.077999 S0i 41.59 Cp0i 25.929001  
V0i 25.860001 IXi 1 Valen 2  
indMT 20 Ri --- Zi ---

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

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## 2) GEMS: dependent components (DComp)

GEM-Selektor 3 (GEMS3) - Geochemical Equilibrium Modelling by Gibbs Energy Minimization - [DComp : Thermochemical/EoS data form...]

Modules Record Record List Database Files Window Help

DComp

1	2	3
131	s CaMgCO	Dis-Dol
132	s CaMgCO	Ord-Dol
133	s CaO	Lim
134	s CaOH	Portlandite
135	s CaSO	Anh
136	s CaSO	Gp
137	s CaSOH	Jennite
138	s CaSOH	Tob-I
139	s CaSOH	Tob-II
140	s CaSiO	C2S
141	s CaSiO	C3S
142	s CaSiOH	CSH3T-T2C
143	s CaSiOH	CSH3T-T5C
144	s CaSiOH	CSH3T-TobH

Portlandite

Ca (OH) 2

Mass (g/mol) charge For activity coefficients

M0 74.092697 Zz 0 ab

Uncertainty

V0d 3.306 Volume (1 J/bar = 10 cm<sup>3</sup>/mol)

G0d -897013 Free energy (J/mol)

H0d -984675 Enthalpy (J/mol)

S0d 83.399986 Entropy (J/mol/K)  $\Delta G = \Delta H - TS$

Cp0d 87.505341 Heat capacity (J/mol/K)

PrTr 1 25

LamST Pressure Temperature

BetAlp --- ---

0 Robie\_Hem:1995:pap: All

1 AUG20\_GEMS:2001:dat: G0 from logK = -22.8

Reference (F2)

Standard state  
thermodynamic data  
of solids and  
aqueous species

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## GEMS: dependent components (DComp)

Modules Record Record List Database Files Window Help

SRef

DComp: Thermochemical/EoS data format for Dependent Components

Page 1 Page 2 07/03/2022, 13:05

Portlandite  
Ca(OH)2

M0 74.092697 Zz

V0d 3.306  
G0d -897013  
H0d -984675  
S0d 83.399986  
Cp0d 87.505341  
PrTr 1  
LamST ---  
BetAlp ---

0 Robie\_Hem:1995:pap:  
1 AUG20\_GEMS:2001:dat:

**Reference (press F2)**

SRef: Scripts or Bibliographic References

Page 1 Page 2 07/03/2022, 13:05

Robie RA, Hemingway BS

Thermodynamic properties of minerals and related substances (10<sup>5</sup> Pascals) pressure and at higher temperatures

United States Geological Survey Bulletin

1995, Vol. 2131

453 pp.

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## GEMS: dependent components (DComp)

GEM-Selektor 3 (GEMS3) - Geochemical Equilibrium Modelling by Gibbs Energy Minimization

Modules Record Record List Database Files Window Help

DComp

DComp: Thermochemical/EoS data format for Dependent Components

Page 1 Page 2 07/03/2022, 13:05

CaO:Portlandite:dn:

122 s CaFeOCH Fe-hemicarbonate  
123 s CaFeOCH Femonocarbonate  
124 s CaFeOsH Fe-ettringite  
125 s CaFeOsH Fe-ettringite05  
126 s CaFeOsH Fe-monosulph05  
127 s CaFeOsH Fe-monosulphate  
128 s CaFeSiOH C3FS0.84H4.32  
129 s CaFeSiCHL  
130 s CaKSOI  
131 s CaMgC  
132 s CaMgCO Ord-Dol  
133 s CaO Lim

TCint  
0 0  
1 426.85001

aiCpT  
0 186.7  
1 -0.021910001  
2 0  
3 -1600  
4 0

**Temperature/Pressure effect on heat capacity**

**Temperature range where equations are valid**

**Right click: further information/help**

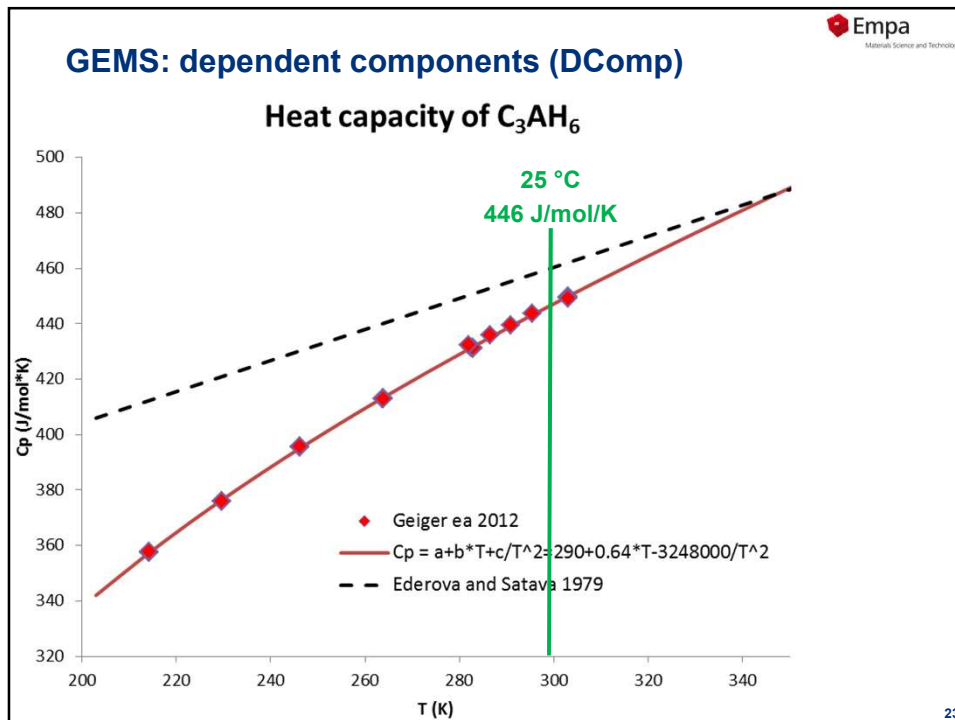
**Equation:**  

$$Cp^0 = a_0 + a_1 T + a_2 T^2 + a_3 T^{0.5} + a_4 T^2 + a_5 T^3 + a_6 T^4 + a_7 T^3 + a_8 T^{-1} + a_9 T^{0.5}$$

**Tabulated values**

	log K <sub>50</sub> <sup>*</sup>	a <sub>0</sub> [J/K/mol]	a <sub>1</sub>	a <sub>2</sub>	a <sub>3</sub>	V° [cm <sup>3</sup> /mol]	Ref
(Al)-ettringite <sup>a,b,c</sup>	-44.9	1939	0.789			707	[3, 4]
CH (portlandite)	-5.2	187	-0.022		-1600	33	[6, 7]
SiO <sub>2,am</sub>	1.476	47	0.034	-1.13·10 <sup>6</sup>		29	[3, 4]

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## 3) GEMS: reactions (ReacDC)

Modules: Record List Database Files Window Help

ReacDC

1 2 3 4

1 a | wS-2 S-2 cn

ReacDC

RTparm

Phase

Compos

ReacDC: Reaction-defined data format for Dependent Components (species)

Page 1 Page 2 01/09/2012, 23:37

**S-2** name  
S|-2|-2 Chemical composition (defined format)

SC	DC	REDC	Uncertainty
0	-1 d	a wS-2 HS-	bnp
1	1 d	a w H+	anp
2	1 n	a wS-2 S-2	cnp

**Reaction component**

V0r	0	2.02095	---
logKr	1e-019	-19	---
G0r	108452.8	120422	---
H0r	108452.8	92236	---
S0r	0	68.1992	---
Cp0r	0	-93.927	---
NiscX	---	---	---

**Pressure Temperature Mass (g/mol) charge**

PrTr	1	25	M0	32.067	-2
BetAl	---	---	ab	4	---

**Reference (F2)**

AUG20\_GEMS:2001:dat: logK

**HS- = H+ + S2-; log K = -19**  
 $\{H^+\}\{S^{2-}\}/\{HS^-\} = 10^{-19}$

**Volume** (1 J/bar = 10 cm<sup>3</sup>/mol)  
**Constant K** (-)  
**Free energy of react** (J/mol)  
**Enthalpy of react** (J/mol)  
**Entropy** (J/mol/K)  $\Delta G = \Delta H - TS$   
**Heat capacity** (J/mol/K)

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

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## 5.) Thermodynamic Phases

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GEM-Selektor 3 (GEMS3) - Geochemical Equilibrium Modelling by Gibbs Energy Minimization

Modules Record Record List Database Files Window Help

Phase

1	2	3	4	5
1	s	C	Graphite	c nagra-psi
2	s	CaCO	Aragonite	c nagra-psi
3	s	CaCO	Calcite	c nagra-psi
4	s	CaO	lime	c cem_
5	s	CaOH	Portlandite	c cem_np_
6	s	CaSO	Anhydrite	c nagra-psi
7	s	CaSO	Gypsum	c nagra-psi
8	s	CaSO	hemihydrate	c cem_
9	s	S	Sulphur	c nagra-psi

Phase: Definition of thermodynamic phase

Page 1 Page 2 Page 3 01/09/2012, 23:37

Portlandite Ca(OH)<sub>2</sub> cryst.  
nagra-psi

0 0 0 0 0 0

0 d s CaOH Portlandite ...

**O: single solid d: DComp**

- 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

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## 6) GEMS: predefined composition

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GEM-Selektor 3 (GEMS3) - Geochemical Equilibrium Modelling by Gibbs Energy Minimization

Modules Record Record List Database Files Window Help

Compos

1	2	3
1	CO <sub>2</sub>	GA Carbon-dioxide_1M_
2	O <sub>2</sub>	GA Oxygen_1M_
3	H <sub>2</sub> SO <sub>4</sub>	AQ Sulfuric-acid_1M_
4	H <sub>2</sub> S	GA Hydrogen-sulfide_1M_
5	H <sub>2</sub>	GA Hydrogen_1M_
6	Ca(OH) <sub>2</sub>	MIN Calcium-hydroxide_1M_
7	CaSO <sub>4</sub>	MIN Calcium-sulfate_1M_
8	Gypsum	MIN Ca-sulfate-2H <sub>2</sub> O_1M_
9	Aqua	AQ 1_mole_H <sub>2</sub> O_
10	CaO	MIN Calcium-oxide_1M_
11	CaCO <sub>3</sub>	MIN Calcium-carbonate_1M_
12	CH <sub>4</sub>	GA Methane_1M_
13	SO <sub>3</sub>	GA Sulfur-trioxide_1M_

ReacDC: Reaction-de Phase: Definition of thermodynamic phase

Compos: Predefined composition objects (PCO)

Page 1 Page 2 01/09/2012, 23:37

Calcium hydroxide 1 mol  
GEMS PCO database

0.0740927 0 0 0 0 0 0

PCO	symIC	CI
0	1 Ca ... M	1
1	2 H ... M	2
2	2 O ... M	2

**Contains chemical compositions of input (e.g. PC, slag, Ca(OH)<sub>2</sub>, HCl, ...)**

**Alternative way of input, no thermodynamic properties needed**

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## 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

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## Thermodynamic data portlandite

- $\text{Ca}(\text{OH})_2$

$$\begin{aligned}
 -K_{\text{s0,H}^+} &= \frac{\{H^+\}^2 \{Ca(\text{OH})_2\}}{\{Ca^{2+}\} \{H_2O^0\}} = \frac{\{H^+\}^2}{\{Ca^{2+}\} \{H_2O^0\}} = 10^{-22.8} & \Delta &= 1 / K_w^2 \\
 -K_{\text{s0,OH}^-} &= \frac{\{Ca(\text{OH})_2\}}{\{Ca^{2+}\} \{OH^-\}^2} = \frac{1}{\{Ca^{2+}\} \{OH^-\}^2} = 10^{5.2} & \Delta &= 1 / (10^{-14})^2 \\
 & & \Delta &= 10^{28}
 \end{aligned}$$

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

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

Portlandite			
Ca(OH)2			
M0	74.0927	Zz	0 ab --- ---
V0d	3.306		0
G0d	$\Delta G_f^\circ$	-897013	---
H0d	$\Delta H_f^\circ$	-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

Flowline test project gem2mt  
GEO THERM Soultz\_1  
Kaolinite Test-JNG

☒ Retain setup of aqueous and gas phases and save all equilibria

☐ Change file configuration of the s ☒ Without speciation

☐ Activate Project Remake wizard ☐ Smart (previous) IA

☐ Create a new project using the sel

Make a new project:

☒ by copying records from default ☐ by linking files from the default

Open Project **New Project** Learn more Cancel

**2. Name it**

Project: Enter a new record key, please

CH:portlandite:

CH Name of the modeling

portlandite Comment to the project

Ok Reset From List Help

**3. Sufficient to select psi-nagra database only**

Basis configuration of a new Modelling Project CH

Step 1 - Selection of databases, data subsets, phase type filters

Phase/DC Filters

☒ Aqueous electrolyte

☒ Gas mixture

Built-in Database

☐ 3rdparty

☒ psi-nagra

☐ supert

☐ supert

Version

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# Portlandite

**4. Select elements**

Ca, Na, Cl

**5. Aqueous electrolyte model:**

Helgeson for NaCl (general)

Setup of aqueous and gas phases in project: CH

Select Aqueous Electrolyte Model | Select Gas/Fluid Mixture Model

☐ Ion-association (IA) with Davies equation, D (default)

☒ IA with extended Debye-Hueckel equation (Helgeson), common b\_gamma and a0, H

☐ IA with extended Debye-Hueckel equation (Shvarov), common b\_gamma and a0, Y

☐ IA with extended Debye-Hueckel equation (Karpov), common b\_gamma, individual a0, Z

☐ IA with Debye-Hueckel equation, no b\_gamma, individual a0, Z

☐ IA with Debye-Hueckel limiting law (very low ionic strength), 1

☐ Do not generate; select a user-defined Phase record from database (Q, S, Z), U

☐ Do not include aqueous electrolyte phase into the system definition, N

Phase record key: a AQELIA aq\_gen aq EDH\_H

Parameters for the aqueous phase model

b\_gamma(1,298) value: 0.064

b\_gamma(P,T) mode NaCl

Common a0 value: 3.72

Gamma (neutral species)

Calculate as b\_gamma\*IS

Gamma (water solvent)

From osmotic coefficient

Molality conversion

Applied to all species

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## 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	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**

Learn more Print OK Cancel

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## 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

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

pH 12.7, 21 mM Ca tot

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## Portlandite: effect of temperature

### 1. Create new process



GEM-Selektor 3 (GEMS3) - Geochemical Equilibrium Modelling by Gibbs Energy Minimization - [Process : Definition of a Process Simulator (batch calculat...

Modules Record Window Help

Process

Controls Sampling Results Config 08/03/2022, 05:18

add SysEq: Please, select a parent System for a new Process

Please, select one record key. Filter: CH:\*\*\*\*\*:

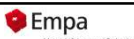
CH	G	port	0	0	1	20	0
<p><i>Process file to calculate effect of temperature on portlandite solubility</i></p>							

Ok Set Filter Help Cancel

Barbara Lot
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## Portlandite

### P: sequential change of temperature



Process: Please, set a new record key

CH:G:port:0:0:1:20:0:Temp\*: GEM-Selektor Process Setup: CH:G:port:0:0:1:20:0:Temp:P:

CH Name of the modeling project

G Thermodynamic potential

port Name of the parent chemical

0 CSD (recipe) variant number

0 Volume of the system, dm<sup>3</sup>

1 Pressure, bar, or 0 for Psat(f)

20 Temperature, C

0 Variant number for addition

Temp Name of this process simulation

P Process simulation mode

Ok Reset From List

**Step 1 - Process Simulator Configuration**

This is a tool for 'batch' calculation of multiple equilibrium states, sampling and plotting of results. In this way, various processes (e.g. mixing, dissolution, hydration, titration, corrosion, weathering) can be simulated.

The Process record can be configured in several modes to perform specific simulation scenarios by execution and simulation output script 'pgExpr'. Simple scripts can be easily produced using this wizard.

Any process simulator belongs to one of three types:

1. 'Sequential': only input GEM parameters are modified (modes P, S, L);
2. 'Reciprocal': next step depends on GEM outputs (e.g. composition of phases) from the previous step (modes R, T);
3. 'Inverse': GEM input adjusted to obtain prescribed values of GEM output (e.g. pH; modes G, T).

Please, choose a process simulation mode:

☒ P Sequential temperature and/or pressure change at fixed bulk composition

☐ S Direct sequential change of bulk composition and/or constraints (default)

☐ G Batch inverse titration sequence for incremented pH values etc.

☐ T One arbitrary inverse titration calculation as defined in Process control script


☐ R - Single flow-through reactor (SFTR) simulation using equilibrium compositions of phases

☐ L Lippmann diagram (transposed) for a binary solid solution

## Portlandite

**P: sequential change of temperature**

*Here: no additional input script needed*



GEM-Selektor Process Setup: CH2:G:port:0:0:1:20:0:Temp:P;

**Step 2 - Process Simulation Controls (click 'Next' to retain the old script)**

	iTm	iV	iP	iTC	iNv	iTau	ipXi	iNu	ipH	ipe
From	1000	0	1	0	0	0	0	0	0	0
Until	1200	0	1	100	0	0	0	0	0	0
Step	0	0	0	2	0	0	0	0	0	0

Start temp  
End temp  
step

☒ No script
 ☐ User-defined script
 ☐ PT phase diagram

Please, check/edit the iP and iT iterator contents, and set Step to 0 in all other iterators.  
 For a PT phase diagram: select phases to plot, then skip the next wizard page.

**Phases**


aq\_gen
gas\_gen
Portlandite

[Learn more](#)

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Next>
Cancel

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## Portlandite



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

**Property**

Scalars

- u
- ue
- b
- Cb
- m\_t
- lgm\_t
- icM
- Xa
- Xwa
- phVol
- phM
- Fa
- bXa(aq\_gen)
- bXa(gas\_gen)
- bXs
- L1
- Yof
- Aalp
- Sigw
- x
- Wxx

**Item Selection**

Mbx	_nnr[0]	F_RT	Fi_3]	iTC[0
pmXs	_nnr[1]	Xw	T	iTC[1
GX	L[0]	Masses[0]	P	iTC[2
IS	L[1]	Masses[1]	RTf[0]	cTC
pH	L[2]	Masses[2]	RTf[1]	cT
pe	L[3]	Masses[3]	RoW[0][0]	iNv[0
Eh	L[4]	Masses[4]	EpsW[0][0]	iNv[1
TC[0]	L[5]	Masses[5]	VisW[0]	iNv[2
TC[1]	Fi[0]	Volumes[0]	iTm[0]	cNV
TK[0]	Fi[1]	Volumes[1]	iTm[1]	iTau[0
TK[1]	Fi[2]	N_	iTm[2]	iTau[1
PG[0]	Fi[0]	L_0]	cTm	iTau[2
PG[1]	Fi[1]	L_1]	iV[0]	cTau
Vx[0]	Fi[2]	L_2]	iV[1]	ipXi[0
Vx[1]	denW[0][0]	L_3]	iV[2]	ipXi[1
It	denW[1][0]	L_4]	cV	ipXi[2
ItEfd	epsW[0][0]	L_5]	iP[0]	cpXi
ItIpm	epsW[1][0]	Fi_0]	iP[1]	cXi
Psi_DK[0]	InP	Fi_1]	iP[2]	iNu[0
Psi_DK[1]	RT	Fi_2]	cP	iNu[1

**Sampling Script**

```

xp[J] =: TC[0];
yp[J][0] =: m_t[{Ca}];
yp[J][1] =: my[{Ca+2}];
yp[J][2] =: my[{CaOH+}];
yp[J][3] =: my[{OH-}];
                    
```

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<sub>2</sub>O

List of static data objects (see tooltip on each object name)

[Learn more](#)

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Cancel

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# Portlandite

GEM-Selektor Process Setup: CHG:port00:1:20:0:Temp:P

Materials Science and Technology

## Step 4 - Important data object dimensions

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

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nPS - Number of steps (1 to 9999 ) to l

1

Number of 'modC' array columns (1 to

4

Number of columns in the 'yp' table (0 nPS.

1

Number of columns in the 'xp' table (0 nPS.

0

Number of rows in the xEp, yEp arrays

1

Number of columns in the xEp, yEp arr

Optional data vectors (of length nPS) can be used allocated using checkboxes below. The assignment vector from the respective process iterator.

Allocation of optional data vectors

☐ CSD variant # ('vTm')
 ☐

☐ Temperature T ('vT')
 ☐

☐ Process extent pXi ('vpXi')
 ☐

## Step 5 - Additional options

On this page, some options of the Process simulator operation can be changed (for specific cases).

Optional modes of operation

☐ Use 'P\_expr' simulation control script (can be turned off in P simulation mode)
 ☐ Save generated SysEq records to the project data base (always saved in G and T modes)
 ☐ Use time dependent calculations and plotting mode (for kinetics simulations, reserved)
 ☐ Use Smart Initial Approximation of GEM IPM algorithm for faster calculations (on your discretion)
 ☐ Use a stepwise mode of Process simulation (for troubleshooting purposes)

The 'P\_expr' simulation control script must be used in most cases except the P mode (e.g. if temperature is changed using ITC Iter system recipe remains constant).

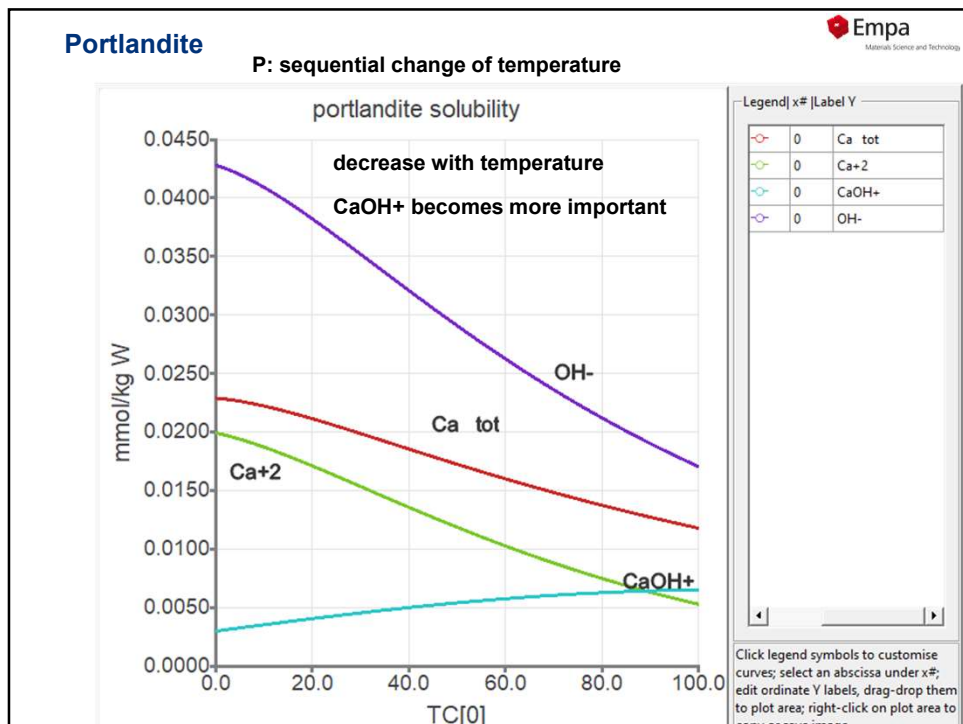
Saving process-generated SysEq records may be necessary for subsequent sampling of results by GtDemo module or for troubleshoot may dramatically increase the size of project database. This flag has no effect on reciprocal and inverse titrations, where optimized records are always saved.

Learn more

Learn more

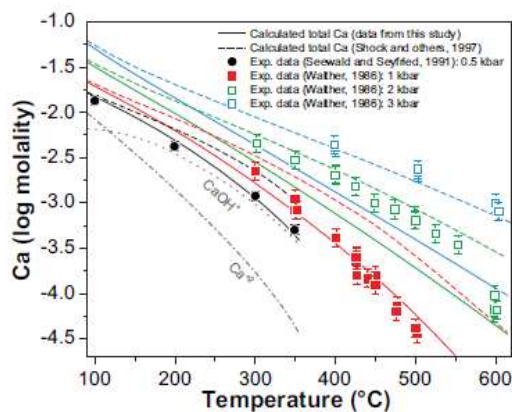
< Back

Next >





## Portlandite



Portlandite solubility decreases with temperature

Agrees well with experimental trends

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

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  $\text{CaOH}^+$  complex, while open symbols represent experimental data points which were not used.

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

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## Portlandite: effect of pH

### 1. Create new process

Process: Please, set a new record key

CH:G:port:0:0:1:20:0:pH:G:

CH Name of the modeling project

G Thermodynamic potential to minimize {G}

port Name of the parent chemical system definition (CSD)

0 CSD (recipe) variant number <Integer>

0 Volume of the system, dm3

1 Pressure, bar, or 0 for Psat(H2O)g

20 Temperature, C

0 Variant number for additional constraints

pH Name of this process simulation task

G Process simulation mode code { P, S, L, G, T, R }

Ok Reset From List Help Cancel

GEM-Selektor Process Setup: CH:G:port:0:0:1:20:0:pH:T:

#### Step 1 - Process Simulator Configuration

This is a tool for 'batch' calculation of multiple equilibrium states, sampling and p geochemical processes (e.g. mixing, dissolution, hydration, titration, corrosion, w

The Process record can be configured in several modes to perform specific simula control script 'P\_expr' and simulation output script 'pgExpr'. Simple scripts can be

Any process simulator belongs to one of three types:

1. 'Sequential': only input GEM parameters are modified (modes P, S, L);
2. 'Reciprocal': next step depends on GEM output parameters (e.g. pH) from p
3. 'Inverse': GEM input adjusted to obtain prescribed values of GEM output (e.g.

Please, choose a process simulation mode:

- ☐ P Sequential temperature and/or pressure change at fixed bulk composition
- ☐ S Direct sequential change of bulk composition and/or constraints (default
- ☐ G Batch inverse titration sequence for incremented pH values etc.
- ☐ T One arbitrary inverse titration calculation as defined in Process control s
- ☐ R Sequential reactor scheme, uses equilibrium bulk compositions of phases
- ☐ L Lippmann diagram (transposed) for a binary solid solution

[Learn more](#)

## G: Batch inverse titration (Variation of pH)

Select 1<sup>st</sup> HCl and 2<sup>nd</sup> NaOH

**Step 2 - Process Simulation Controls (click 'Next' to retain the old script)**

	iTm	iV	iP	ITC	iNv	iTau	ipXi	iNu	ipH	ipe
From	1000	0	1	20	0	0	0	0	0	0
Until	1200	0	1	20	0	0	0	0	0	0
Step	1	0	0	0	0	0	0	0	0	0

☒ Property-vs-pH diagram    ☐ Constant-pH isotherm

To plot a property-vs-pH diagram: select acid and base from the 'AcidBase' list; set the 'ipH' iterator to a desired pH range and step; set the 'ipXi[0]' iterator to maximum allowed addition of acid (negative value) and 'ipXi[1]' to that of base (positive value) for use by the inverse titration algorithm; and go to the next wizard page.

To plot a constant-pH isotherm: select acid and base from the 'AcidBase' list; set the 'ipH' iterator to a desired pH value and zero step; set the 'ipXi[0]' iterator to maximum addition of acid (negative value) and 'ipXi[1]' to that of base (positive value); select the trace element in the 'AcidBase' list, and in the 'ipe' iterator set its addition amount interval and step in log10 scale; select aqueous species in the 'Molality' list for abscissa; finally, select one or more sorbed species from the 'Sorbed' list for ordinate(s), then skip the next wizard page.

AcidBase	Molality	Sorbed
Aqua	KOH	
Ca(OH)2	NaCl	
CaCl2	NaClO4	
CaO	NaOH	
H2	O2	
HCl		
HClO4		
KCl		

```

$ pH sequence of inverse titrations
if ( Next=1) begin
  cNu =: cpH-pH; end
if (Next=2) begin
  xa_[(NaOH)] =: ((cEh < 0)? 1e-9: cEh);
  xa_[(HCl)] =: ((0<cEh < 0)? 1e-9: 0-cEh);
  modC[J] =: cEh;
end
$ modC[J]: acid or base addition
  
```

[Learn more](#)    < Back    Next >    Cancel

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## Output

pH as x-axis (right hand click)  
log(Ca tot), Ca<sup>2+</sup> and CaOH<sup>+</sup>

GEM-Selektor Process Setup: CH:G:port:0:1:20:0:pH:G:

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

Property	Item Selection	Sampling Script
Yof	Ca+2	xp[J] =: pH;
Aalp	CaOH+	yp[J][0] =: lgm_t[{Ca}];
Sigw		yp[J][1] =: my[{Ca+2}];
x	Na+	yp[J][2] =: my[{CaOH+}];
Wcx	NaOH@	
my	ClO4-	
v	Cl-	
vEx	H2@	
Iga	O2@	
gamma	OH-	
InGam	H+	

$my\{Ca+2\}$  = Ca<sup>2+</sup> concentration (in mol/kg H<sub>2</sub>O)


$m\_t\{Ca\}$  = total concentration (in mol/kg H<sub>2</sub>O) = Ca<sup>2+</sup> + CaOH<sup>+</sup> + ...

$lgm\_t\{Ca\}$  = log(10) of total concentration (in mol/kg H<sub>2</sub>O) = Ca<sup>2+</sup> + CaOH<sup>+</sup> + ...

$lg(my\{Ca+2\})$  = log(10) of Ca<sup>2+</sup> concentration (in mol/kg H<sub>2</sub>O)

(lg(...) has to be adapted afterwards)

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

CH:G:port:0:0:1:20:0:pH:G:

Controls Sampling Results Config 08/03/2022, 08:10

pH effect on portlandite

--- temperature Max amount of acid/base pH interval

	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

accuracy

```


$ pH sequence of inverse titrations
if ( Next=1) begin
  A
  cNu =: cpH-pH; end
if (Next=2) begin
  B
  xa_[(NaOH)] =: ((cEh < 0)? 1e-9: cEh);
  xa_[(HCl)] =: ((0-cEh < 0)? 1e-9: 0-cEh);
  modC[J] =: cEh;
end
$ modC[J]: acid or base addition
C
  
```

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

<sup>B</sup> \$ 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.\$

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

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**Collection of data** 

pH, total concentrations  
concentrations of species  
( use lg() = log<sub>10</sub> for better readability)

GEM-Selektor 3 (GEMS3) - Geochemical Equilibrium Modelling by Gibbs Energy Minimization - [Process :: Definition of a Process Simulator (batch calculation)]

Modules Record Window Help

CH:G:port:0:0:1:20:0:Port:S:

Controls Sampling Results Config 21/03/2017, 11:03

NeIt	9999	31	Next	0	I	0	J	30	Jp	30
pSTkey	CH:G:port:0:0:1:20:0:	cTm	1030	cNV	0					
cTau	0	cpXi	0	cXi	1	cNu	3.1			
cpH	0	cpe	0	cEh	0.82481019	cT	293.15			

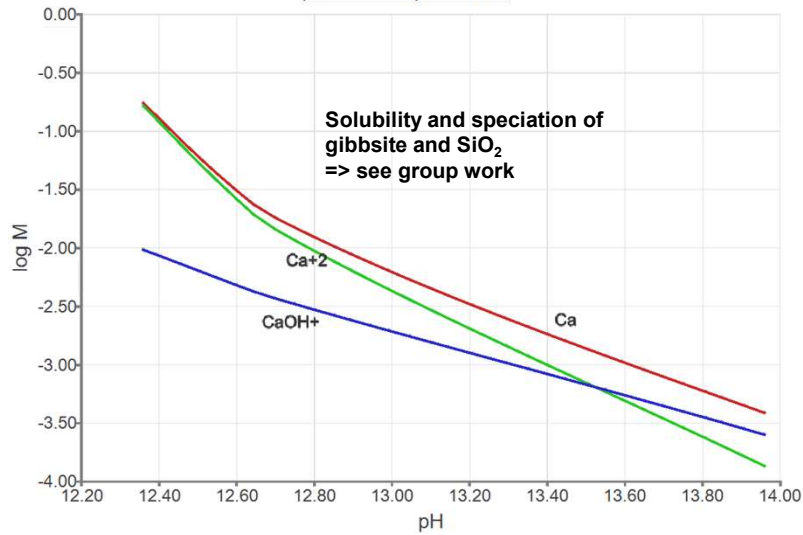
```

xp[J] =: pH;
yp[J][0] =: lgm_t[{Ca}];
yp[J][1] =: lg(my[{Ca+2}]);
yp[J][2] =: lg(my[{CaOH+}]);
  
```

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- Lower Ca concentrations at high pH
  - $K_{s0} = \{Ca^{2+}\} \cdot \{OH^{-}\}^2$  :  $pH \uparrow = OH^{-} \uparrow \Rightarrow Ca^{2+} \downarrow$
  - pH increase: more  $CaOH^{+}$

pH effect on portlandite



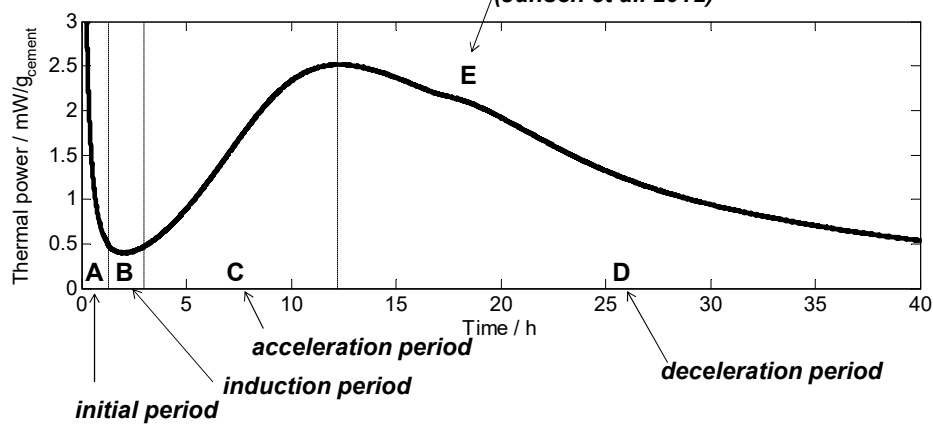
45

## Cement hydration: calorimetry ⇔ enthalpy

Isothermal calorimetry

„sulfate depletion peak“:

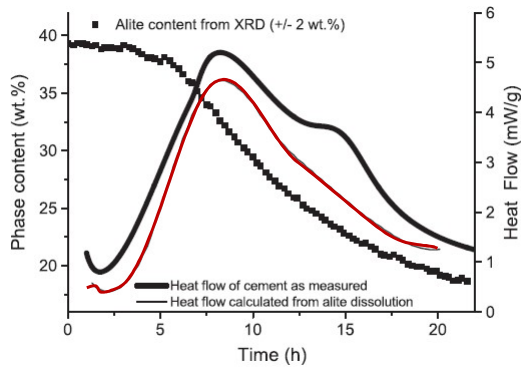
second alumininate reaction  
(Jansen et al. 2012)



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## Heat of hydration (I)

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



	$\Delta H_f$ [kJ/Mol]	Mol weight [g/Mol]
Alite	-2929	228.2
H <sub>2</sub> O	-286	18
C-S-H	-2890	201.9
Portlandite	-986	73.97

Enthalpy of alite reaction  
 $= -(-2929 - 3.9 \cdot 286) + (-2890 - 1.3 \cdot 986)$   
 $= -127 \text{ kJ/mol}$   
 $\Rightarrow -558 \text{ J/g Alite}$

Table 3  
Enthalpies of reaction for the assumed reactions.

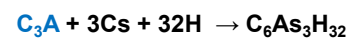
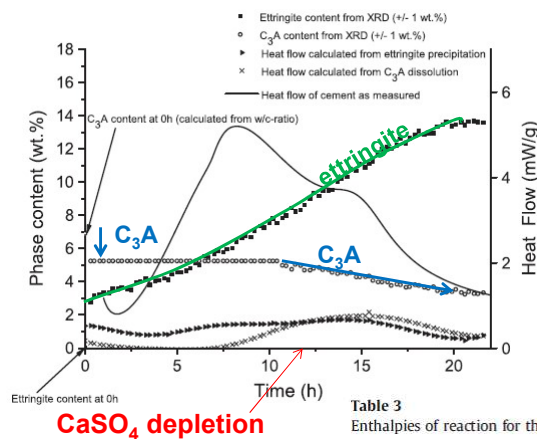
Reaction	Enthalpy
Eq. (1) (Silicate reaction)	-561 J/g <sub>Alite</sub>
Eq. (3) (Dissolution C <sub>3</sub> A)	-868 J/g <sub>C<sub>3</sub>A</sub>
Eq. (4) (Dissolution anhydrite)	-50 J/g <sub>Anhydrite</sub>
Eq. (5) (Dissolution gypsum)	59 J/g <sub>Gypsum</sub>
Eq. (6) (Precipitation ettringite)	-214 J/g <sub>Ettringite</sub>

23°C, w/c = 0.50

Jansen et al. 2012, CCR

## Heat of hydration (III)

Main early reaction:  $C_3A(\text{aluminate}) + CaSO_4 + H_2O \rightarrow \text{ettringite}$



two  $C_3A$  dissolution events

- 1<sup>st</sup> minutes
- Depletion of  $CaSO_4$

Ettringite forms continuously

Table 3  
Enthalpies of reaction for the assumed reactions.

Reaction	Enthalpy
Eq. (1) (Silicate reaction)	-561 J/g <sub>Alite</sub>
Eq. (3) (Dissolution C <sub>3</sub> A)	-868 J/g <sub>C<sub>3</sub>A</sub>
Eq. (4) (Dissolution anhydrite)	-50 J/g <sub>Anhydrite</sub>
Eq. (5) (Dissolution gypsum)	59 J/g <sub>Gypsum</sub>
Eq. (6) (Precipitation ettringite)	-214 J/g <sub>Ettringite</sub>

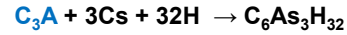
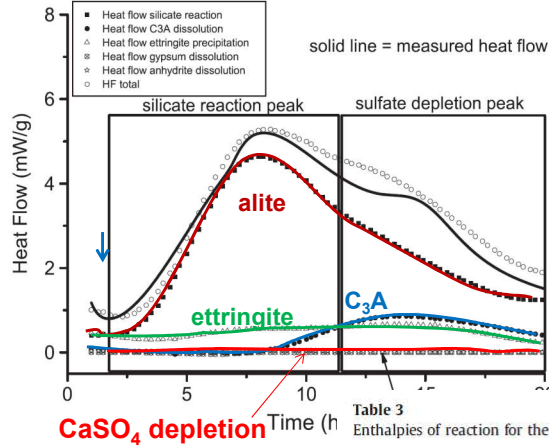
23°C, w/c = 0.50

Jansen et al. 2012, CCR



## Heat of hydration (II)

Main early reaction:  $C_3A(\text{aluminate}) + CaSO_4 + H_2O \rightarrow \text{ettringite}$



two  $C_3A$  dissolution events

- 1<sup>st</sup> minutes

- Depletion of  $CaSO_4$

Ettringite forms continuously

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 <sub>alite</sub>
Eq. (3) (Dissolution $C_3A$ )	-868 J/g <sub><math>C_3A</math></sub>
Eq. (4) (Dissolution anhydrite)	-50 J/g <sub>anhydrite</sub>
Eq. (5) (Dissolution gypsum)	59 J/g <sub>gypsum</sub>
Eq. (6) (Precipitation ettringite)	-214 J/g <sub>ettringite</sub>

## How to calculate heat

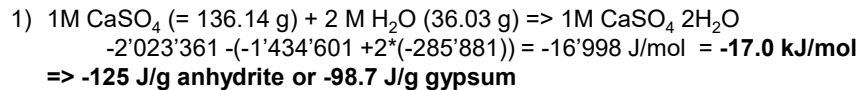
	log K <sub>50</sub>	Δ <sub>r</sub> G° [kJ/mol]	Δ <sub>r</sub> H° [kJ/mol]	S° [J/K/mol]	a <sub>0</sub>	a <sub>1</sub>	a <sub>2</sub>	a <sub>3</sub>	V° [cm³/mol]	Ref
(Al)-ettringite <sup>a,b,q</sup>	-44.9	-15205.94	-17535	1900	1939	0.789			707	[1,2]
$C_4As_3H_{30}$ <sup>q</sup>		-14728.1	-16950.2	1792.4	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 <sup>a</sup>	-46.5	-14565.64	-16792	1858	2042	0.559	-7.78e6		650	[2,1]
Fe-ettringite <sup>b</sup>	-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]
$C_3AH_6$ <sup>c</sup>	-20.50	-5008.2	-5537.3	422	290	0.644	-3.25e6		150	[10]
$C_3AS_{0.41}H_{5.18}$ <sup>c</sup>	-25.35	-5192.9	-5699	399	310	0.566	-4.37e6		146	[11]
$C_3AS_{0.84}H_{4.32}$ <sup>d</sup>	-26.70	-5365.2	-5847	375	331	0.484	-5.55e6		142	[11]
$C_3FH_6$ <sup>e,f</sup>	-26.30	-4122.8	-4518	870	330	1.237	-4.74e6		155	[11]
$C_3FS_{0.84}H_{4.32}$ <sup>d,e</sup>	-32.50	-4479.9	-4823	840	371	0.478	-7.03e6		149	[11]
$C_3(A,F)S_{0.84}H_{4.32}$ <sup>d</sup>	-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]
$C_4AH_{19}$ <sup>f</sup>	-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 !  
 $\Delta_f H^\circ (H_2O) = -285.88 \text{ kJ/mol}$

## How to calculate heat

	log K <sub>SO</sub>	Δ <sub>r</sub> G° [kJ/mol]	Δ <sub>f</sub> H° [kJ/mol]	S° [J/K/mol]	a <sub>0</sub>	a <sub>1</sub>	a <sub>2</sub>	a <sub>3</sub>	V° [cm³/mol]	Ref
Cs (anhydrite)	-4.357	-1322.12	-1434.60	106.7	70.2	-0.099			46	[6,7]
CsH <sub>2</sub> (gypsum)	-4.581	-1797.76	-2023.36	193.8	91.4	-0.318			75	[6,7]
β-CsH <sub>0.5</sub> (hemihyd)	-3.59 <sup>iv</sup>	-1436.34 <sup>iv</sup>	-1575.3 <sup>iv</sup>	134.3	124.1				62	[19]

Example: hydration of anhydrite to gypsum



$$\begin{aligned}\Delta_r H^\circ &= \Delta_f H^\circ_{\text{gypsum}} - \Delta_f H^\circ_{\text{anhydrite}} - 2 \Delta_f H^\circ_{\text{water}} \\ &= -2022.63 - (-1434.11) - 2(-285.830) \\ &= -16.86 \text{ kJ mol}^{-1}\end{aligned}$$

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.

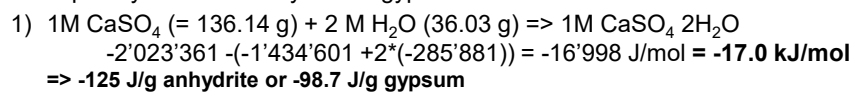
Anderson (2017): Thermodynamics of Natural Systems

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## How to calculate heat

	log K <sub>SO</sub>	Δ <sub>r</sub> G° [kJ/mol]	Δ <sub>f</sub> H° [kJ/mol]	S° [J/K/mol]	a <sub>0</sub>	a <sub>1</sub>	a <sub>2</sub>	a <sub>3</sub>	V° [cm³/mol]	Ref
Cs (anhydrite)	-4.357	-1322.12	-1434.60	106.7	70.2	-0.099			46	[6,7]
CsH <sub>2</sub> (gypsum)	-4.581	-1797.76	-2023.36	193.8	91.4	-0.318			75	[6,7]
β-CsH <sub>0.5</sub> (hemihyd)	-3.59 <sup>iv</sup>	-1436.34 <sup>iv</sup>	-1575.3 <sup>iv</sup>	134.3	124.1				62	[19]

Example: hydration of anhydrite to gypsum



2) Dissolution of CaSO<sub>4</sub> in water: 1 g anhydrite (in 1 L H<sub>2</sub>O)

Input	M	g/mol	H (J/mol)	g/L	J/g CaSO <sub>4</sub>
CaSO <sub>4</sub>	0.0073	136	-1434601	1	-10537
output					
Ca <sup>2+</sup>	0.0055	40	-543069	0.22105834	-2995
SO <sub>4</sub> <sup>2-</sup>	0.0055	96	-909697	0.5298638	-5018
CaSO <sub>4</sub> aq	0.0018	136	-1448430	0.2490777	-2650
<b>Dissolution</b>					<b>-126</b>

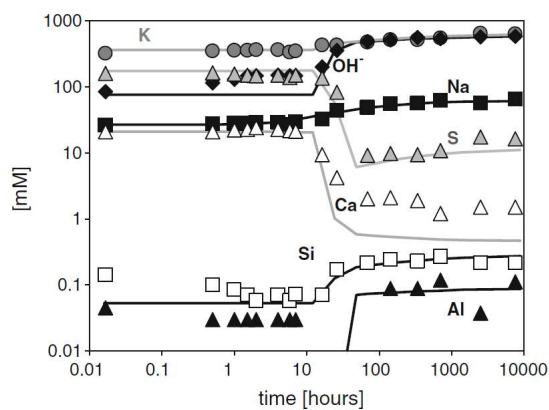
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## Thermodynamic data

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

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## Poresolution PC



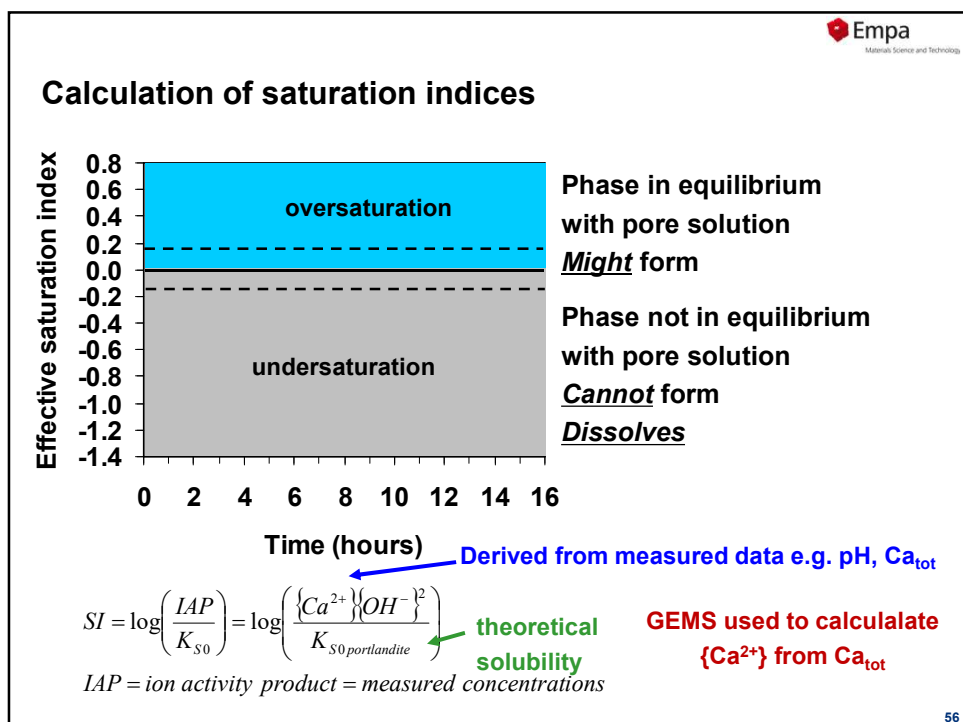
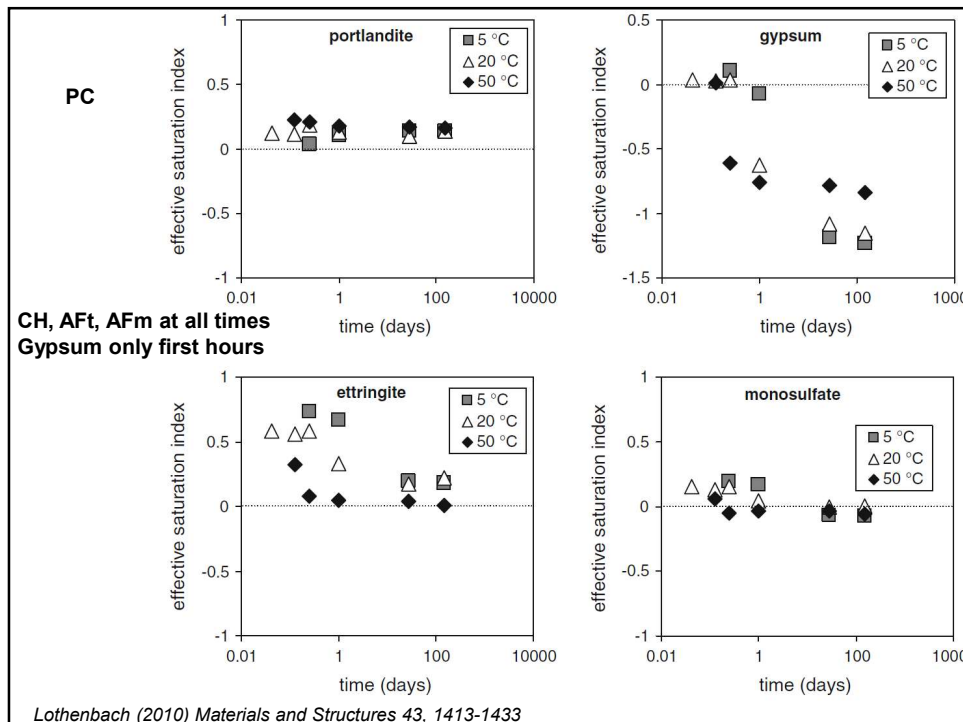
Composition changes  
during cement reaction  
In particular for calcium  
and sulfate:

Calculation of saturation  
indices  
=> indicate changes in  
solid phases

**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

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## 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

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Make a new project:  
by copying records from default d... by linking files from the default d...

Open Project New Project Learn more Cancel

### Step 1 - Selection of databases, data subsets, phase type filters

Phase/DC Filters

☒ Aqueous electrolyte

☒ Gas mixture

Built-in Database

☒ 3rdparty

☒ psi-nagra

☐ supert

☐ support

Built-in Database

Version

☒ 3rdparty

☒ cemdata 18.01

☐ .

☐ aam 18.01

☐ pc 18.01

☒ .

☒ csh

☐ csh2o 18.01

☐ csh3t 18.01

☐ cshkn 18.01

☒ cshq 18.01

☐ ht 18.01

☒ ss-fe3 18.01

☒ ss 18.01

Setup of aqueous and gas phases in project: SI

Select Aqueous Electrolyte Model

Select Gas/Fluid Mixture Model

☐ Ion-association (IA) with Davies equation, D (default)

☒ IA with extended Debye-Hueckel equation (Helgeson), common b\_gamma and a0, H

☐ IA with extended Debye-Hueckel equation (Shvarov), common b\_gamma and a0, Y

☐ IA with extended Debye-Hueckel equation (Karpov), common b\_gamma, individual a0, 3

☐ IA with Debye-Hueckel equation, no b\_gamma, individual a0, 2

☐ IA with Debye-Hueckel limiting law (very low ionic strength), 1

☐ Do not generate; select a user-defined Phase record from database ( Q, S, Z ), U

☐ Do not include aqueous electrolyte phase into the system definition, N

Parameters for the aqueous phase model

b\_gamma(1,298) value: 0.123

b\_gamma(P,T) mode: KOH

Common a0 value: 3.67

Gamma (neutral species)

## Calculation of saturation indices

Empa  
Materials Science and Technology

Input Recipe of Single Thermodynamic System: SI\_G:MySystem:0:0:1:20:0:

Title: caclaution of saturation indices  
Comment: course

Property

- Compos (xa\_)
- DComp (xd\_)
- IComp (bi\_)
- Phase (xp\_)
- Kin.lower (dll\_)
- Kin.upper (dul\_)
- G0 shift (gEx\_)
- Other Inputs

Selection

- K2O
- K2SO4
- KOH
- Na2O
- Na2SO4
- NaOH
- O2
- SO3
- SiO2

Recipe Input

Property	Name	Quantity	Units
1	Al(OH)3	0.0094	h
2	Aqua	1000	g
3	CaO	21	h
4	KOH	395	h
5	NaOH	76	h
6	O2	0.1	g
7	SO3	168	h
8	SiO2	0.11	h

Input quantities of Compos(itions) contributing to B\_ vector

Learn more   Print   OK   Cancel

1 kg of water  
h: mmol  
=> mmol/l

O<sub>2</sub> => oxidising cond.

**Al(OH)<sub>3</sub>, CaO, KOH, NaOH, SO<sub>3</sub>, SiO<sub>2</sub> used as proxy for measured total Ca, Al, ...concentrations [mmol/l]**  
**=> Input of uncharged species**

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Window Help

SL-G:SI:0:0:1:20:0:

Compos   **DComp**   Phase   IComp   Surfaces   Config   25/04/2019, 16:44

	mDC	DCvp		dll	dul	
46	G	g	S-2 H2S	...	B	0 1000000 M
47	I	s	CaSiOH CSHQ-JenD	...	B	0 0 M
48	I	s	CaSiOH CSHQ-JenH	...	B	0 0 M
49	I	s	CaSiOH CSHQ-TobD	...	B	0 0 M
50	I	s	CaSiOH CSHQ-TobH	...	B	0 0 M
51	I	s	KSiOH KSiOH	...	B	0 0 M
52	I	s	NaSiOH NaSiOH	...	B	0 0 M
53	I	s	CaAlOSH straetlingite	...	B	0 0 M
54	I	s	CaAlOSiHstraetlingite7...	...	B	0 0 M
55	I	s	CaAlOSH ettringite	...	B	0 0 M
56	I	s	CaAlOSH ettringite30	...	B	0 0 M
57	J	s	CaAlOH C4AH13	...	B	0 0 M
58	M	s	CaAlOSH monosulphate12...	...	B	0 0 M
59	M	s	CaAlOH C4AH13	...	B	0 0 M
60	J	s	CaAlOSH monosulphate12...	...	B	0 0 M
61	O	s	AlOH AlOHam	...	B	0 0 M
62	O	s	AlOH AlOHmic	...	B	0 0 M
63	O	s	AlOH Gbs	...	B	0 0 M
64	O	s	AlSiOH Kln	...	B	0 0 M
65	O	s	CaAlO C12A7	...	B	0 0 M
66	O	s	CaSiO C2S	...	B	0 0 M
67	O	s	CaAlO C3A	...	B	0 0 M
68	O	s	CaSiO C3S	...	B	0 0 M
69	O	s	CaAlO CA	...	B	0 0 M

3) Scroll down to 2<sup>nd</sup> table

4) Select all dul of solids

5) Press F8, Ok-do it

dul = upper limit  
 dul = 0  
**Solid cannot form**  
 But saturation is calculated

dll = lower limit

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Empa  
Materials Science and Technology

Input: System Definition Results: Equilibrium State

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

PC pore solution after 1 hour  
Oversaturated: logSI > 0  
with respect to

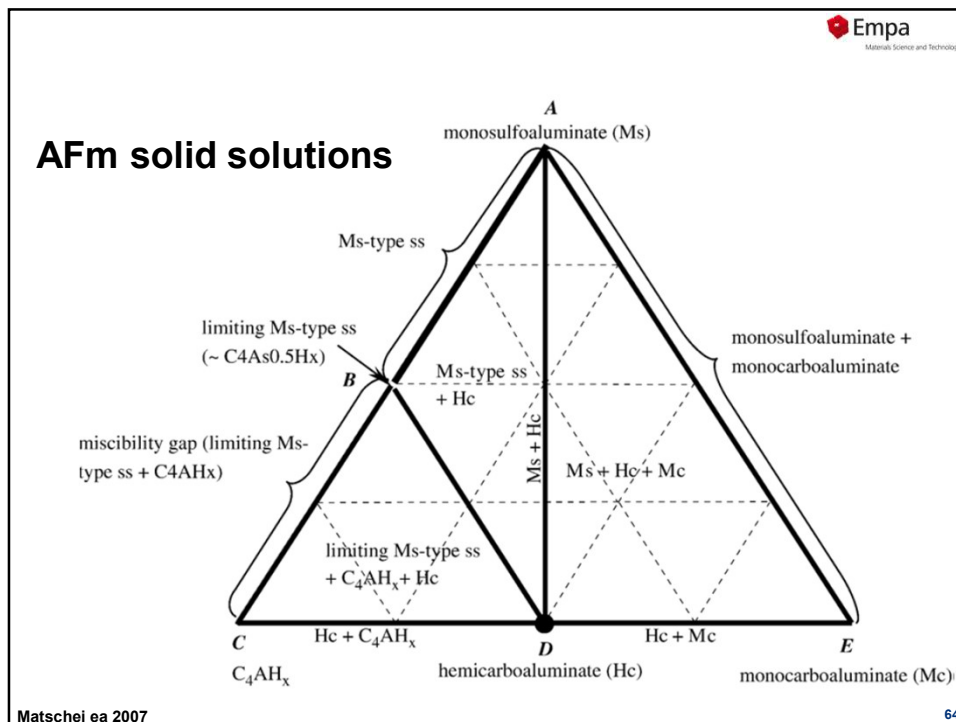
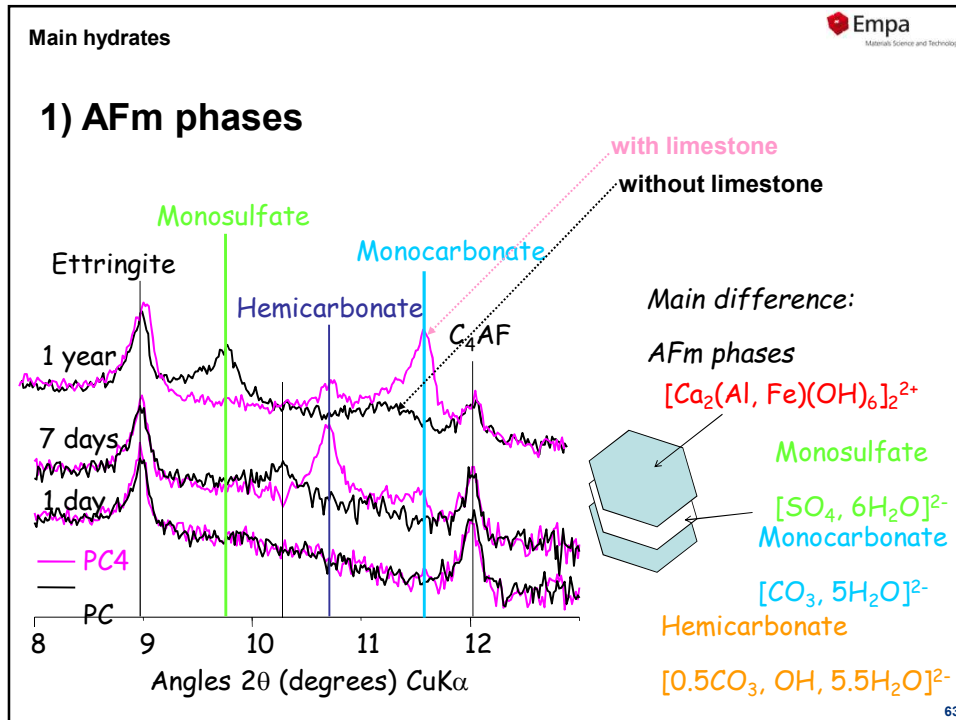
- C-S-H
- Ettringite
- Monosulfate
- Portlandite
- Gypsum

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

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## 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

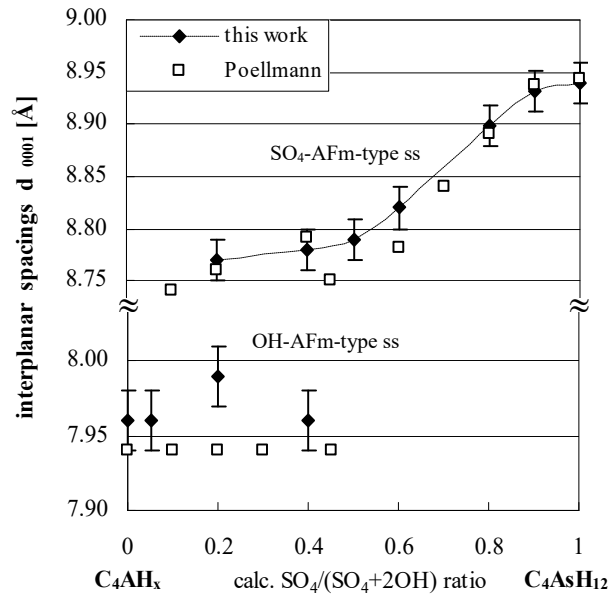


## 1) AFm phases

Characteristics  
solid solutions:

- XRD peak shift
- change of concentrations

$C_4AH_{13}$  –  
monosulfate:  
solid solution



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

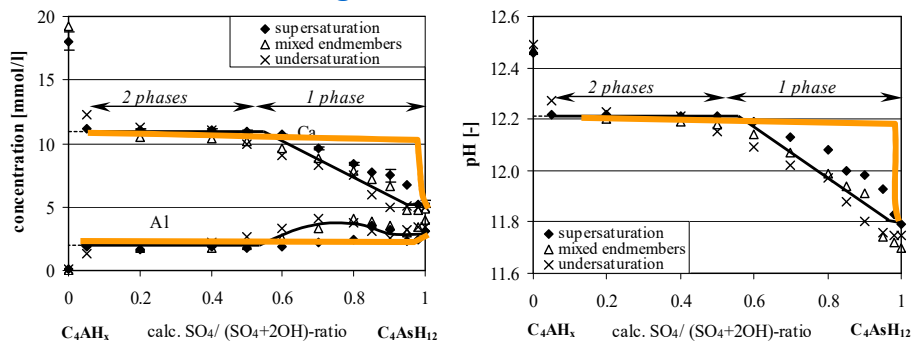
65

## 1) AFm phases

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
- no solid solution

- miscibility gap 0.03-0.5

66

Empa  
Materials Science and Technology

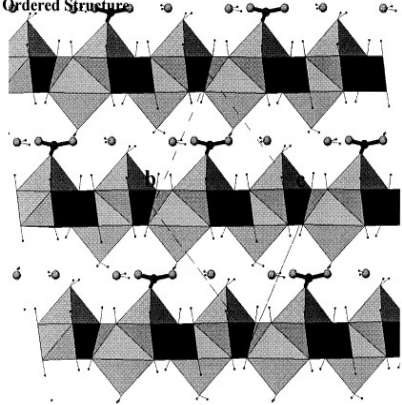
**Solid solutions probable**

- Similar charge
- Similar structure
- Similar size

**AFm:  $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaX} \cdot n\text{H}_2\text{O}$**

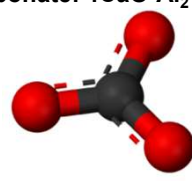
$\text{CO}_3^{2-}$     $\text{H}_2\text{O}$

**Ordered Structure**



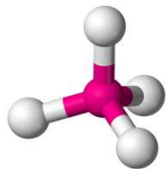
**Monocarbonate:  $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaCO}_3 \cdot 11\text{H}_2\text{O}$**

$\text{CO}_3^{2-}$



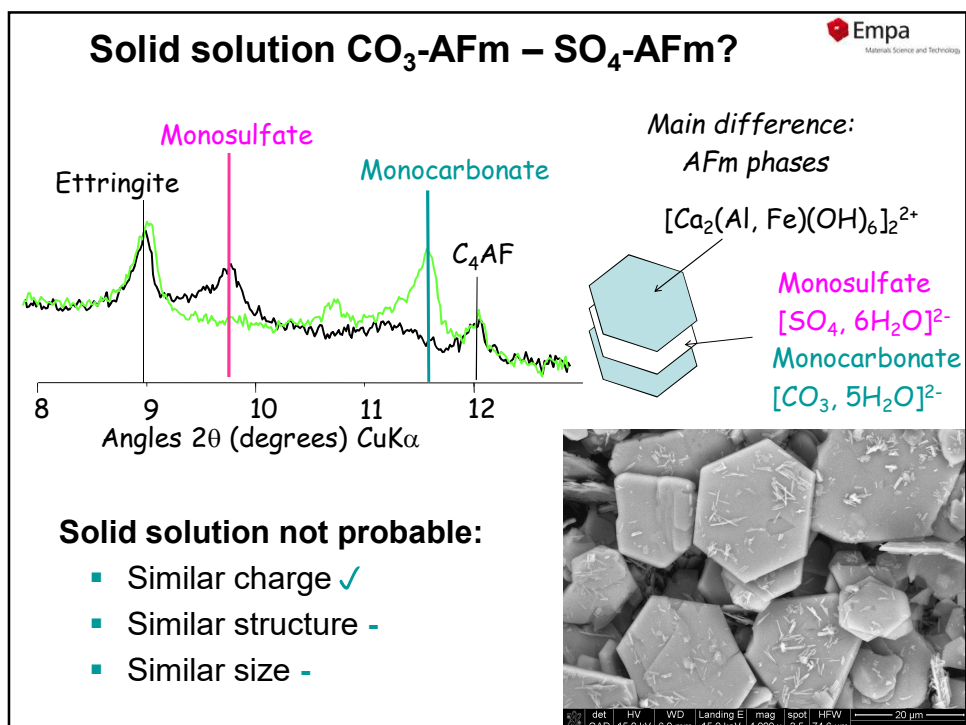
**Monosulfate:  $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O}$**

$\text{SO}_4^{2-}$

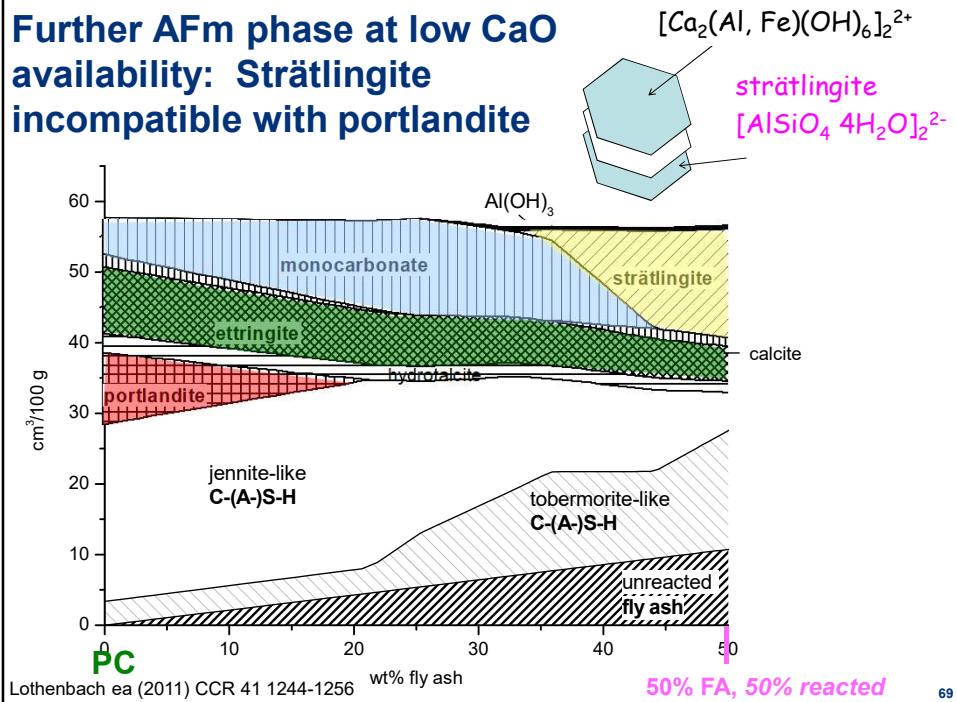


$[\text{Ca}_4\text{Al}_2(\text{OH})_{12}]^{2+}$    Renaudin 1999

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



**Ettringite:**



high water content

-> voluminous

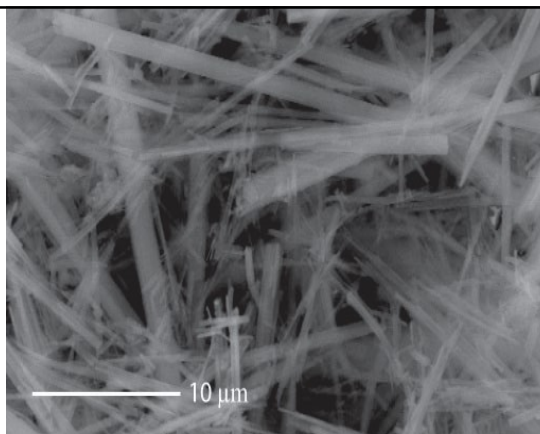
-> low density 1.8 kg/dm³

-> good space filling

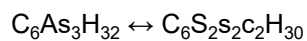
Takes up other ions  
(solid solutions)

->  $Al \leftrightarrow Fe$

->  $SO_4^{2-} \leftrightarrow CO_3^{2-}, CrO_4^{2-}, \dots$

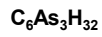


solid solution with thaumasite



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**Ettringite:**



high water content

-> voluminous

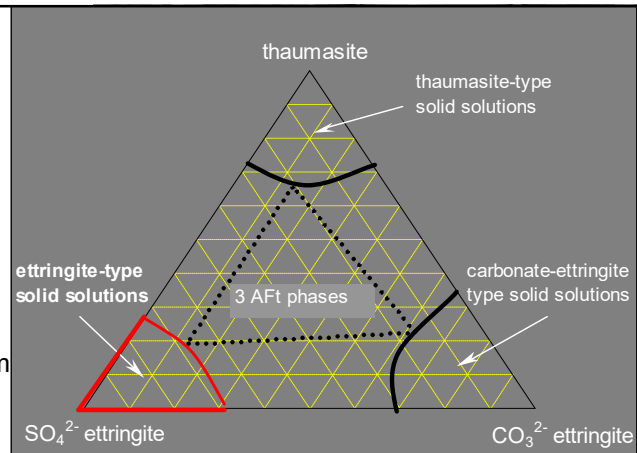
-> low density 1.8 kg/dm<sup>3</sup>

-> good space filling

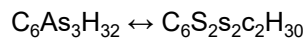
Takes up other ions  
(solid solutions)

-> Al ↔ Fe

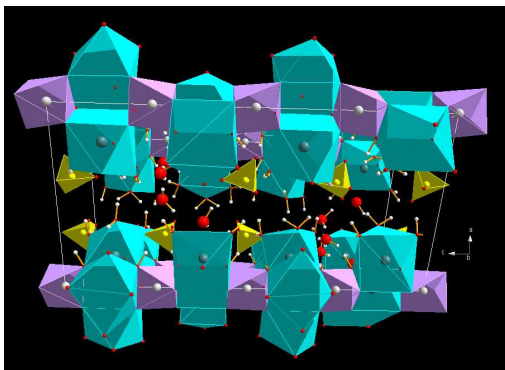
->  $\text{SO}_4^{2-} \leftrightarrow \text{CO}_3^{2-}$ ,  $\text{CrO}_4^{2-}$ , ...



solid solution with thaumasite

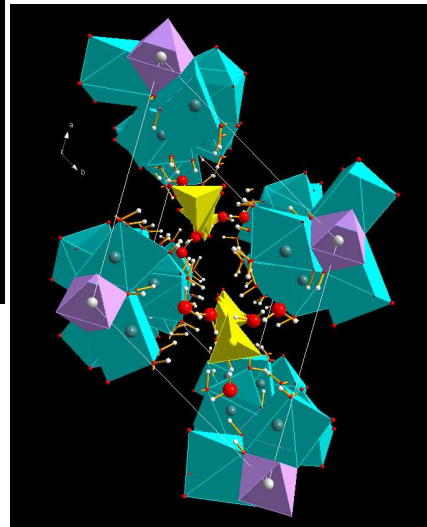


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ettringite  
crystal system: hexagonal  
a=1.12 nm  
c=2.14 nm

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





## Hydrogarnets:



Solid solutions

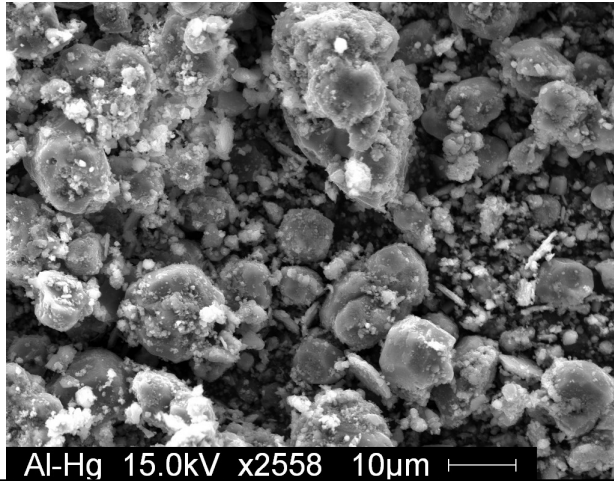
->  $\text{Al} \leftrightarrow \text{Fe}$

->  $\text{SiO}_2^0 \leftrightarrow 2\text{H}_2\text{O}$

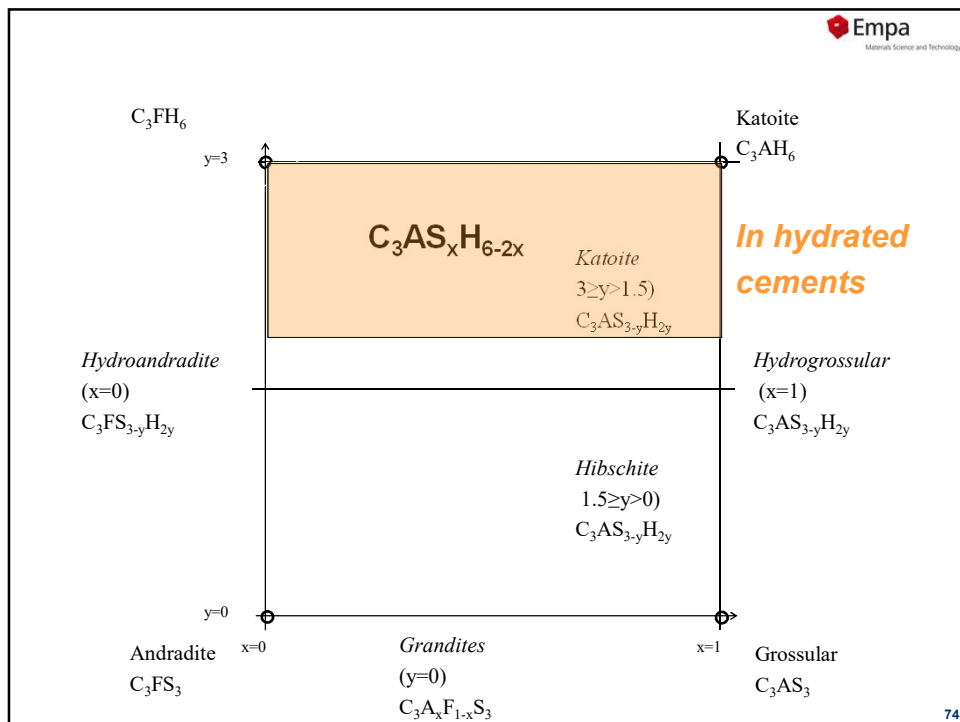
low water content

-> higher density

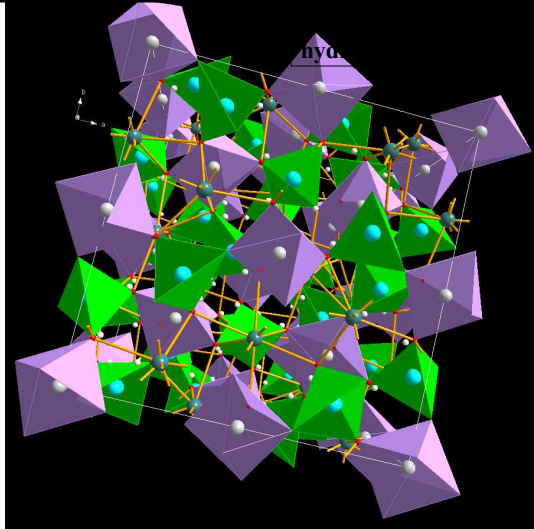
>  $2.5 \text{ kg/dm}^3$



Al-Hg 15.0kV x2558 10μm



## Hydrogarnets:



Katoite ( $y=1.9$ ):

crystal system: cubic

$a=1.22\text{ nm}$

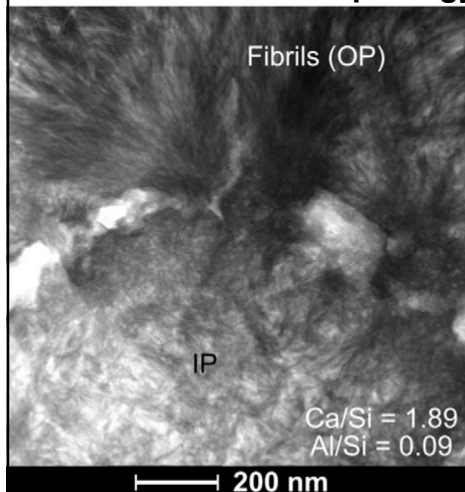
\* Ferro et al. European J. Min. 15 (2003) 419- 426

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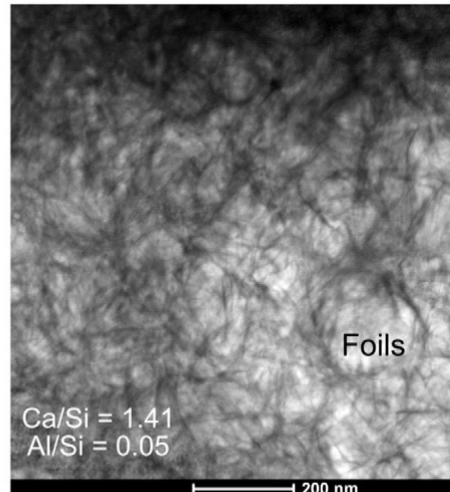
## C-S-H in cements



### Foil like morphology at low Ca/Si



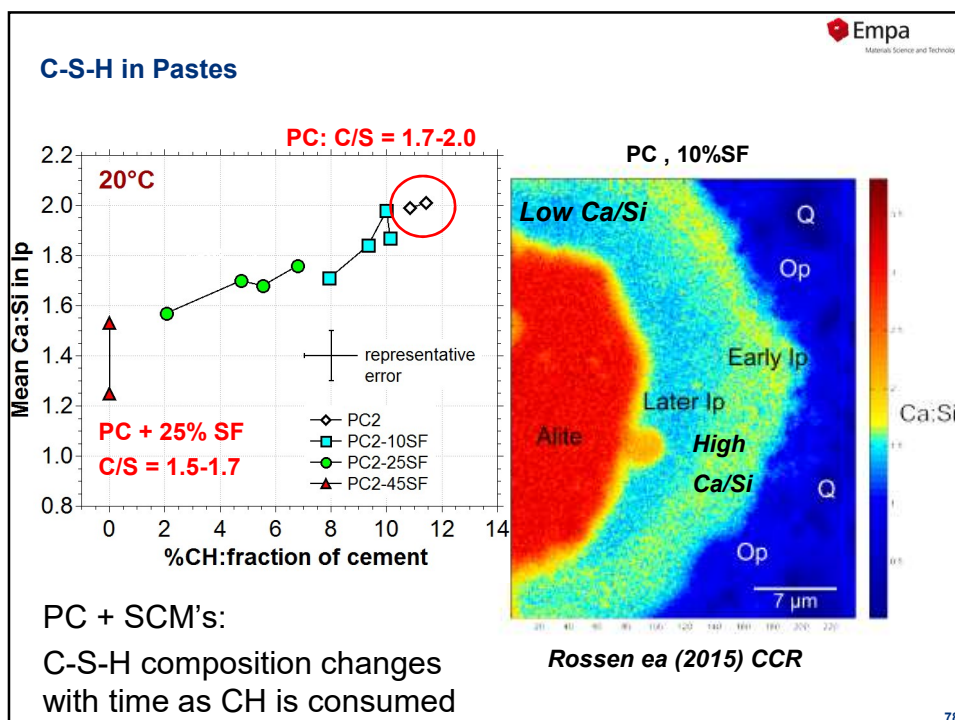
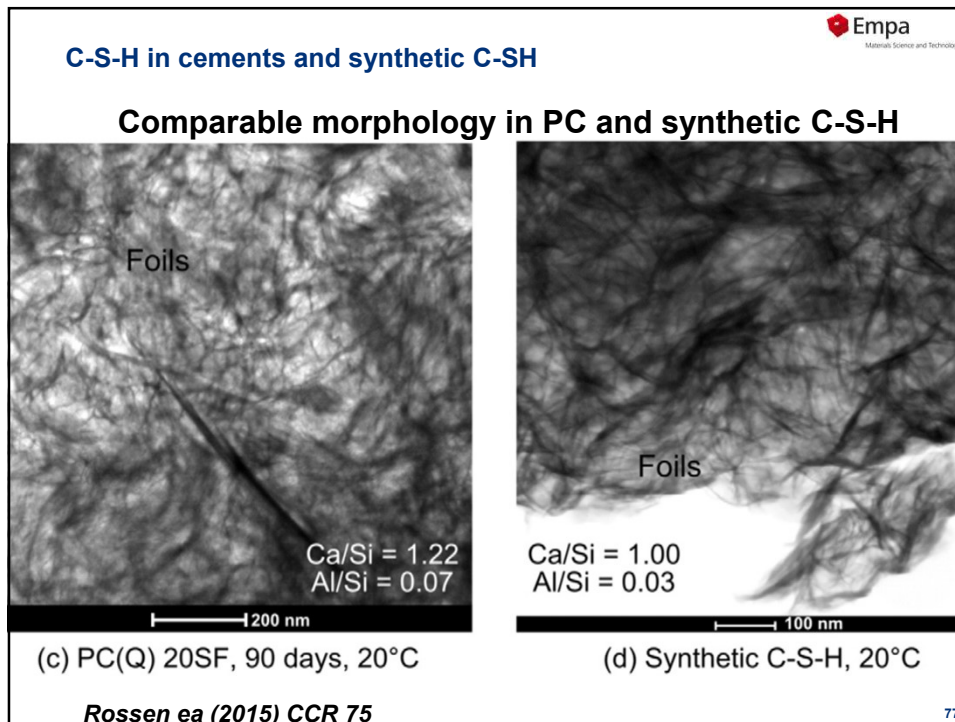
a) Plain cement (PC), 90 days, 20°C

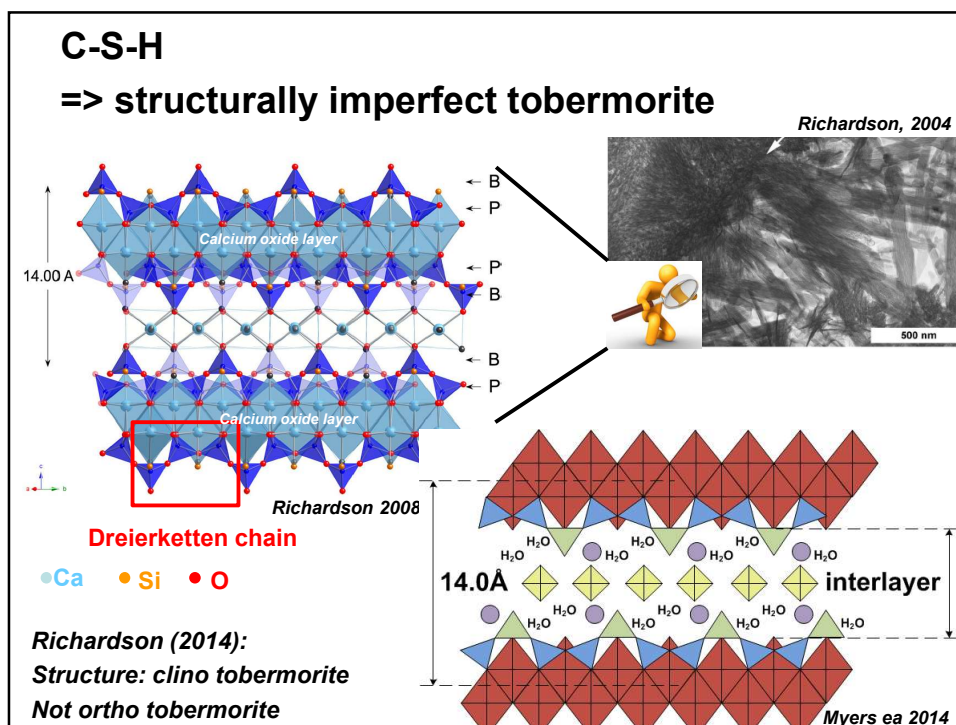
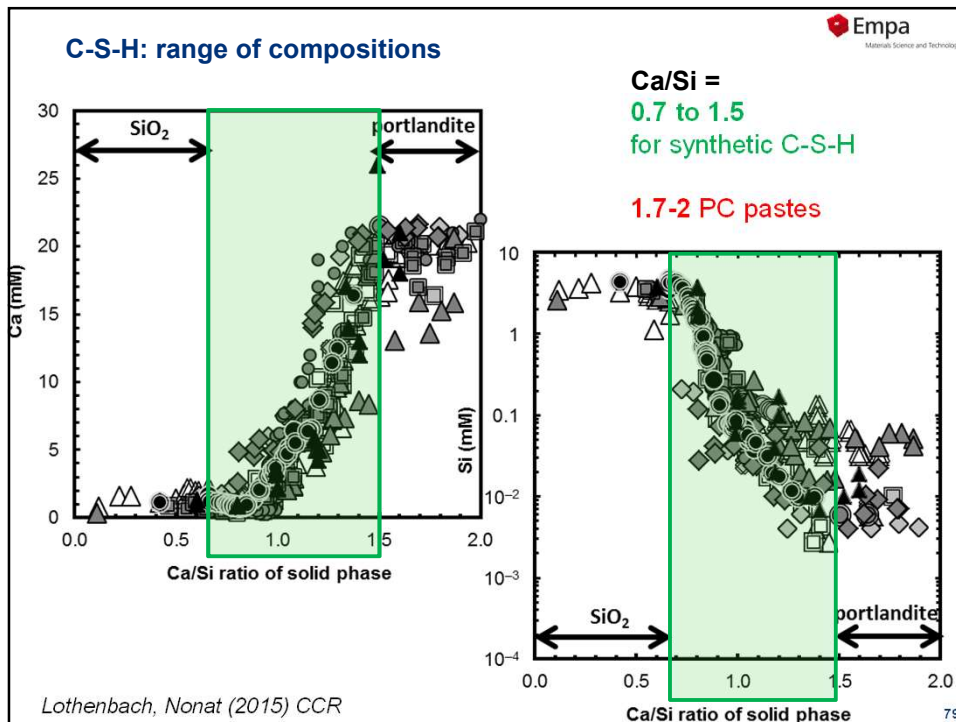


(b) PC 10SF, 90 days, 20°C

Rossen et al (2015) CCR 75

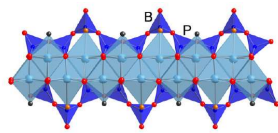
76





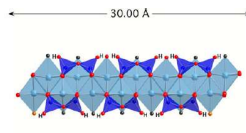
## C-S-H structure: Variation of Ca/Si ratio

Richardson 2008



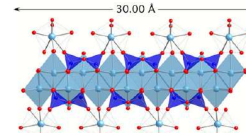
Ca/Si=0.67

- Infinite chain



Ca/Si=1.0

- Dimer, pentamer, ...

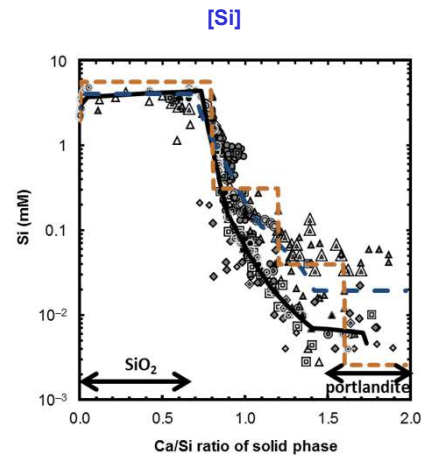
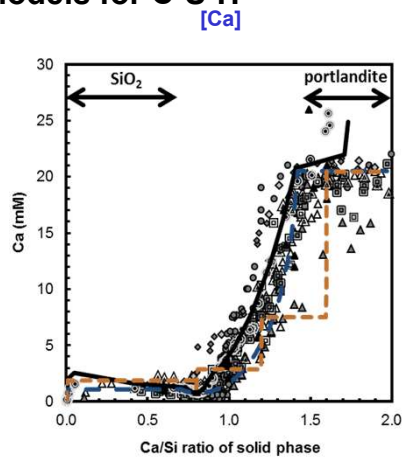


Ca/Si=1.50

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

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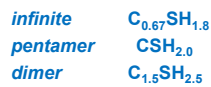
## Different types of thermodynamic (geochemical) models for C-S-H



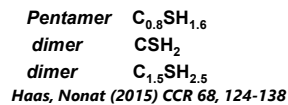
### 3 different CSH



### Solid solution



### Surface reaction model

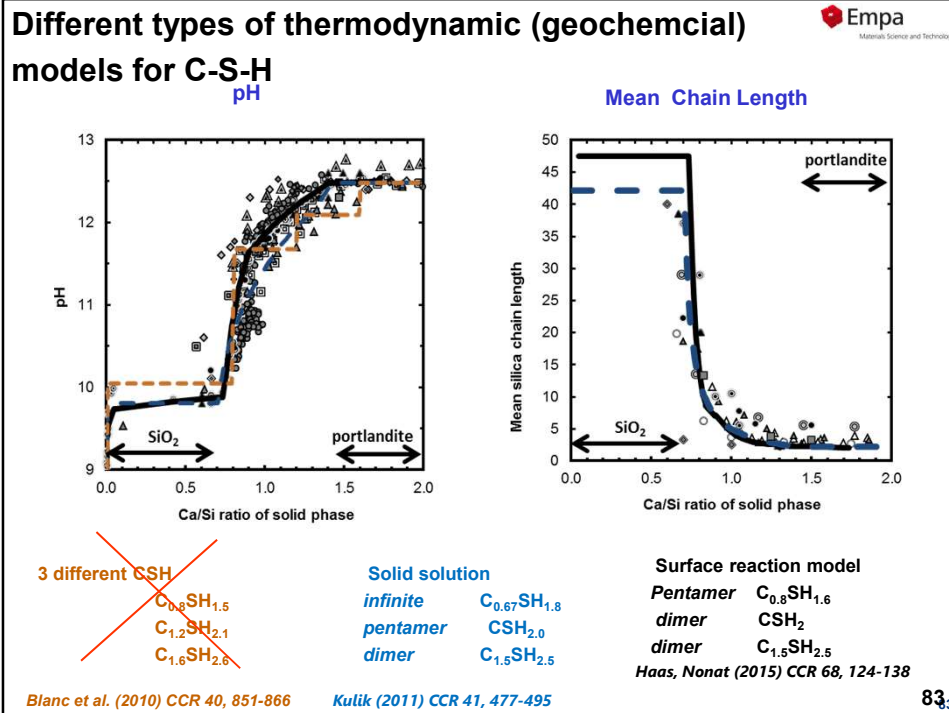


Blanc et al. (2010) CCR 40, 851-866

Kulik (2011) CCR 41, 477-495

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## 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



Make a new project:  
by copying records from default d by linking files from the default d

Open Project **New Project** Learn more Cancel

**Step 1 - Selection of databases, data subsets, phase type**

Phase/DC Filters

☒ Aqueous electrolyte  
☒ Gas mixture

Built-in Databases Version

☐ support  
☐ supcrt  
☒ psi-nagra  
☐ 3rdparty

**Step 2: Select Independent Components (not available)**

	I	II	III	IV	V	VI	VII	VIII
1	H							He
2	Li	Be	B	C	N	O	F	Ne
3	Na	Mg	Al	Si	P	S	Cl	Ar
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe
								Co
								Ni

Setup of aqueous and gas phases in project: CaO2H2

Select Aqueous Electrolyte Model Select Gas/Fluid Mixture Model

Ion-association (IA) with Davies equation, D (default)  
IA with extended Debye-Hueckel equation (Helgeson), common b\_gamma and a0, H  
IA with extended Debye-Hueckel equation (Shvarov), common b\_gamma and a0, Y  
IA with extended Debye-Hueckel equation (Karpov), common b\_gamma, individual a0, 3  
IA with Debye-Hueckel equation, no b\_gamma, individual a0, 2  
IA with Debye-Hueckel limiting law (very low ionic strength), 1

Do not generate: select a user-defined Phase record from database ( Q, S, Z ), U  
Do not include aqueous electrolyte phase into the system definition, N

Phase record key: |a AQELIA aq\_gen aq EDH\_H

Parameters for the aqueous phase model  
b\_gamma(L,298) value: [0.064]  
b\_gamma(P,T) mode: [HSC]  
Common a0 value: [3.72]  
Gamma (neutral species): [Calculate as b\_gamma]  
Gamma (water solvent): [From osmotic coefficient]  
Molality conversion: [Applied to all species]

GEM-Selektor 3 (GEMS3) - Geochemical Equilibrium

Modules Record Data Calculate View Print Win

SingleSys

Input: System Definition

Phase/species

☒ aq\_gen  
☒ gas\_gen  
☒ Portlandite

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

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

DComp: Please, set a new record key

s:CaOH:Portlandite:exam:

s Phase state of Dependent Component (species) { a g s l h x c }

CaOH Group to which Dependent Component belongs

Portlandite Name of Dependent Component

exam Name of thermodynamic data subset (e.g. database)

Ok Reset From List Help Cancel

Phase state (s ... solid; a ... aqueous; g ... gaseous; l ... liquid; h ... hexamer; c ... cluster)

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  
Optional: 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)

GEM-Selektor DComp Setup: s:CaOH:Portlandite:exam:

**Step 1 - Defining the dependent component (DC) type and the calculation method codes**

Select here to which class this DC belongs

This class code will be copied into Phase definition (can be changed there too):

0 Dependent Component of a single-component condensed phase

By setting the codes below, configure the DComp record data and tell the program how the molar properties of this DC should be corrected for T and P.

## DComp– creation of new entries

GEM-Selektor DComp Setup: s:CaOH:Portlandite:exam:

**Step 1 - Defining the dependent component (DC) type and the calculation method codes**

Select here to which class this DC belongs:

This class code will be copied into Phase definition (can be changed there too):

0 Dependent Component of a single-component condensed phase

By setting the codes below, configure the DComp record data and tell the program how the molar properties of this DC should be corrected for T and P.

Select here the methods for temperature T and pressure P corrections:

General method code for T corrections of molar thermodynamic properties:

C Calculation on the basis of standard S<sup>0</sup> and Cp<sup>0</sup> integration

Method variant code for EoS T corrections of molar thermodynamic properties:

S Calculation of g<sup>0</sup>T, h<sup>0</sup>T, S<sup>0</sup>T from standard entropy integration

Method code for P corrections of molar thermodynamic properties:

C Pressure correction assuming constant molar volume V<sup>0</sup>

Codes for species-dependent EoS subroutines

N No fluid model routine

**Optional parameters for experienced users, else leave default values**

**Default: “CS”**

$$\Delta_a G_T^o = \Delta_f G_{T_0}^o - \int_{T_0}^T S_T^o dT$$

**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 molar 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

**Step 2 - Specific dimensions and settings**

Dimensions to change only in special cases

1

Number of Cp(T) equations can be changed here if Cp(T) coefficients are available for more than one temperature interval. Default is 1, maximum 5 intervals.

0

Number of phase transitions can be changed here, if necessary (usually one less than the number of Cp=f(T) equations). Default is 0, maximal 4.

0

Number of EoS coefficients can be set here if certain EoS models for fluids will be used (default: 0). The coefficients will be collected automatically into Phase record.

☐ Check here to allocate the Vm=f(P, T) vector of coefficients (reserved)

Units of measurement (cannot be changed in this version of GEMS)

J /mol/(K)

Units of energy (default: J)

J /bar = 0.1 cm<sup>3</sup>/mol

Units of volume (default: J)

b bar = 10<sup>5</sup> Pa

Units of pressure (default: b)

C Celsius

Units of temperature (default: C)

Learn more

< Back

Next >

Cancel

**Optional parameters for experienced users, else leave default values**

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**DComp :: Thermochemical/EoS data format for Dependent Components**

Page 1 Page 2 03/05/2017, 10:09

Portlandite  
Ca (OH) 2

M0 --- Zz --- ab

V0d	3.306	---
G0d	-897013	---
H0d	---	---
S0d	83.4	---
Cp0d	---	---
PrTr	1	25
LamST	---	---
BetAlp	---	---

Robie\_Hem:1995:pap: All

**Press calculate**

Modules Record Record List Database Files Window Help

**Temperature range**

Enter G (in J/mol) and S  
H will be calculated  
Cp on page 2

**DComp :: Thermochemical/EoS data format**

Page 1 Page 2 03/05/2017, 10:09

C S C N O j j b C + -

TCint	0
1	426.85

aiCpT	0	186.7
1	---	-0.02191
2	---	0
3	---	-1600
4	---	0
5	---	0
6	---	0
7	---	0
8	---	0
9	---	0
10	---	0
11	---	0

$$C_p^0 = a_0 + a_1T + a_2T^2 + a_3T^{0.5} + a_4T^2 + a_5T^3 + a_6T^4 + a_7T^{-3} + a_8T^{-1} + a_9T^{0.5}$$

$$= 186.7 - 0.022 \cdot 298.15 - 1600 / \sqrt{(298.15)} = 87.5$$

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**DComp :: Calculation finished OK (elapsed time: 8.533 s).**

Page 1 Page 2 03/05/2017, 10:12

Portlandite  
Ca (OH) 2

Mass (g/mol) from composition charge Activity coefficients

M0 74.0927 Zz 0 ab ---

Uncertainty

V0d	3.306	0
G0d	-897013	---
H0d	-984671.48	---
S0d	83.4	---
Cp0d	87.5053	0
PrTr	1	25
LamST	---	---
BetAlp	---	---

**Empa**  
Materials Science and Technology

**name**  
**Chemical composition (defined format)**

**Volume** (1 J/bar = 10 cm<sup>3</sup>/mol)  
**Free energy** (J/mol)  
**Enthalpy** (J/mol) calculated from S and G  
**Entropy** (J/mol/K) ΔG = ΔH-TS  
**Heat capacity** (J/mol/K): calculated from page 2  
**Pressure Temperature**

	log K <sub>50</sub> <sup>*</sup>	Δ <sub>r</sub> G° [kJ/mol]	Δ <sub>r</sub> H° [kJ/mol]	S° [J/K/mol]	a <sub>0</sub> [J/K/mol]	a <sub>1</sub>	a <sub>2</sub>	a <sub>3</sub>	V° [cm <sup>3</sup> /mol]
CH (portlandite)	-5.2	-897	-985	83	187	-0.022	---	-1600	33
SiO <sub>2,am</sub>	1.476	-848.90	-903	41	47	0.034	-1.13·10 <sup>6</sup>	---	29

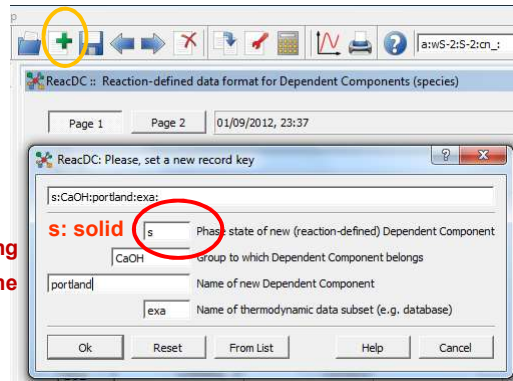
### 3) GEMS: reactions (ReacDC): new

Portlandite solubility:

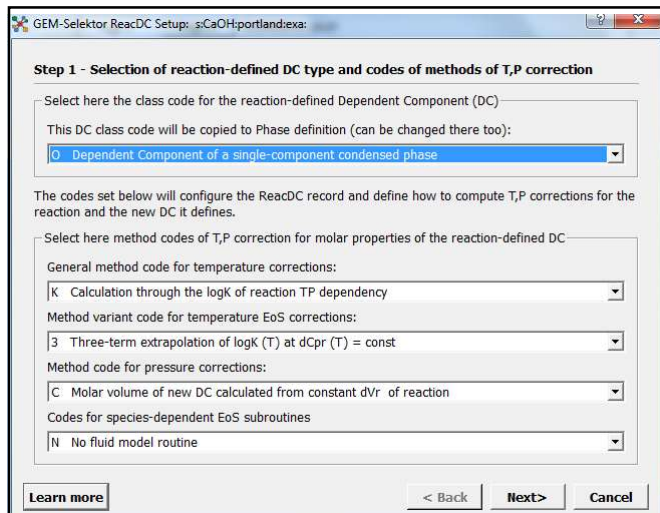


$$\{\text{Ca}^{2+}\}\{\text{OH}^-\}/\{\text{Ca(OH)}_2\} = 10^{-5.2}$$

Elements: ordering  
Component name  
Data base: «example»



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

K) 3

Three-term extrapolation of  $\log K(T)$  at  $dCpr(T) = \text{const}$  (preferable). Enter non-[empty] values into the Cp0x[0,0] cell, and into either H0x[0,0] or S0x[0,0] cells (another must contain [empty]); enter a non-empty value in either logKx[0,0], logKx[0,1] or G0x[0,0] cells (the other two cells and G0x[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  $V^\circ$  (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:



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

GEM-Selektor ReacDC Setup: s:CaOH:portland:exa:

**Step 2 - Specific dimensions and settings**

Dimension to change only in special cases (e.g. to find properties of reaction between existing DCs)

**b** Number of DCs in the reaction (usually set automatically after selecting the DCs)

Dimensions to set only for the logK array for T,P corrections by interpolation (KZZ method codes)

0 Number of interpolation points along T (> 2, < 20)

0 Number of interpolation points along P (> 1, < 10)

Units of measurement (cannot be changed in this version of GEMS)

j J/mol(K) Units of energy (default: j)

j J/bar = 0.1 cm<sup>3</sup>/mol Units of volume (default: j)

b bar = 10<sup>5</sup> Pa Units of pressure (default: b)

C Celsius Units of temperature (default: C)

Learn more < Back Next> Cancel

Ca<sup>2+</sup>, OH<sup>-</sup>, Ca(OH)<sub>2</sub>

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### 3) GEMS: reactions (ReacDC)

Portlandite solubility:



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

GEM-Selektor ReacDC Setup: s:CaOH:portland:exa:

**Step 3 - Useful hints**

Optional

**1** Set here the number of links to SDref bibliography records (default 0)

What will happen after you click "Finish"

(1) A list of available ReacDC records will appear, asking you to mark those selected into the reaction. Next, a list of available DComp records appears, to mark those taken into reaction. In total, minimum one DC (DComp or ReacDC) must be selected if the reaction defines a new DC, or at least two DCs must be selected if only the properties of reaction shall be calculated.

(2) When Page 1 appears, fill out RDname field and enter the formula of new (last) DC into RDform field. Next, enter the reaction stoichiometry coefficients into the SC\_DC column (convention: positive for products, negative for reactants). Then enter the available dVr; K or logK or dGr; dHr or dSr; dCpr values. If some properties are unknown (e.g. dHr), enter the 'empty' value '---' there.

(3) Click on 'Calculate' toolbar button: the missing properties of the reaction and the newly defined DC (the last one) will appear on Page 1. Save the ReacDC record to database. You may test T,P corrections for properties of the reaction or its new DC by creating a RTParm tabulator on this ReacDC record later on.

Learn more < Back Finish Cancel

Literature reference

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### 3) GEMS: reactions (ReacDC)

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

Please, mark one or more record keys. Filter: \*.\*.\*.\*.\*

d	a	Ca	Ca+2	an
d	a	Ca	CaOH+	cn
d	a	wH0	H2O	bn
d	a	wO0	O2	bn
d	a	wX	OH-	bn
d	a	w	H+	an
d	a	w	H2O	an
d	g	H0	H2	en
d	g	O0	O2	en
d	s	CaOH	Portlandite	dn
d	s	CaOH	Portlandite	exam

Ok Set Filter Select All

Chose existing compounds;

New compound «Ca(OH)<sub>2</sub>» will be made by the programme

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### 3) GEMS: reactions (ReacDC)

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

ReacDC: Calculation finished OK (elapsed time: 0 s)

Page 1 Page 2 02/04/2013, 15:48

Portlandite  
Ca(OH)<sub>2</sub>

SC	DC	REsDC
0	1 d a	Ca Ca+2 an
1	2 d a	wX OH- bn
2	-1 p s	CaOH Portl exa

V0r -6.0914  
logKr -5.2  
G0r  
H0r  
S0r -161.306  
Cp0r -391.104  
NisoX

PrTr 1 25 M0 74.0927  
BetAl

Reaction coefficients  
 New component  
 Volume changes  
 Log K  
 S reaction  
 Cp reaction

96



### 3) GEMS: reactions (ReacDC)

ReacDC :: Reaction-defined data format for Dependent Components

ReacDC :: Calculation finished OK (elapsed time: 0 s).

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Portlandite  
Ca (OH) 2

M0 74.0927 Z:

V0d 3.306  
G0d -897013  
H0d -984675  
S0d 83.4  
Cp0d 87.5053  
PrTr 1  
LamST ---  
BetAlp ---

Page 1 Page 2 02/04/2013, 15:48

Portl  
Ca (OH) 2

	SC DC		REsDC		
0	1 d	a	Ca	Ca+2	an
1	2 d	a	wX	OH-	bn
2	-1 n	s	CaOH	Portl	exa

V0r -6.0914 3.30596  
logKr 6.3095734e-006 -5.2  
G0r 29681.819 -897011.82  
H0r -18411.565 -984675.43  
S0r -161.306 83.399  
Cp0r -391.104 87.505

Volume  
Gf  
S  
Cp

	log K <sub>50</sub> *	Δ <sub>r</sub> G° [kJ/mol]	Δ <sub>r</sub> H° [kJ/mol]	S° [J/K/mol]	a <sub>0</sub> [J/K/mol]	a <sub>1</sub>	a <sub>2</sub>	a <sub>3</sub>	V° [cm <sup>3</sup> /mol]
CH (portlandite)	-5.2	-897	-985	83	187	-0.022		-1600	33
SiO <sub>2</sub>	1.476	-848.90	-903	41	47	0.034	-1.13·10 <sup>6</sup>		29

ReacDC :: Calculation finished OK (elapsed time: 0 s).

Page 1 Page 2 03/09/2012, 14:14

portlandite  
Ca (OH) 2

SC DC REsDC

0	1 d	a	Ca	Ca+2	an
1	2 d	a	wX	OH-	bn
2	-1 n	s	CaOH	portland	exa

V0r -6.0914 3.30596  
logKr 6.3095734e-006 -5.2  
G0r 29681.819 -897011.82  
H0r -18411.597 -984675.4  
S0r -161.306 83.4  
Cp0r -391.104 87.5053

TCint P int allgKr

	TCint	P int	allgKr
0	0	0	128.397
1	426.85	1	0
2			-5129.11
3			-20.4287
4			0
5			0
6			0
7			0
8			0
9			0
10			0

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**  $\Delta C p_T = \Delta C p_{T_0} = \text{const}$

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

$$A_0 = \frac{0.4343}{R} \cdot [\Delta_r S_{T_0}^0 - \Delta_r C p_{T_0} (\ln T_0 + 1)]$$

$$A_2 = -\frac{0.4343}{R} \cdot (\Delta_r H_{T_0}^0 - \Delta_r C p_{T_0} T_0)$$

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

#### 4.) Plot of temperature/pressure dependent thermodynamic data

**new**

Please, select a source record from:

DComp ReacDC Cancel

logKsp = f(TC) of ettringite  
Please, change the script and/or remake, if necessary

logK(T) experim.  
logK(T) experim.

rpMode 2 rpNpT 1 17

5  
85  
5

2 1000 2 5

tExpr xT[TP] =: twTC;  
xB[TP] =: twB;  
yF[TP][0] =: tlogK;

**Helps to determine S or H for Temperature extrapolations**

**Temperature/pressure dependent thermodynamic data**

ReacDC: Select one key of a source ReacDC record

Please, select one record key. Filter: \*

s CaOH Port1 exa

**number**

RTParm: Please, set a new record key

s:CaOH:Port1:exa:r:001:

s Phase state of source Dependent Component (DComp or ReacDC)

CaOH Group to which source Dependent Component belongs

Port1 Name of source Dependent Component

exa Code of source thermodynamic data set

r Source of input data for DC { r d }

001 Variant number of this RTParm calculation task <integer>

Ok Reset From List Help Cancel

Ok Set Filter Help Cancel

100

**Temperature/pressure dependent thermodynamic data**

GEM-Selektor RTParm Setup: s:CaOH:Port:exacr:001

**Step 1 - Thermodynamic data tabulator (RTParm) configuration**

This is a tool for tabulating and plotting thermodynamic data against temperature T and/or pressure P. The input is taken from a DComp or ReacDC record specified in this RTParm record key.

Upon calculation, results will be tabulated on the 'Tables' page, as specified in 'tExpr' math script. Results can be plotted, exported into text files, or copy-pasted to other programs.

Simple 'tExpr' scripts can be created using a selection dialog on the next page of this wizard. Example scripts are also provided under 'Help' 'View Scripts...' menu command in the RTParm window.

2 T then P increments Select mode for iterating xP and xT arguments. Default mode: 2.

Temperature T  
Units: C Celsius  
Minimal: 0.00  
Maximal: 350.00  
Step: 25.00  
Number of points: 15  
Plot as abscissa xT

Pressure P  
Units: b bar  
Minimal: 1.00  
Maximal: 1.00  
Step: 0.00  
Number of points: 1  
Plot as abscissa xP

**Initial Final step**

**Step 2 - Selection of items to sample (to retain the old script, just click 'Next >')**

Property Item Selection Sampling Script

Scalars

twG twEw  
twH twRT  
twS twP  
twCp twTC  
twV twTK  
twK tw[0]  
tlogK xT  
tdGr xP

yF[jTP][0] =: tlogK;

Learn more < Back

**Temperature/pressure dependent thermodynamic data**

GEM-Selektor RTParm Setup: s:CaOH:Ca(OH)2:cmr:01

**Step 1 - Thermodynamic data tabulator (RTParm) configuration**

This is a tool for tabulating and plotting thermodynamic data against temperature T and/or pressure P. The input is taken from a DComp or ReacDC record specified in this RTParm record key.

Upon calculation, results will be tabulated on the 'Tables' page, as specified in 'tExpr' math script. Results can be plotted, exported into text files, or copy-pasted to other programs.

Simple 'tExpr' scripts can be created using a selection dialog on the next page of this wizard. Example scripts are also provided under 'Help' 'View Scripts...' menu command in the RTParm window.

2 T then P increments Select mode for iterating xP and xT arguments. Default mode: 2.

Temperature T  
Units: C Celsius  
Minimal: 0.00  
Maximal: 350.00  
Step: 25.00  
Number of points: 15  
Plot as abscissa xT

Pressure P  
Units: b bar  
Minimal: 1.00  
Maximal: 1.00  
Step: 0.00  
Number of points: 1  
Plot as abscissa xP

**calc. values**

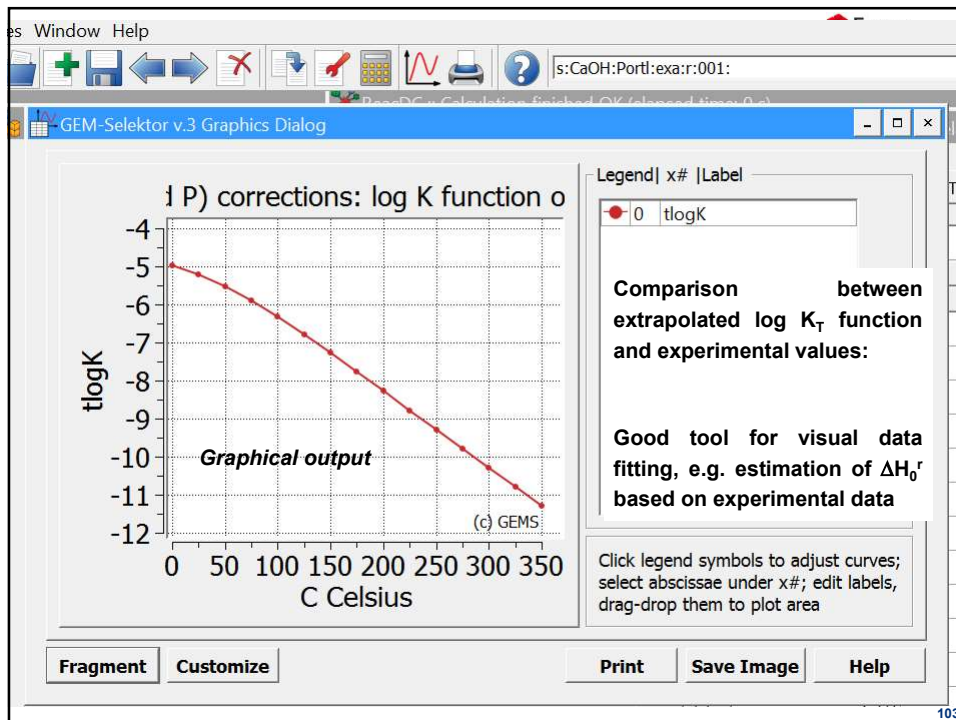
**Start value Stop value Step**

RTParm : Calculation finished OK (elapsed time: 0.687 s).

Scripts Tables TPwork Setup 03/05/2017, 14:50

tXName C Celsius tlogK

	xT	xP	yF
0	0	1	-4.9854588
1	25	1	-5.2
2	50	1	-5.5140215
3	75	1	-5.8965457
4	100	1	-6.3261795
5	125	1	-6.7876229



### 5.) Thermodynamic Phases – creation of entries

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Phase: Please, set a new record key

s:CaOH:Portlandite:c:exa:

s Code of phase state { a g f p l m h s d x }

CaOH Group identifier for such phases (letters, digits)

Portlandite Name of this phase definition (letters, digits)

c Phase class { c d l gm ss ssd ls aq xsd xc }

exa Comment to phase definition

Ok Reset From List Help Cancel

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:

GEM-Selektor Phase Setup: s:CaOH:Portlandite:c:exa:

Step 1 - Defining the Phase and the Model of Mixing

Selection of the codes below will configure the Phase record and tell the program what kind of phase and which model of (ideal) mixing should be used, and how it should be calculated.

Select a phase aggregate state code:

s Condensed solid phase, also multi-component solid solution

Select a model of mixing for this phase:

I Ideal mixture or pure phase (default)

Select a mode of calculation of activity coefficients of end members:

I Activity coefficients will be set to 1 (pure phase, simple ideal mixing), default

Select a mode of execution of DcEq user-defined script for end-members:

## 5.) Thermodynamic Phases – creation of entries

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

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

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## 5.) Thermodynamic Phases – creation of entries

**Step 2 - Phase Model-Specific Settings**

Optional dimensions to set when built-in functions or scripts for the mixing model shall be used.

Attention! ForTSMMod built-in mixing models that use dc\_cf and/or ipxT, pc\_cf data objects, the appropriate dimensions will usually be allocated automatically. Otherwise, the array will be allocated only if all its dimensions are not zeros.

dc\_cf array: number of columns (coefficients per phase end member).

ipxT and ph\_cf arrays: number of rows (interaction parameters) for the non-ideal mixing model.

ipxT array for indexation of interaction parameters: set here the maximum order of a parameter (e.g. 3 if binary and ternary parameters will be used).

ph\_cf array of interaction parameter coefficients: number of columns (max. number of coefficients per parameter).

Set items in this box only if this is a sorption phase

☐ Check if surface complexation will be considered in this (sorption) phase

Set the number of surface types (minimum 1, maximum 6) to allocate surface complexes

Enter here the specific surface area A of the sorbent (in m<sup>2</sup> per gram), A>0

[Learn more](#) [< Back](#) [Next >](#)

**Step 3 - Final Settings and Hints**

Optional

Set here the number of links to SDref bibliography records (default 0)

☐ Extract parameters from DComp/ReacDC records and refresh DC class codes upon "Calculate"?

What will happen after you click "Finish"

(1) A list of available ReacDC ("Y") and DComp ("D") records will appear; mark those to be the phase components (end-members). At least one species for a pure phase, or two for a solution phase must be marked.

(2) In Phase window, fill out PhName and PhNote comments. Depending on setup, enter numbers in DisPar, text in DisEq and/or PhEq, parameter coefficients in ipxT, ph\_cf, dc\_cf arrays on Phase window pages.

(3) Click on "Calculate" toolbar button, then look at the PhDCC columns; correct DC codes, if needed ("T" for H+; "W" for H<sub>2</sub>O-solvent; "M", "J", or "I" for solid-solution end members). Save Phase record to project database.

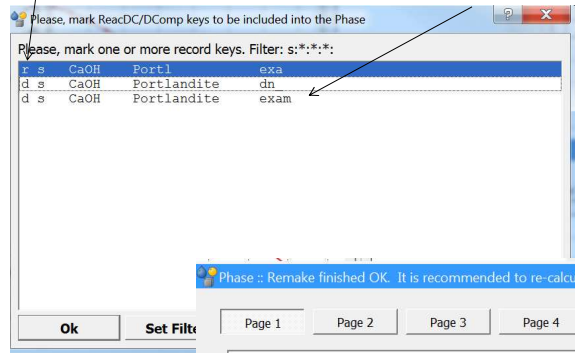
**Optional parameters only for experienced users, otherwise leave default values**

## 5.) Thermodynamic Phases – creation of entries

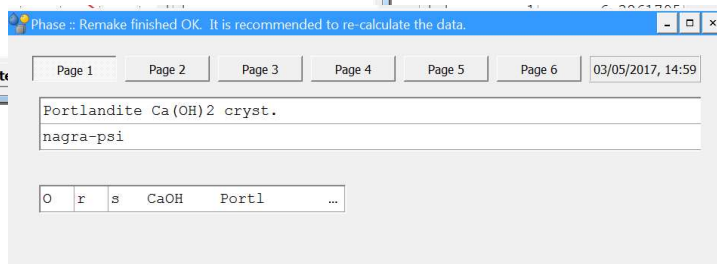
Mark dependent component to be included in the project database

a) either from ReacDC

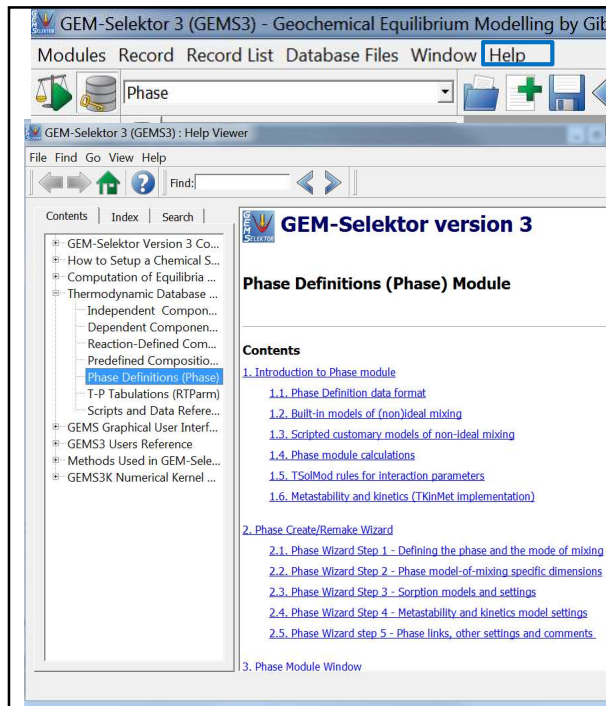
b) or from DComp



See “help” for additional information or hints  
(Partially still under construction)



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• See “Help:Help” for additional information or hints (Partially still under construction)

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## 5.) Thermodynamic Phases – creation of entries

### b) Solid solution

Phase

	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

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CSH-quaternary model  
cement database

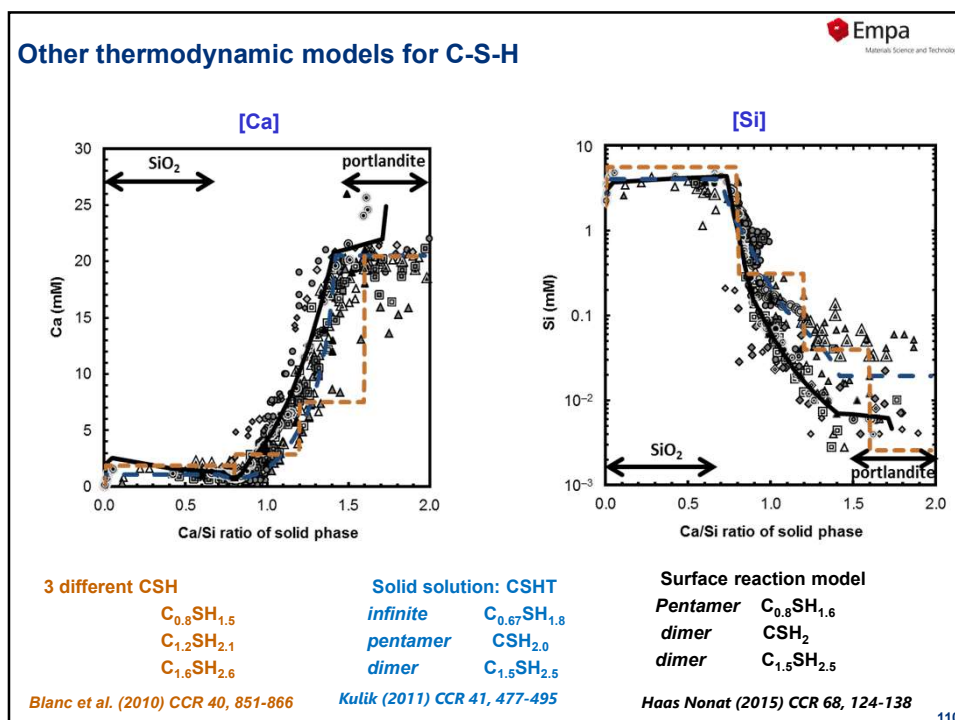
Kulik:2011:pap:   all

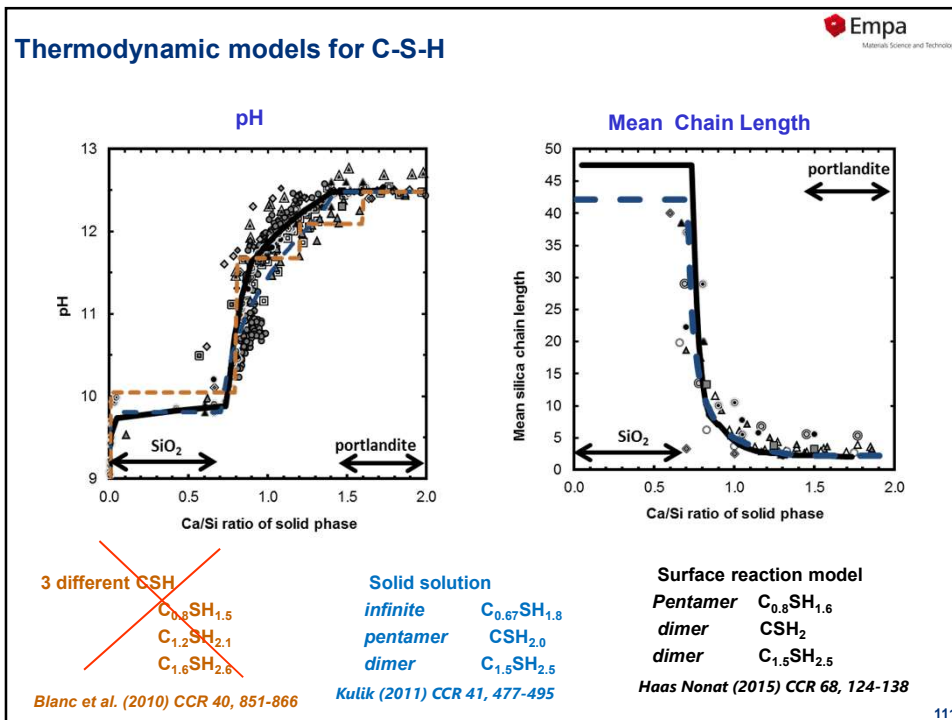
0	r	s	CaSiOH	CSH-JenD	...	
1	I	r	s	CaSiOH	CSH-JenH	...
2	I	r	s	CaSiOH	CSH-TobD	...
3	I	r	s	CaSiOH	CSH-TobH	...
4	I	d	s	KSIOH	KSIOH	...
5	I	d	s	NaSiOH	NaSiOH	...

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

Plus  $(\text{KOH})_{2.5}\text{SiO}_2\text{H}_2\text{O}$  and  $(\text{NaOH})_{2.5}\text{SiO}_2\text{H}_2\text{O}$  to **estimate** alkali uptake

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## Selection of CSH model

- 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"

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## Selection of CSH models


  
 Materials Science and Technology

modules record record list database files window help

Phase

	1	2	3	4	5
54	s	CaFeSiOH	C3S1.34H5.32	c	cem_
55	s	CaFSH	C3(AF)S0.84H	ss	cem_
56	s	CaMgCO	Dolomite-dis	c	nagra-psi_
57	s	CaMgCO	Dolomite-ord	c	nagra-psi_
58	s	CaO	lime	c	cem_
59	s	CaOH	Portlandite	c	nagra-psi_
60	s	CaSO	Anhydrite	c	nagra-psi_
61	s	CaSO	Gypsum	c	nagra-psi_
62	s	CaSO	hemihydrate	c	cem_
63	s	CSH	CSH3T	ss	cem_
64	s	CSH	CSHQ	ss	cem_
65	s	Fe	Iron	c	nagra-psi_
66	s	FeCO	Fe-carbonate	d	nagra-psi_
67	s	FeCO	Siderite	c	nagra-psi_
68	s	FeO	Hematite	c	nagra-psi_
69	s	FeO	Magnetite	c	nagra-psi_
70	s	FeOH	Ferrihydrite-am	d	nagra-psi_
71	s	FeOH	Ferrihydrite-mc	c	cem_
72	s	FeOH	Goethite	c	nagra-psi_

Phase: Definition of thermodynamic phase

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CSH3T (downscaled) solid solution model

cement database


Kulik:2011:pap: all

0	I	d	s	CaSiOH	CSH3T-T2C	...
1	I	d	s	CaSiOH	CSH3T-T5C	...
2	I	d	s	CaSiOH	CSH3T-TobH	...

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

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## 5.) Thermodynamic Phases – Treatment of solid solutions


  
 Materials Science and Technology

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

GEM-Selektor Phase Setup: s:CSH:CSHT:ss:cem\_

**Step 1 - Defining the Phase and the Model of Mixing**

Selection of the codes below will configure the Phase record and tell the program what kind of phase and which model of (non-ideal) mixing should be used, and how it should be calculated.

Select a phase aggregate state code:

s Condensed solid phase, also multi-component solid solution

Select a model of mixing for this phase:

I Ideal mixture or pure phase (default)

Select a mode of calculation of activity coefficients of end members:

I Activity coefficients will be set to 1 (pure phase, simple ideal mixing), default

Select a mode of execution of DcEq user-defined script for end-members:

N No DcEq script will be provided in this Phase definition (default)

Select a mode of execution of PhEq user-defined script for the whole phase:

N No PhEq script will be provided in this Phase definition (default)

Select a mode of a linking user-defined DcEq script to phase end members:

N No DcEq script will be provided (pure phase, built-in or ideal model), default

Select specific mixing rules (temperature corrections) for EoS and activity models:

N Default mixing rule or form of interaction parameter coefficients

To set up a (new) sorption, metastable layer- or a kinetically-controlled phase, please proceed to next wizard pages.

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## GEMS – Database management

### 5.) Thermodynamic Phases – Treatment of solid solutions

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

Please, mark one or more record keys. Filter: s:\*,\*:\*,\*:

r	s	CaSiOH	CSH-JenD	ce
r	s	CaSiOH	CSH-JenH	ce
r	s	CaSiOH	CSH-TobD	ce
r	s	CaSiOH	CSH-TobH	ce
d	s	CSH	T2C-CNASHss	CA
d	s	CSH	T5C-CNASHss	CA
d	s	CSH	TobH-CNASHss	CA
d	s	CaO	Lim	ce
d	s	CaOH	Portlandite	dn
d	s	CaSOH	Jennite	ce
d	s	CaSOH	Tob-I	ce
d	s	CaSOH	Tob-II	ce
d	s	CaSiO	C2S	ce
d	s	CaSiO	C3S	ce
d	s	CaSiOH	T2C	ce
d	s	CaSiOH	T5C	ce
d	s	CaSiOH	TobH	ce
d	s	SiO	Amor-S1	ce
d	s	SiO	Qtz	dn

Ok Set Filter Select All

➔

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CSH-ternary tobermorite model  
cement database

Kulik:2011:pap: all

0	I	d	s	CaSiOH	T2C	...
1	I	d	s	CaSiOH	T5C	...
2	I	d	s	CaSiOH	TobH	...

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

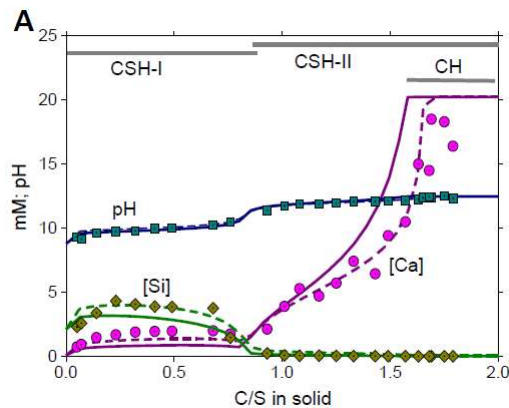
Ideal solid solution phase

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### CSH «Tob-Jennite»: used in Cemdata07

#### CSHII: Ca/Si 0.83 to 1.67

- i) CSH-I solid solution system with the end-members  $\text{SiO}_2$  (am) and tobermorite (Tob-I:  $(\text{CaO})_2(\text{SiO}_2)_{2.4}(\text{H}_2\text{O})_{3.2}$ ) and
- ii) CSH-II solid solution system with the end-members jennite  $(\text{CaO})_{1.67}(\text{SiO}_2)_1(\text{H}_2\text{O})_{2.1}$  and tobermorite (Tob-II:  $(\text{CaO})_{0.83}(\text{SiO}_2)_1(\text{H}_2\text{O})_{1.3}$ ).



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

**CSH «Tob-Jennite»: used in Cemdata07** Empa  
Materials Science and Technology

Record List Database Files Window Help

Phase: Definition of thermodynamic phase

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Tob-jen ideal ss  
cement database

Lothenbach\_ea:pap:2007:

0	I	d	s	CaSOH	Jennite	...
1	I	d	s	CaSOH	Tob-II	...
2	I	r	s	KOHSi	K_sorption	...
3	I	r	s	NaOHSi	Na_sorption	...

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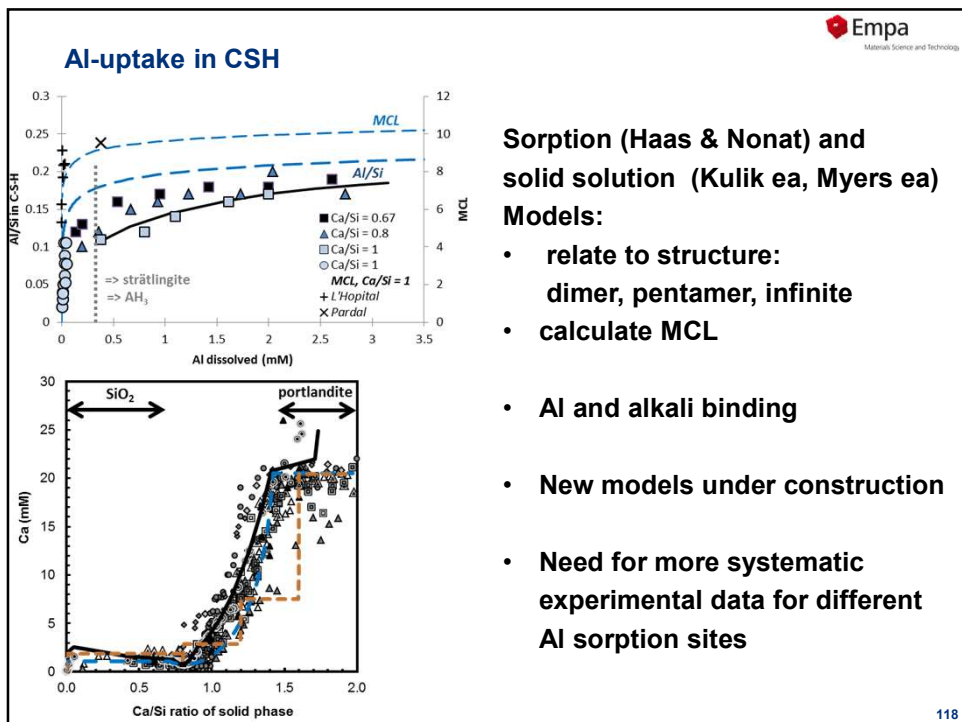
Tob-SiO2 ideal ss  
cement database

Lothenbach\_ea:pap:2007: all

0	I	d	s	CaSOH	Tob-I	...
1	I	d	s	SiO	Amor-Si	...

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

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

### Based on CSHT (Kulik 2011)

SEM-Selektor 3 (GEMS3) - Geochemical Equilibrium Modelling by Gibbs Energy Minimization

File Edit Record List Database Files Window Help

Phase

1	2	3	4	5
1 s	C2S	Belite	c	cem_
2 s	C3S	Alite	c	cem_
3 s	CNASH	CNASH_ss	ss	RJM_
4 s	CSH	CSHQ	ss	cem_
5 s	CaO	lime	c	cem_
6 s	CaOH	Portlandite	c	nagra-psi_
7 s	SiO	Quartz	c	psi-nagra_
8 s	SiO	Silica-amorph	c	nagra-psi_

Phase :: Definition of thermodynamic phase

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CNASH\_ss  
5CA-INFCA-5CNA-INFCA-INFCA-T2C-T5C-TobH\_ss

Myers:2014:pap: all

0	I	r	s	CASH	5CA	...
1	I	r	s	CASH	INFCA	...
2	I	r	s	CNASH	5CNA	...
3	I	r	s	CNASH	INFCA	...
4	I	r	s	CNSH	INFCA	...
5	I	d	s	CSH	T2C-CNASHss	...
6	I	d	s	CSH	T5C-CNASHss	...

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

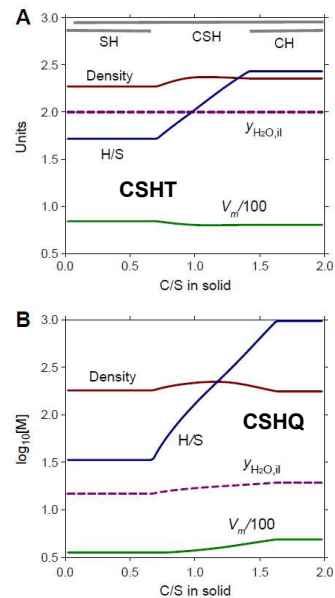


Fig. 8. Variations of density (in g cm<sup>-3</sup>), volume  $V_m$  (in cm<sup>3</sup> mol<sup>-1</sup>), interlayer H<sub>2</sub>O mole fraction  $y_{H_2O,il}$  and H<sub>2</sub>O/SiO<sub>2</sub> mole ratio H/S of the C-S-H phase, as predicted by the downscaled CSHT simple ideal model Table 5 (A) and by the downscaled CSHQ simple ideal model Table 6 (B).