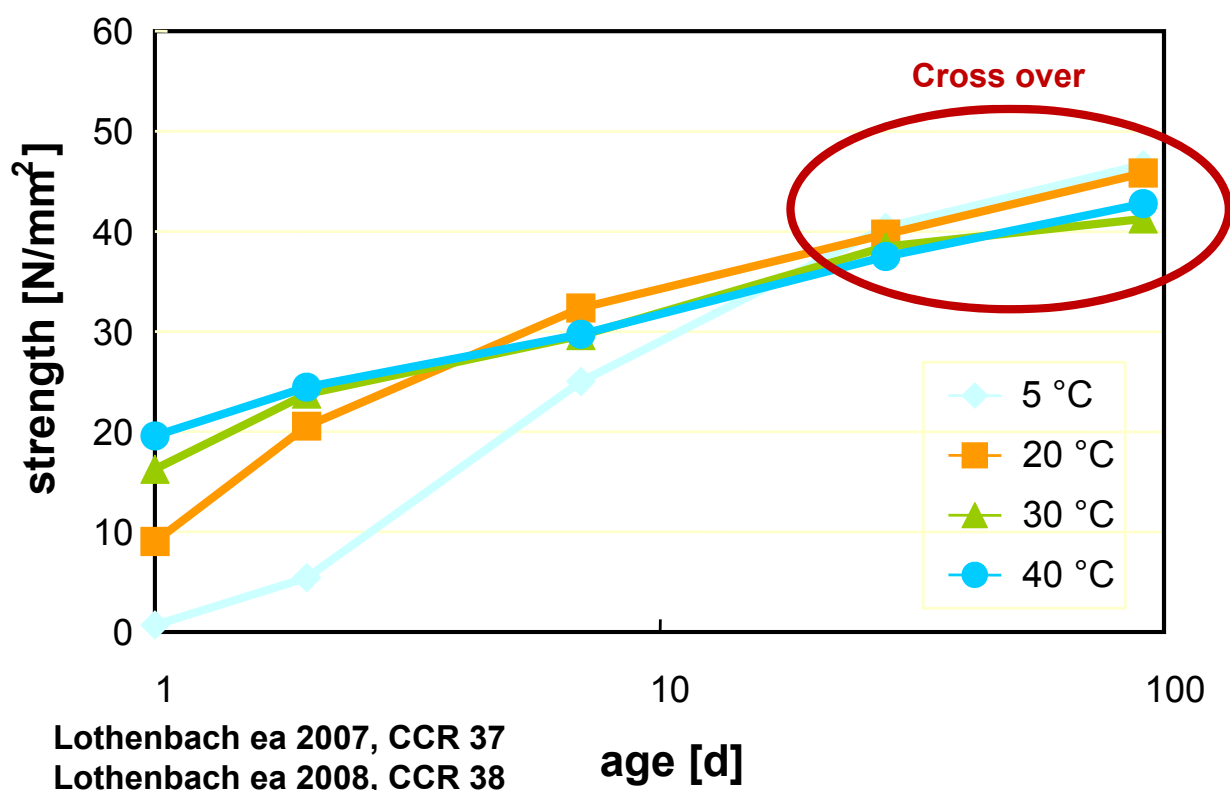




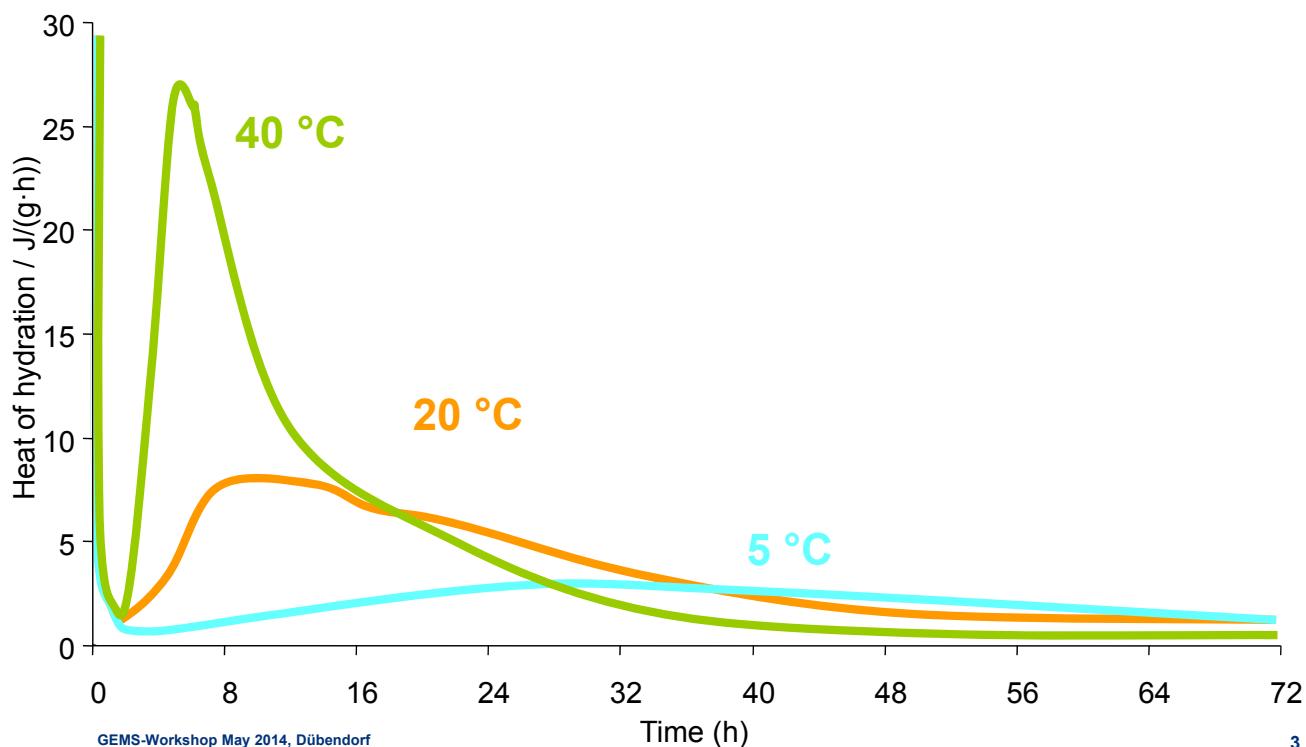
2) Influence of temperature

- a. Experimental evidence**
- b. Temperature extrapolation**
- c. Blended systems**

Influence of temperature: Compressive strength

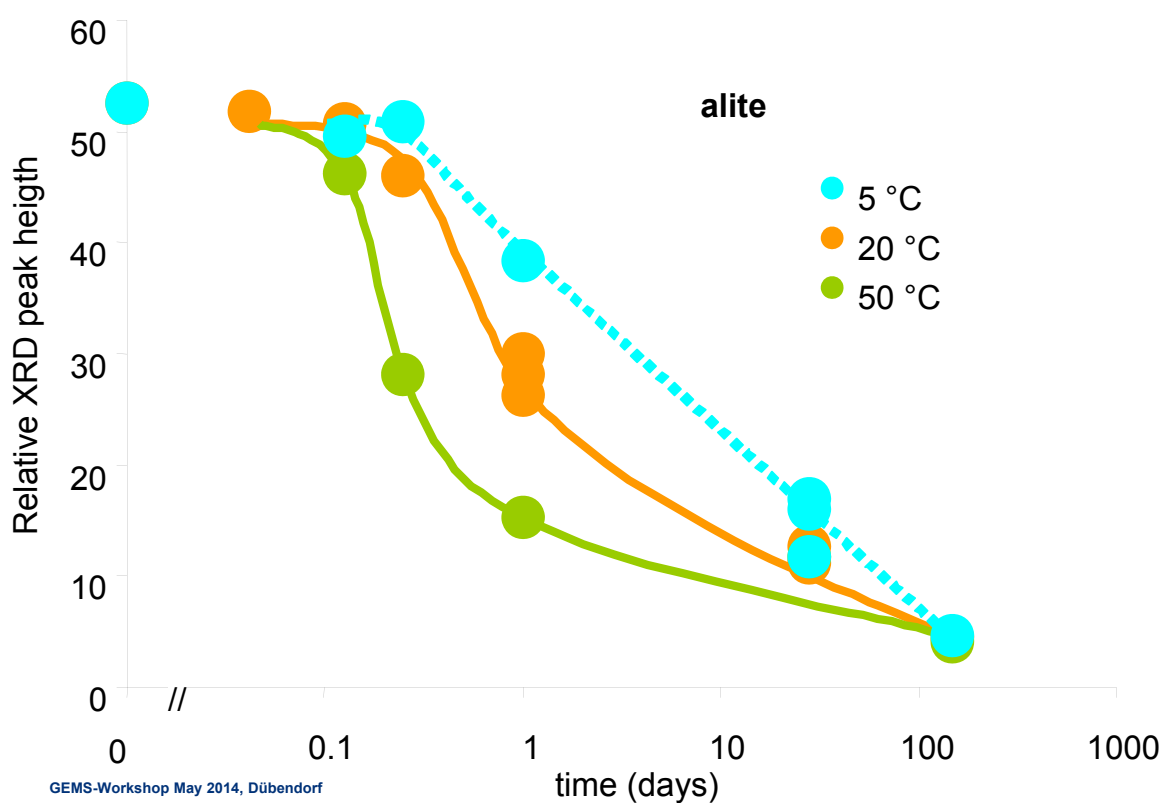


Calorimetry



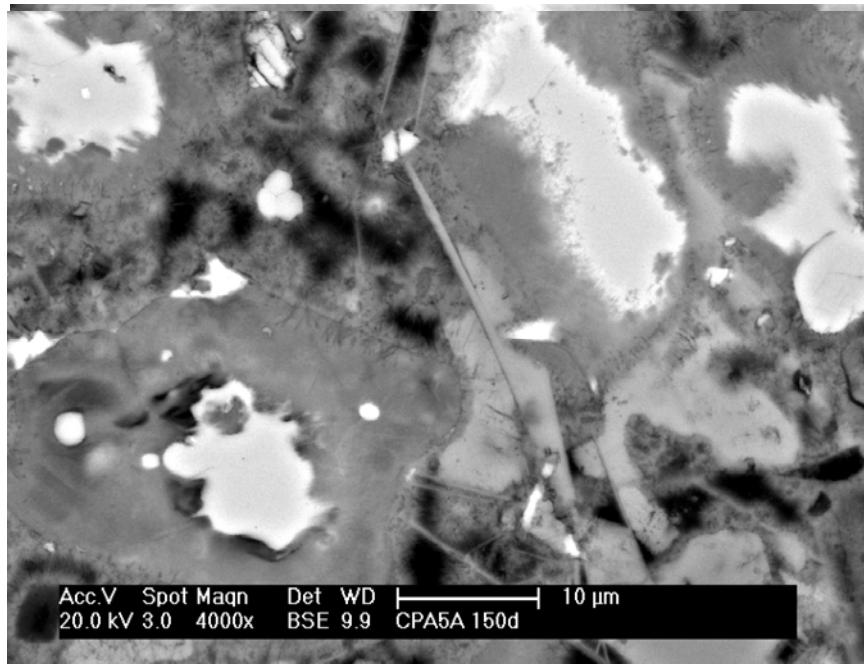
3

Progress of hydration

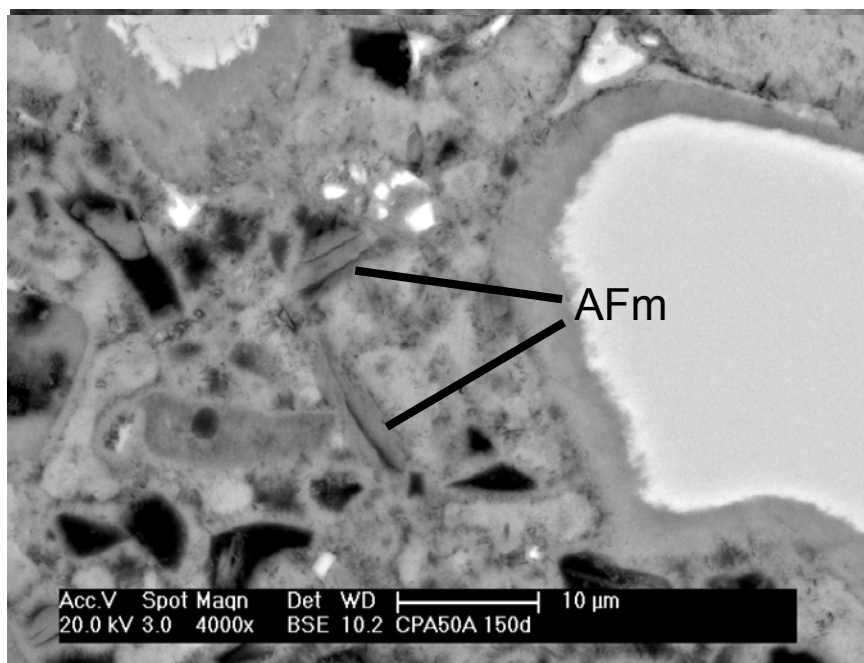


4

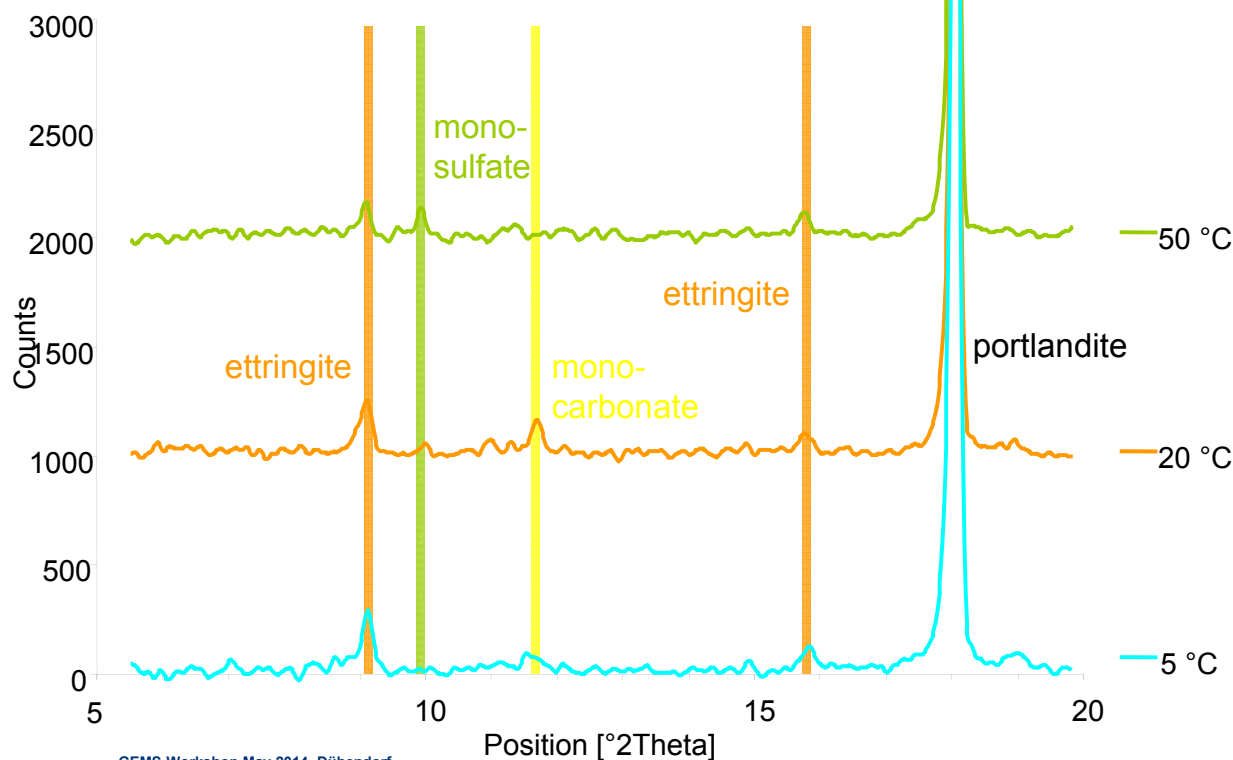
5 °C, 150 days



50 °C, 150 days

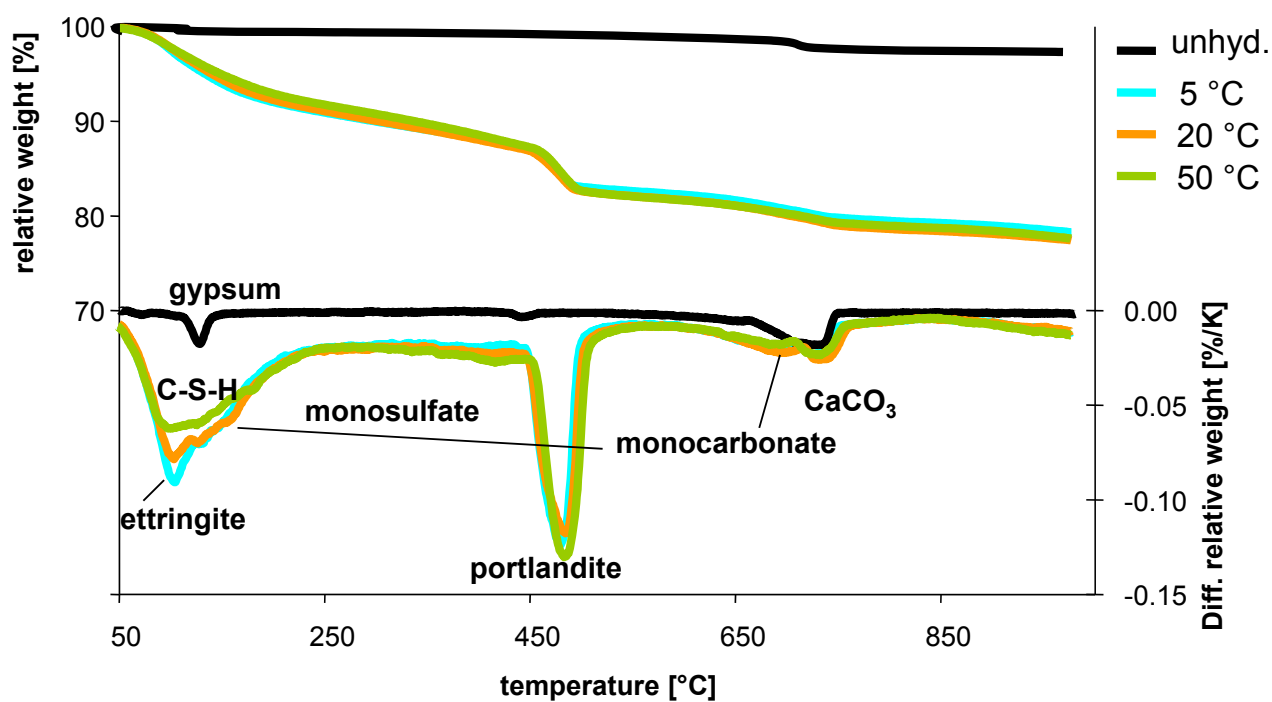


XRD, 150 days



7

150 days



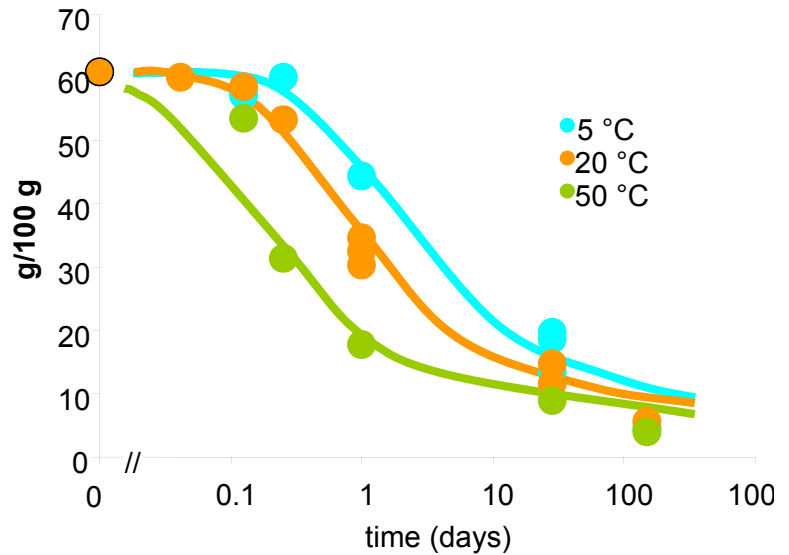
8

Modeling: Temperature

Arrhenius equation

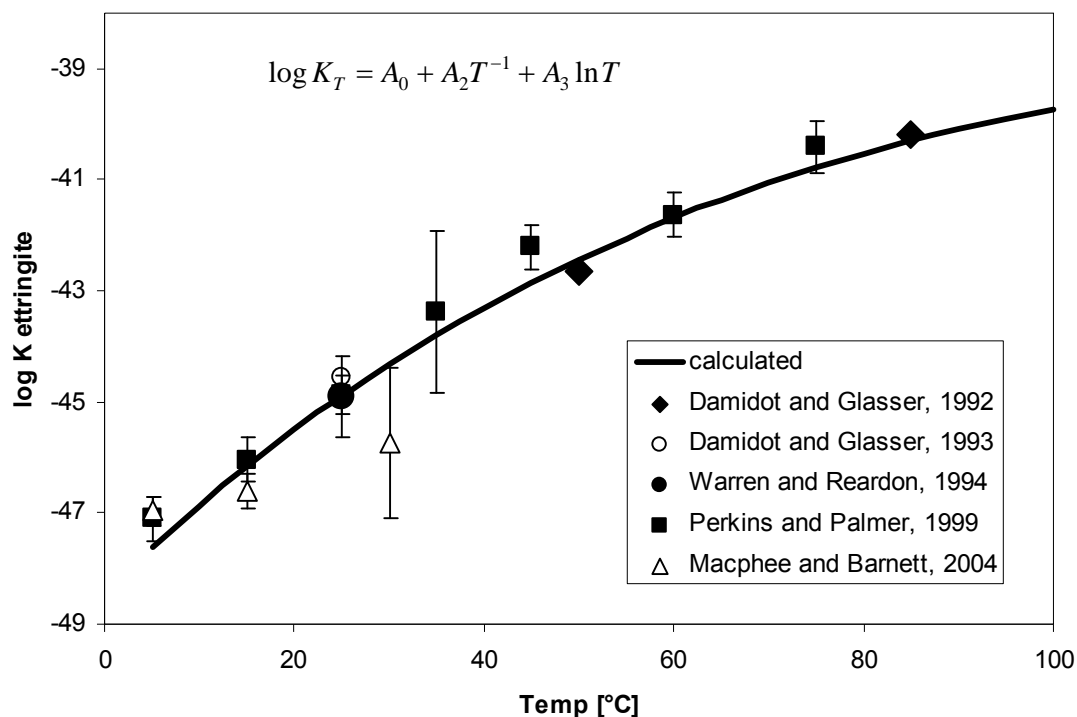
$$R_T = A e^{-\frac{E_a}{RT}}$$

E_a : activation energy

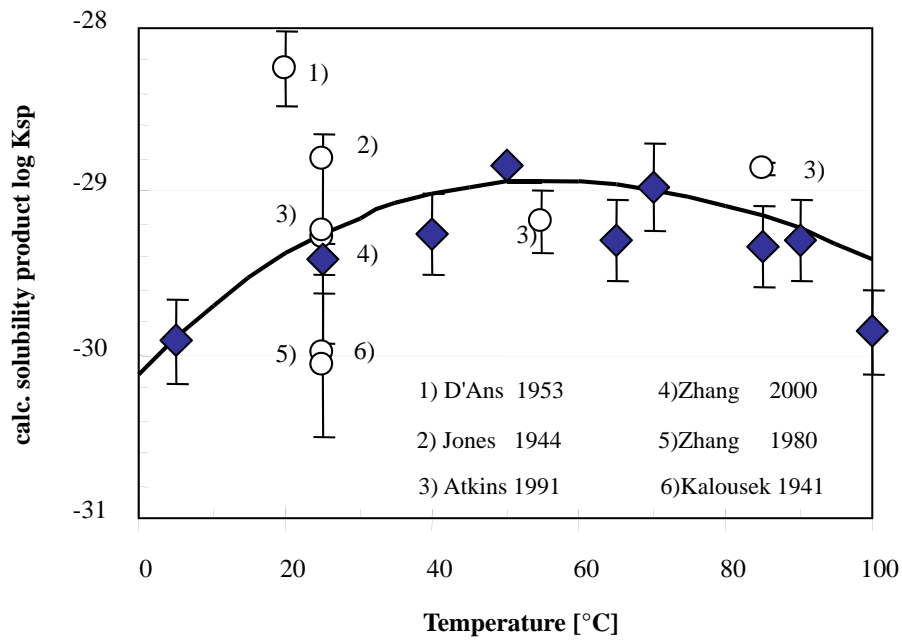


Chemical reactions accelerate with increasing temperature

Solubility of ettringite as f(T)



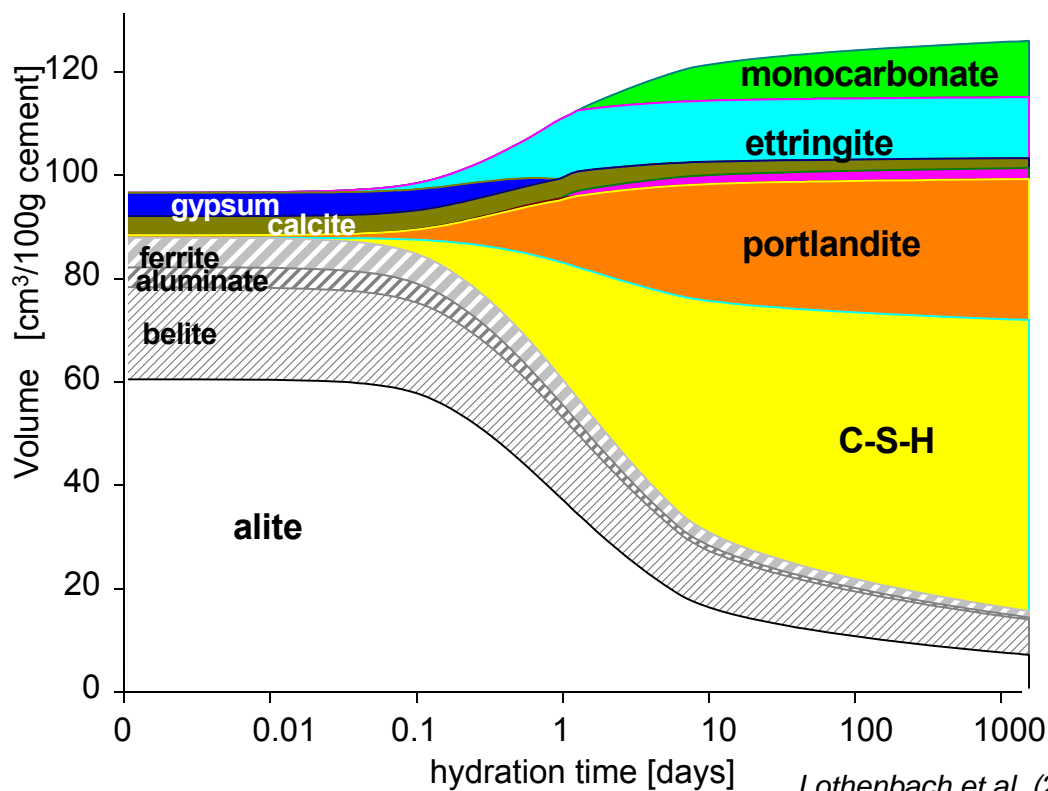
Solubility of monosulfate



Matschei et al. (2007), CCR 37, 1379-1410

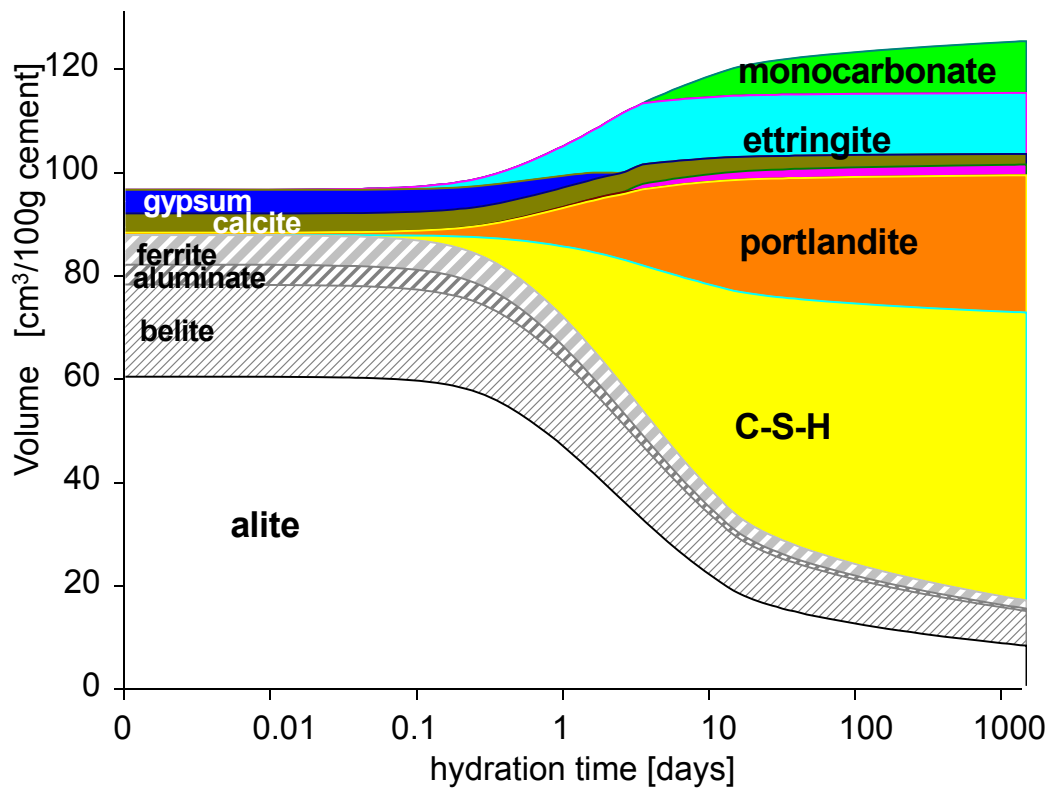


Hydration: 20 °C

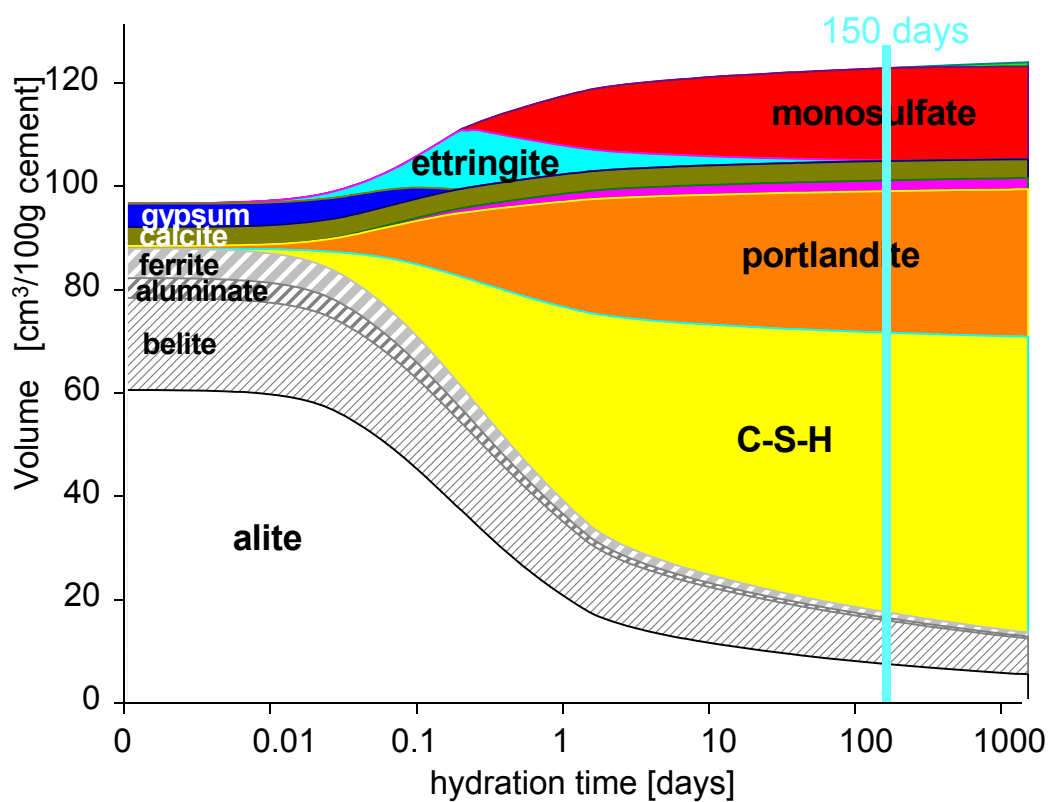


Lothenbach et al. (2008), CCR 38,

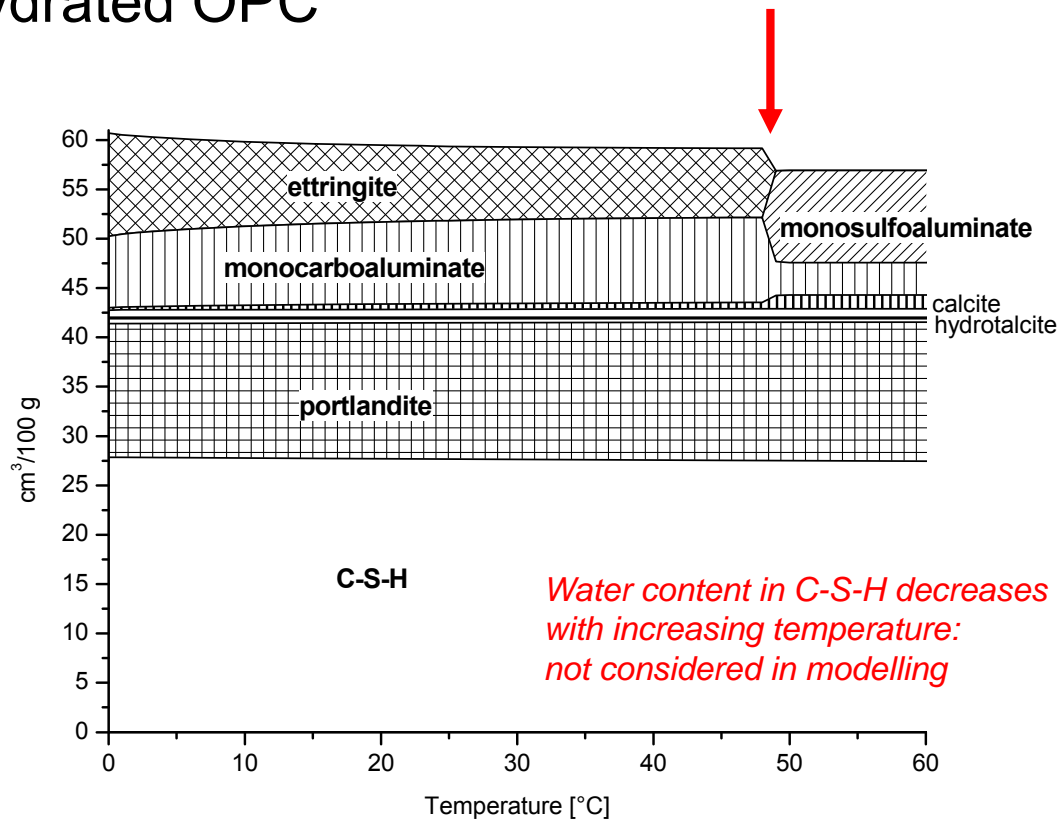
hydration: 5 °C



hydration: 50 °C

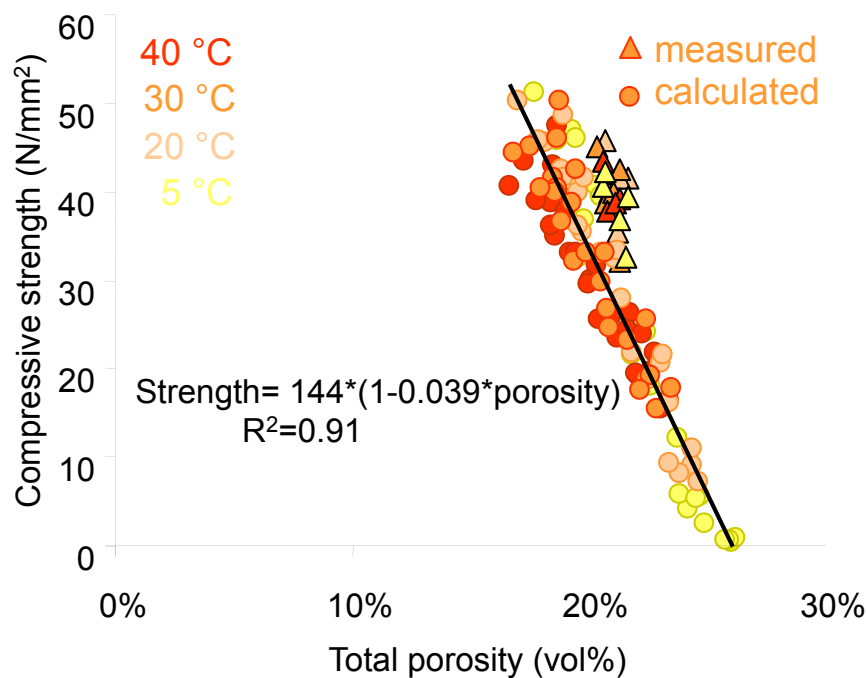


Hydrated OPC



Lothenbach et al. (2010), *Advances Cem Res* 22, 211-223

Strength-porosity



Influence of temperature

Higher temperature:

- kinetic of hydration
- morphology (inhomogenous), denser C-S-H
- coarser porosity
- pore solution (SO_4 , Al)
- hydrates (ettringite, monocarb. → monosulfate)
 - volume decrease
 - decrease in strength

Solubility of ettringite increases with temperature
 -> less stable

Influence of temperature: tutorial

■ Cement: «OPC» in project «Temp»

Input Recipe of Single Thermodynamic System: Temp:G:OPC:0:0:1:20:0:

tname OPC-all reacted 5% of calcite (2.8 g CaO, 2.2 g CO₂)

Property	Name	Quantity	Units
1 xa_	Al ₂ O ₃	5	g
2 xa_	Aqua	50	g
3 xa_	CO ₂	2.2	g
4 xa_	CaO	67	g
5 xa_	Fe ₂ O ₃	1	g
6 xa_	K ₂ O	0.1	g
7 xa_	MgO	1	g
8 xa_	Na ₂ O	0.1	g
9 xa_	O ₂	0.1	g
10 xa_	SO ₃	4	g
11 xa_	SiO ₂	21.8	g

Input quantities of Compos(itions) contributing to B_ vector

Learn more | Print | OK | Cancel

Cement composition in g/100 g:
 => All reacts!

w/b = 0.5

Some O₂ to ensure oxic conditions

Window Help

Input: System Definition Results: Equilibrium State

Phase/species	L	T	On/	UC	Add to BC	UG	G0
aq_gen	69	a	+	g	0	J	0
gas_gen	5	g	+	g	0	J	0
C3(AF)S0.84H	2	s	-	g	0	J	0
CSHQ	4	s	+	g	0	J	0
CSH-JenD		I	+	M	0	J	0
CSH-JenH		I	+	M	0	J	0
CSH-TobD		I	+	M	0	J	0
CSH-TobH		I	+	M	0	J	0
ettringite-Al	2	s	-	g	0	J	0
ettringite-Fe	2	s	-	g	0	J	0
monosulphate-Al	2	s	-	g	0	J	0
monosulphate-Fe	2	s	-	g	0	J	0
SO4_OH_AfM	2	s	+	g	0	J	0
OH_SO4_AfM	2	s	+	g	0	J	0
SO4_CO3_AfT	2	s	+	g	0	J	0
CO3_SO4_AfT	2	s	+	g	0	J	0
hydrotalc-pyro	2	s	+	g	0	J	0
Al(OH)3mic	1	s	+	g	0	J	0
Gibbsite	1	s	+	g	0	J	0
Kaolinite	1	s	+	g	0	J	0
Graphite	1	s	+	g	0	J	0
Mayenite	1	s	+	g	0	J	0
Belite	1	s	+	g	0	J	0
Aluminate	1	s	+	g	0	J	0
Alite	1	s	+	g	0	J	0
Ferrite	1	s	+	g	0	J	0
CA	1	s	+	g	0	J	0
CA2	1	s	+	g	0	J	0
C2AH75	1	s	+	g	0	J	0
C3AH6	1	s	+	g	0	J	0
C4AH13	1	s	+	g	0	J	0
C4AH10	1	s	+	g	0	J	0
C4AsH12	1	s	-	g	0	J	0
C2ASH8	1	s	+	g	0	J	0
C4Ac0.5H12	1	s	+	g	0	J	0
C4AcH11	1	s	+	g	0	J	0
ettringite	1	s	-	g	0	J	0
Aragonite	1	s	+	g	0	J	0

No siliceous hydrogarnet (C3(AF)S0.84H) dolomite, quartz, ... formation at room temperature and short time frames

Quarternary solid solution model for C-S-H (Kulik 2010); Ca/Si varies from 0.67 to ≈ 1.5 (in the presence of portlandite)

Al-Fe monosulphate and Al-Fe-ettringite excluded for this example (duplicates can cause mathematical problems; iron more stable in hydroandradite: $C_3FS_{0.84}H_{4.32}$)

Single solids (ettringite/monosulphate) deactivated as already considered as solid solutions

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Input: System Definition Results: Equilibrium State

Phase/species	L	T	On/	UC	Add to BC	UG	G0 cor
C2ASH8	1	s	+	g	0	J	0
C4Ac0.5H12	1	s	+	g	0	J	0
C4AcH11	1	s	+	g	0	J	0
ettringite	1	s	-	g	0	J	0
Aragonite	1	s	+	g	0	J	0
Calcite	1	s	+	g	0	J	0
C3FH6	1	s	+	g	0	J	0
C4FH13	1	s	+	g	0	J	0
C3FS0.84H4.32	1	s	+	g	0	J	0
C3FS1.34H3.32	1	s	+	g	0	J	0
C4Fc05H10	1	s	+	g	0	J	0
C4FcH12	1	s	+	g	0	J	0
Dolomite-dis	1	s	-	g	0	J	0
Dolomite-ord	1	s	-	g	0	J	0
lime	1	s	+	g	0	J	0
Portlandite	1	s	+	g	0	J	0
Anhydrite	1	s	+	g	0	J	0
Gypsum	1	s	+	g	0	J	0
hemihydrate	1	s	+	g	0	J	0
thaumasite	1	s	-	g	0	J	0
Iron	1	s	+	g	0	J	0
Fe-carbonate	1	s	+	g	0	J	0
Siderite	1	s	+	g	0	J	0
Hematite	1	s	-	g	0	J	0
Magnetite	1	s	+	g	0	J	0
Ferrihydrite-am	1	s	+	g	0	J	0
Ferrihydrite-mo	1	s	+	g	0	J	0
Goethite	1	s	-	g	0	J	0
Pyrite	1	s	+	g	0	J	0
Troilite	1	s	+	g	0	J	0
Melanterite	1	s	+	g	0	J	0
syngenite	1	s	+	g	0	J	0
OH-hydrotalcite	1	s	+	g	0	J	0
Magnesite	1	s	+	g	0	J	0
Brucite	1	s	+	g	0	J	0
Sulphur	1	s	+	g	0	J	0
Quartz	1	s	+	g	0	J	0
Silica-amorph	1	s	+	g	0	J	0

C_on [33]: Selection of Phases to be included into GEM task { + - }

Single solids deactivated as already considered as solid solutions

No thaumasite, hematite, dolomite, goethite, quartz, ... formation at room temperature and short time frames

Amorphous SiO₂

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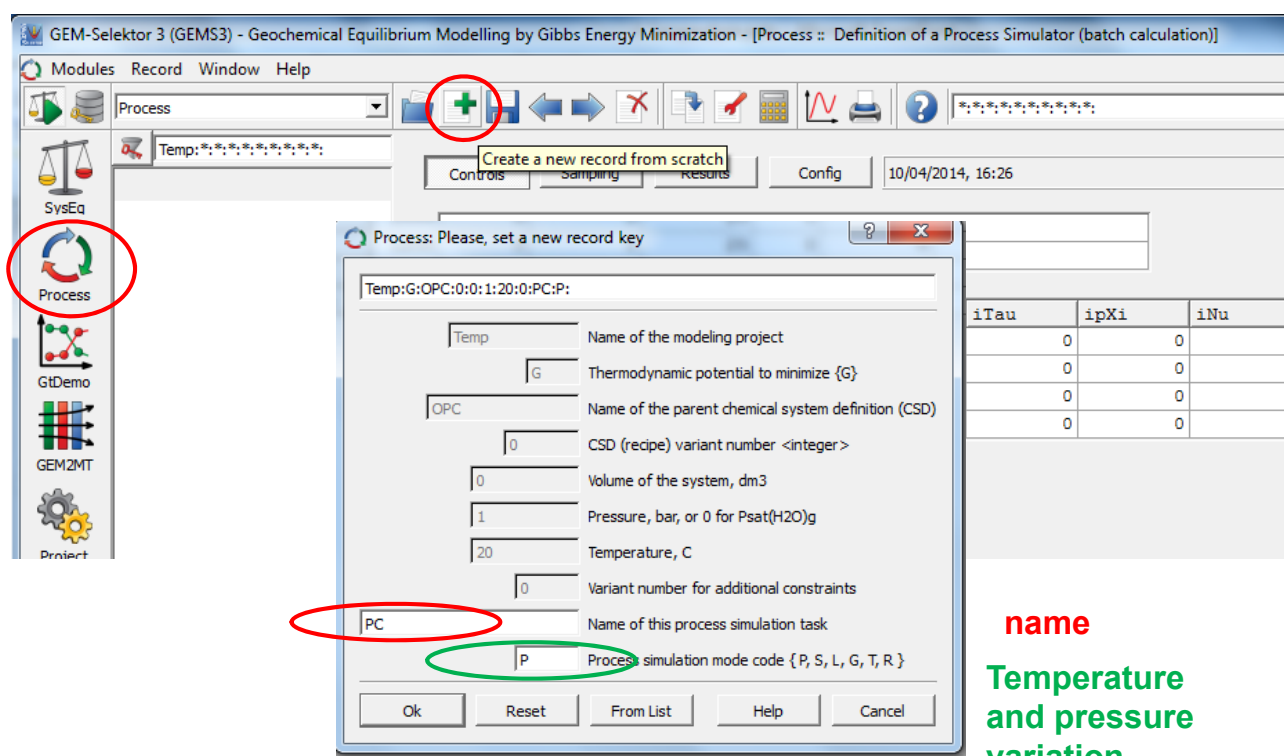
Input: System Definition		Results: Equilibrium State			
Phase/species	L	T	Amount (mol)	logSI/Activity	Concentration
a aq_gen	69	a	0.43500338	2.192e-09	
g gas_gen	5	g	0.0031158762	-2.094e-11	
s CSHQ	4	s	0.46917649	1.379e-09	
s SO4 OH AFm	2	s	0	-1	
s OH SO4 AFm	2	s	0	-1	
s SO4 CO3 AFt	2	s	0.018717018	-3.32e-09	
s CO3 SO4 AFt	2	s	2.9848203e-007	0.0001596	
s hydrotalc-pyro	2	s	0	-8.646	
s Al(OH)3mic	1	s	0	-3.192	
s Gibbsite	1	s	0	-2.669	
s Kaolinite	1	s	0	-15.11	
s Graphite	1	s	0	-83.76	
s Mayenite	1	s	0	-145.1	
s Belite	1	s	0	-1.856	
s Aluminate	1	s	0	-38.91	
s Alite	1	s	0	-14.11	
s Ferrite	1	s	0	-36.62	
s CA	1	s	0	-13	
s CA2	1	s	0	-18.96	
s C2AH75	1	s	0	-4.162	
s C3AH6	1	s	0	-2.668	
s C4AH13	1	s	0	-3.239	
s CAH10	1	s	0	-5.212	
s C2ASH8	1	s	0	-2.895	
s C4Ac0.5H12	1	s	0	-0.7397	
s C4AcH11	1	s	0.024117778	2.299e-09	
s Aragonite	1	s	0	-0.1441	
s Calcite	1	s	0.01959412	5.851e-09	
s C3FH6	1	s	0	-2.316	
s C4FH13	1	s	0	-2.476	
s C3FS0.84H4.32	1	s	0.0062622026	0	
s C3FS1.34H3.32	1	s	0	-0.6439	
s C4Fc05H10	1	s	0	-4.76	
s C4FcH12	1	s	0	-2.433	
s lime	1	s	0	-9.956	
s Portlandite	1	s	0.36532113	-3.761e-10	
s Anhydrite	1	s	0	-3.092	
s Gypsum	1	s	0	-2.838	

Solution
 C-S-H
 CH
 Ettringite
 Monocarbonate
 Calcite
 Hydroandradite ($C_3FS_{0.84}H_{4.32}$)
 Hydrotalcite

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Influence of temperature: tutorial

■ New process file to calculate variation of temperature



The screenshot shows the GEM-Selektor 3 (GEMS3) software interface. The 'Process' module is selected in the left sidebar. A dialog box titled 'Process: Please, set a new record key' is open, showing the following fields:

- Temp:G:OPC:0:0:1:20:0:PC:P:
- Temp: Name of the modeling project
- G: Thermodynamic potential to minimize {G}
- OPC: 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
- PC: Name of this process simulation task
- P: Process simulation mode code {P, S, L, G, T, R}

The 'Process' module icon in the sidebar is circled in red. The 'PC' field in the dialog box is circled in red. The 'P' field in the dialog box is circled in green.

name
 Temperature and pressure variation

Influence of temperature: tutorial

GEM-Selektor Process Setup: blended:G:OPC:0:0:1:25:000:Temp:P:

Step 1 - Process Simulator Configuration

This is a tool for 'batch' calculation of multiple equilibrium states, sampling and plotting of results. In this way, irreversible geochemical 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 of process control script 'P_expr' 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 output parameters (e.g. pH) from previous step (mode R);
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 Sequential reactor scheme, uses equilibrium bulk compositions of phases

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

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

Temperature and pressure variation

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Influence of temperature: tutorial

GEM-Selektor Process Setup: Temp:G:OPC:0:0:1:20:0:PC:P:

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

	iTm	iP	iTC	iNu	iTau	ipXi	iNu	ipH	ipe
From	1000	0	1	4	0	0	0	0	0
Until	1200	0	1	96	0	0	0	0	0
Step	1	0	2	0	0	0	0	0	0

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

Please, check iP and iT iterator contents, and set Step to 0 in all other iterators.

For PT phase diagram: select phases to plot, then skip the next wizard page.

Phases

aq_gen	C3AH6	Iron
gas_gen	C4AH13	Fe-carbonate
CSH0	C4AH10	Siderite

Numbering of the single calculations

Start temperature
Stop temperature
Step size

No script needed

GEM-Selektor Process Setup: Temp:G:OPC:0:0:1:20:0:PC:P:

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**
- phVol
- Fa
- bXa(aq_gen)
- bXa(gas_gen)
- bXa(CSHQ)
- bXa(SO4_OH_)
- bXa(OH_SO4_)
- bXa(SO4_CO3_)
- bXa(CO3_SO4_)
- bXa(hydratalc-)
- bXs
- L1
- Yof
- Aalp
- Sigw
- x

Item Selection

aq_gen	C4Ac0.5H12	Melanterite
gas_gen	C4AcH11	syngenite
CSHQ	Aragonite	OH-hydratalcite
SO4_OH_AfM	Calcite	Magnesite
OH_SO4_AfM	C3FH6	Brucite
SO4_CO3_AfT	C4FH13	Sulphur
CO3_SO4_AfT	C3FS0.84H4.32	Silica-amorph
hydratalc-pyro	C3FS1.34H3.32	
Al(OH)3mic	C4Fc05H10	
Gibbsite	C4FcH12	
Kaolinite	lime	
Graphite	Portlandite	
Mayenite	Anhydrite	
Belite	Gypsum	
Aluminate	hemihydrate	
Alite	thaumasite	
Ferrite	Iron	
CA	Fe-carbonate	
CA2	Siderite	
C2AH75	Magnetite	
C3AH6	Ferrihydrite-am	
C4AH13	Ferrihydrite-mc	
CAH10	Pyrite	
C2ASH8	Troilite	

Sampling Script

```

xp[] =: J;
yp[] [0] =: phVol[{CSHQ}];
yp[] [1] =: phVol[{Portlandite}];
yp[] [2] =: phVol[{Calcite}];
yp[] [3] =: phVol[{SO4_CO3_AfT}];
yp[] [4] =: phVol[{SO4_OH_AfM}];
yp[] [5] =: phVol[{C2ASH8}];
yp[] [6] =: phVol[{C4Ac0.5H12}];
yp[] [7] =: phVol[{C4AcH11}];
yp[] [8] =: phVol[{C3FS0.84H4.32}];
yp[] [9] =: phVol[{C3FS1.34H3.32}];
yp[] [10] =: phVol[{OH-hydratalcite}];
yp[] [11] =: phVol[{Gibbsite}];
yp[] [12] =: phVol[{Anhydrite}];
yp[] [13] =: phVol[{Gypsum}];
yp[] [14] =: phVol[{C3AH6}];
yp[] [15] =: phVol[{Brucite}];

```

To be changed later

**Solid phases sampled:
appear in the order selected**

**Be careful to forget no
relevant phase!**

Volumes of phases (in cm3) in equilibrium

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

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GEM-Selektor Process Setup: Temp:G:OPC:0:0:1:20:0:PC:P:

Step 4 - Important data object dimensions

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

Dimensions of sampled and experimental data

47	nPS - Number of steps (1 to 9999) to be performed in this simulation (default: 21); also length of the 'xp' vector.
1	Number of 'modC' array columns (1 to 40, 0 - not used) to store process control values; number of rows will be nPS.
16	Number of columns in the 'yp' table (0 to 200) to keep the simulated data sampled by the pgExpr script; number of rows will be nPS.
1	Number of columns in the 'xp' table (0 to 4) to keep the simulated data sampled by the pgExpr script; number of rows will be nPS.
0	Number of rows in the xEp, yEp arrays for experimental data (optional)
1	Number of columns in the xEp, yEp arrays for experimental data (optional)

Optional data vectors (only allocated using checkboxes) vector from the respective

Allocation of optional data

- ☐ CSD variant # ('vTn')
- ☐ Temperature T ('vT')
- ☐ Process extent pxi ('vxi')

[Learn more](#)

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 TBM algorithm for factor calculations (on your discretion)

GEMS-Workshop

Temp:G:OPC:0:0:1:20:0:PC:P:

Controls Sampling Results Config 10/04/2014, 16:26

NeIt 9999 0 Next 1 I 0 J 0 Jp 0

pSTkey cTm 1000 cNV 0

cTau 0 cpXi 0 cXi 1 cNu 0

cpH 0 cpe 0 cEh 0 cT 277.15

xp[J] =: cTC;

cTC: Temperature in °C

yp[J][0] =: phVol[{CSHQ}];
 yp[J][1] =: phVol[{Portlandite}];
 yp[J][2] =: phVol[{Calcite}];
 yp[J][3] =: phVol[{SO4_CO3_Aft}]+phVol[{CO3_SO4_Aft}];
 yp[J][4] =: phVol[{SO4_OH_Afm}]+phVol[{OH_SO4_Afm}];
 yp[J][5] =: phVol[{C2ASH8}];
 yp[J][6] =: phVol[{C4Ac0.5H12}];
 yp[J][7] =: phVol[{C4AcH11}];
 yp[J][8] =: phVol[{C3FS0.84H4.32}];
 yp[J][9] =: phVol[{C3FS1.34H3.32}];
 yp[J][10] =: phVol[{OH-hydrotalcite}];
 yp[J][11] =: phVol[{Gibbsite}];
 yp[J][12] =: phVol[{Anhydrite}];
 yp[J][13] =: phVol[{Gypsum}];
 yp[J][14] =: phVol[{C3AH6}];
 yp[J][15] =: phVol[{Brucite}];

Ettringite and monosulphate: both parts of the solid solution needed

cT temperature in K

Influence of temperature: tutorial

Modelling by Gibbs Energy Minimization - [Process :: Remake of the new record finished OK. It is recommended to re-calculate data]

Temp:G:OPC:0:0:1:20:0:PC:P:

Controls Sampling Results Config 10/04/2014, 16:26

--- pY Nam phVol

pX Nam	Temp C	CSHQ	Portlandite	Calcite	Ettringite	monosulfate	C2ASH8
0	0	0	0	0	0	0	0
1	0	0	0	0	0	0	0
2	0	0	0	0	0	0	0
3	0	0	0	0	0	0	0
4	0	0	0	0	0	0	0
5	0	0	0	0	0	0	0
6	0	0	0	0	0	0	0
7	0	0	0	0	0	0	0
8	0	0	0	0	0	0	0
9	0	0	0	0	0	0	0
10	0	0	0	0	0	0	0
11	0	0	0	0	0	0	0
12	0	0	0	0	0	0	0
13	0	0	0	0	0	0	0
14	0	0	0	0	0	0	0
15	0	0	0	0	0	0	0
16	0	0	0	0	0	0	0
17	0	0	0	0	0	0	0
18	0	0	0	0	0	0	0
19	0	0	0	0	0	0	0
20	0	0	0	0	0	0	0

yp [2,4] : Data table of c

Cement:
«OPC_noCc»
in project
«Temp»

Clone
existing
OPC

OPC without
calcite

GEMS-Workshop May 2014, Dübendorf

Influence of temperature: tutorial



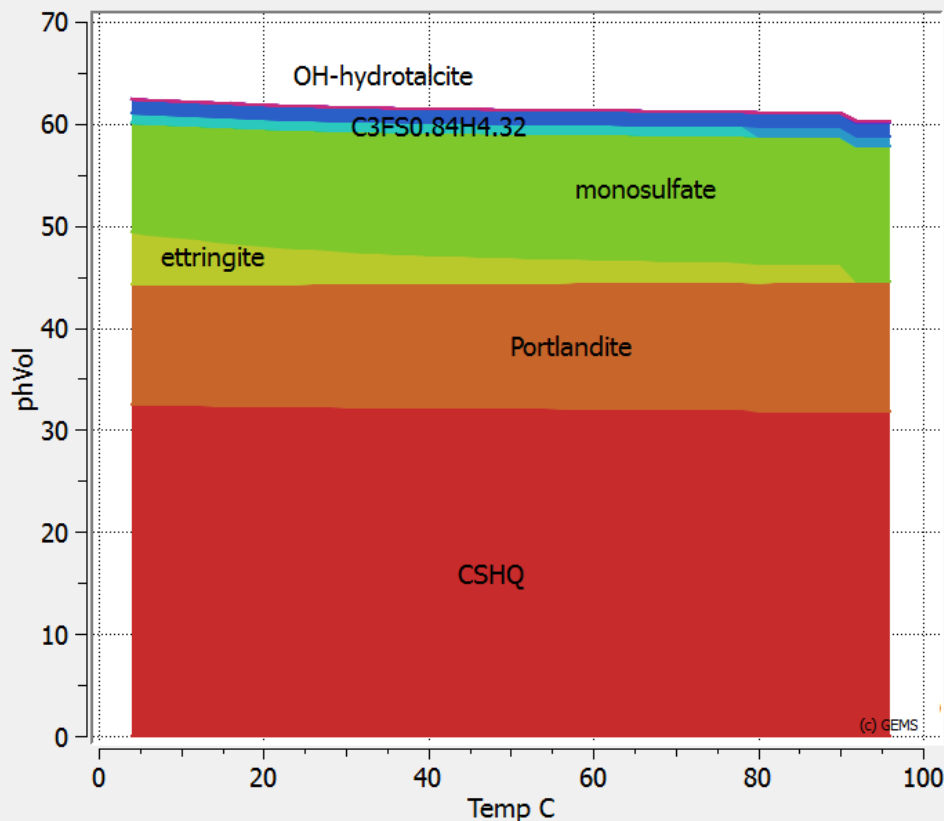
■ Cement: «OPC_noCc» in project «Temp»

Cement
composition
in g/100 g:
=> All reacts!

Remove
CO2

Reduce CaO

Influence of temperature: no Cc



Legend | x# | Label

0	CSHQ
0	Portlandite
0	Calcite
0	ettringite
0	monosulfate
0	C2ASH8
0	C4Ac0.5H12
0	C4AcH11
0	C3FS0.84H4.32
0	C3FS1.34H3.32
0	OH-hydroxalite
0	Gibbsite
0	Anhydrite
0	Gypsum
0	C3AH6
0	Brucite

Click legend symbols to adjust curves; select abscissae under x#; edit labels, drag-drop them to plot area

Fragment Customize

Print Save Image Help

Influence of temperature: 5% Cc



Temp:G:OPC:0:0:1:20:0:CSH_pH:P

Process - Remake finished OK. It is recommended to re-calculate the data

GEM-Selektor Process Setup: Temp:G:OPC:0:0:1:20:0:CSH_pH:P

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)
- bXa(CSHQ)
- bXa(SO4_OH_)
- bXa(OH_SO4_)
- bXa(SO4_CO3_)
- bXa(CO3_SO4_)
- bXa(hydroxalite)
- bXs
- L1
- Yof
- Aalp
- Sigw
- x

Item Selection

Mbx	L[3]	Volumes[1]	iV[1]	cXi	vpXi
GX	L[4]	N_	iV[2]	iNu[0]	vNu
IS	L[5]	L_[0]	cV	iNu[1]	vKin
pH	Fi[0]	L_[1]	iP[0]	iNu[2]	moc
pe	Fi[1]	L_[2]	iP[1]	cNu	xp
Eh	Fi[2]	L_[3]	iP[2]	ipH[0]	yp
TC[0]	Fi[0]	L_[4]	cP	ipH[1]	xEp[
TC[1]	Fi[1]	L_[5]	iTC[0]	ipH[2]	yEp[
TK[0]	Fi[2]	Fi_[0]	iTC[1]	cpH	
TK[1]	denW[0][0]	Fi_[1]	iTC[2]	ipe[0]	
PG[0]	denW[1][0]	Fi_[2]	cTC	ipe[1]	
PG[1]	epsW[0][0]	Fi_[3]	cT	ipe[2]	
Vx[0]	epsW[1][0]	T	iNv[0]	cpe	
Vx[1]	InP	P	iNv[1]	cEh	
It	RT	RTf[0]	iNv[2]	Next	
ItEfd	F_RT	RTf[1]	cNV	I	
Itlpm	Xw	RoW[0][0]	iTau[0]	J	
Psi_DK[0]	Masses[0]	EpsW[0][0]	iTau[1]	Jp	
Psi_DK[1]	Masses[1]	VisW[0]	iTau[2]	vTm	
_nnr[0]	Masses[2]	iTm[0]	cTau	vNV	
_nnr[1]	Masses[3]	iTm[1]	ipXi[0]	vP	
L[0]	Masses[4]	ipXi[1]	vV		
L[1]	Masses[5]	cTm	ipXi[2]	vT	
L[2]	Volumes[0]	iV[0]	cpXi	vTau	

Sampling Script

```

xp[] =: J;
yp[] [0] =: pH;
yp[] [1] =: bXa[{CSHQ}][{Ca}];
yp[] [2] =: bXa[{CSHQ}][{Si}];
yp[] [3] =: my[{OH-}];
    
```

Plotting of changes in pH, OH⁻ and C-S-H

bXa[{CSHQ}][{Ca}]:
mol Ca in C-S-H solid solution

my[{OH-}]:
OH⁻ concentration (in mol/kg H₂O)

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

Influence of temperature: 5% Cc

Controls	Sampling	Results	Config	17/04/2014, 11:19
NeIt	9999	47	Next	0
I	0	J	46	Jp
Jp	46			
pSTkey	Temp:G:OPC:0:0:1:20:0:			cTm
cTm	1000	cNV	0	
cTau	0	cpXi	0	cXi
cXi	1	cNu	0	
cpH	0	cpe	0	cEh
cEh	0	cT	369.15	

```

xp[J] =: cTC;
yp[J][0] =: pH;
$ plotting Ca/Si in CSH
yp[J][1] =: bXa[{CSHQ}][Ca]/bXa[{CSHQ}][Si];
$ plotting H/Si in CSH: H/2 = H2O
yp[J][2] =: bXa[{CSHQ}][H]/2/bXa[{CSHQ}][Si];
$ log OH- conc
yp[J][3] =: 14+lg(my[{OH-}]);
    
```

Plotting of changes in pH, OH- and C-S-H

$bXa[{CSHQ}][Ca]/bXa[{CSHQ}][Si]$:

molar Ca/Si in C-S-H solid solution

$bXa[{CSHQ}][H]/2/bXa[{CSHQ}][Si]$:

molar H/Si in C-S-H solid solution (H/2 = H₂O)

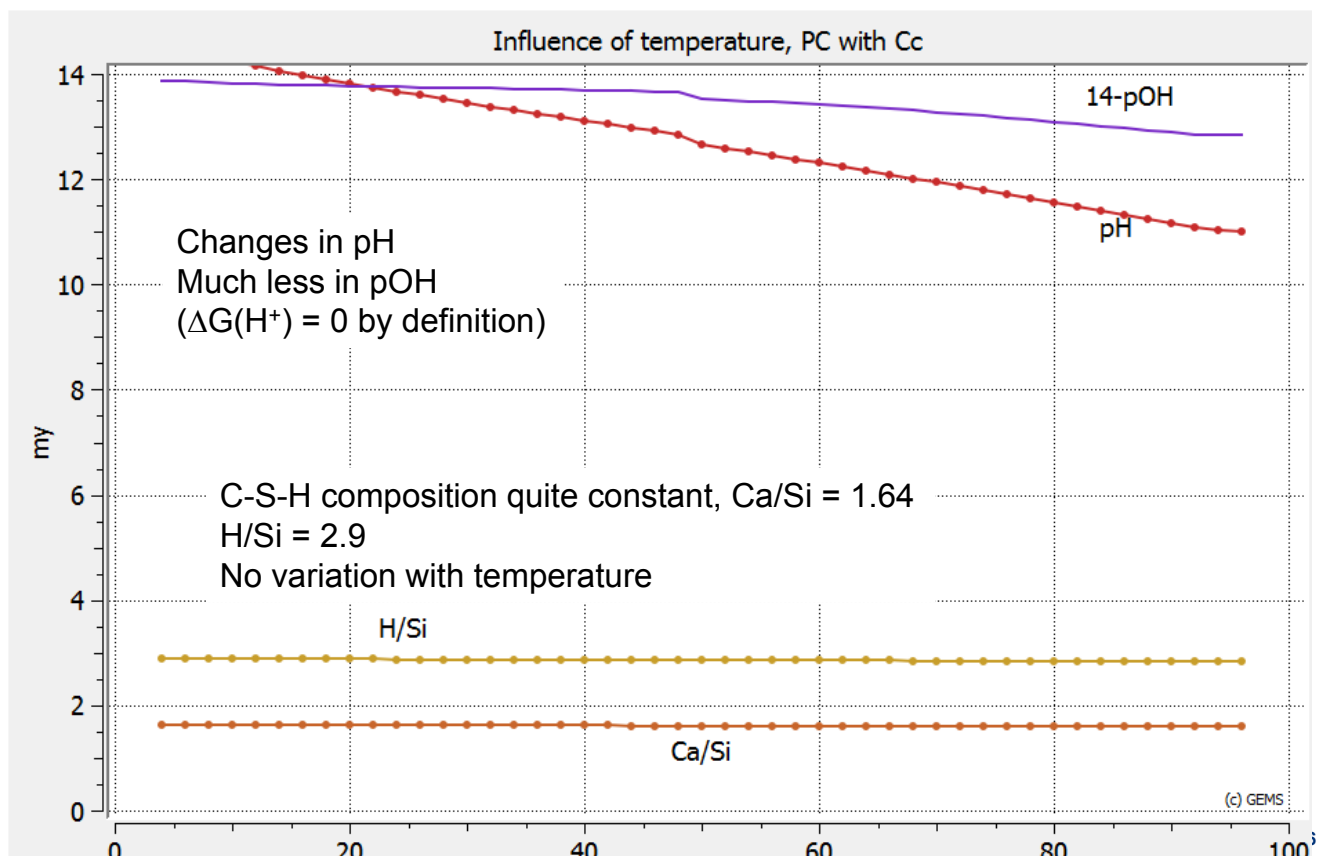
14+lg(my[{OH-}]) equals pH at 25 °C

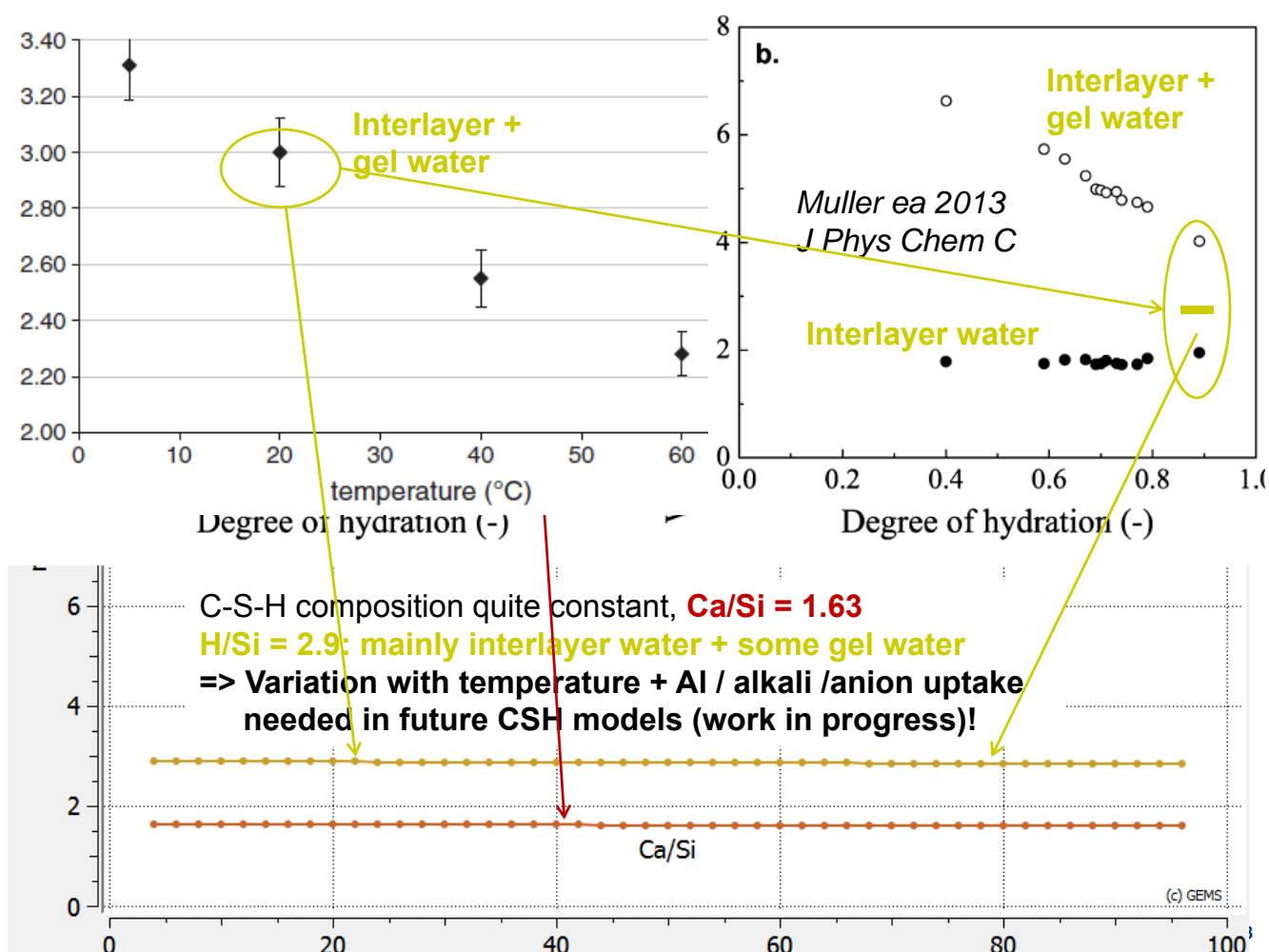
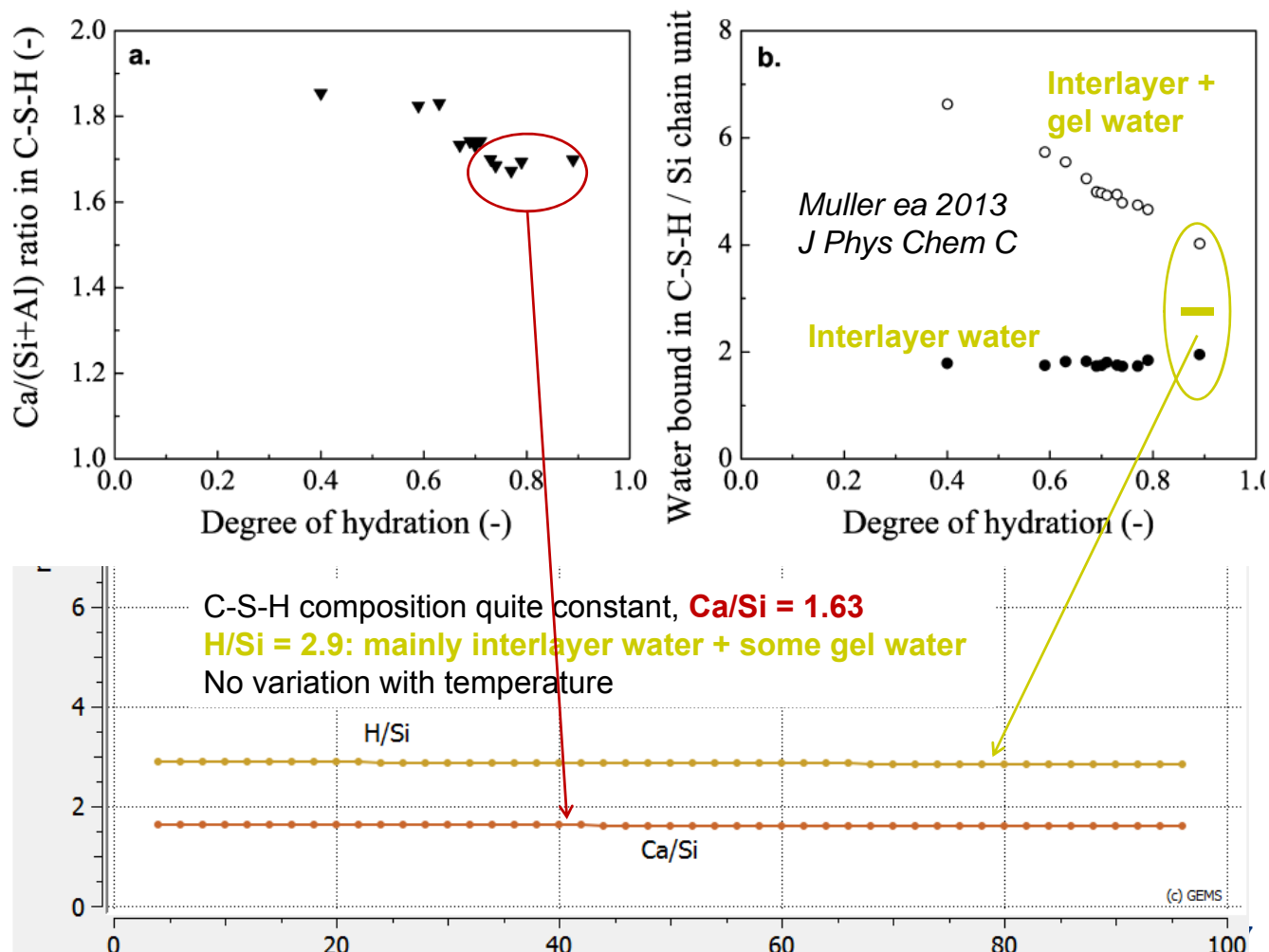
=> to illustrate temperature effect on pH:

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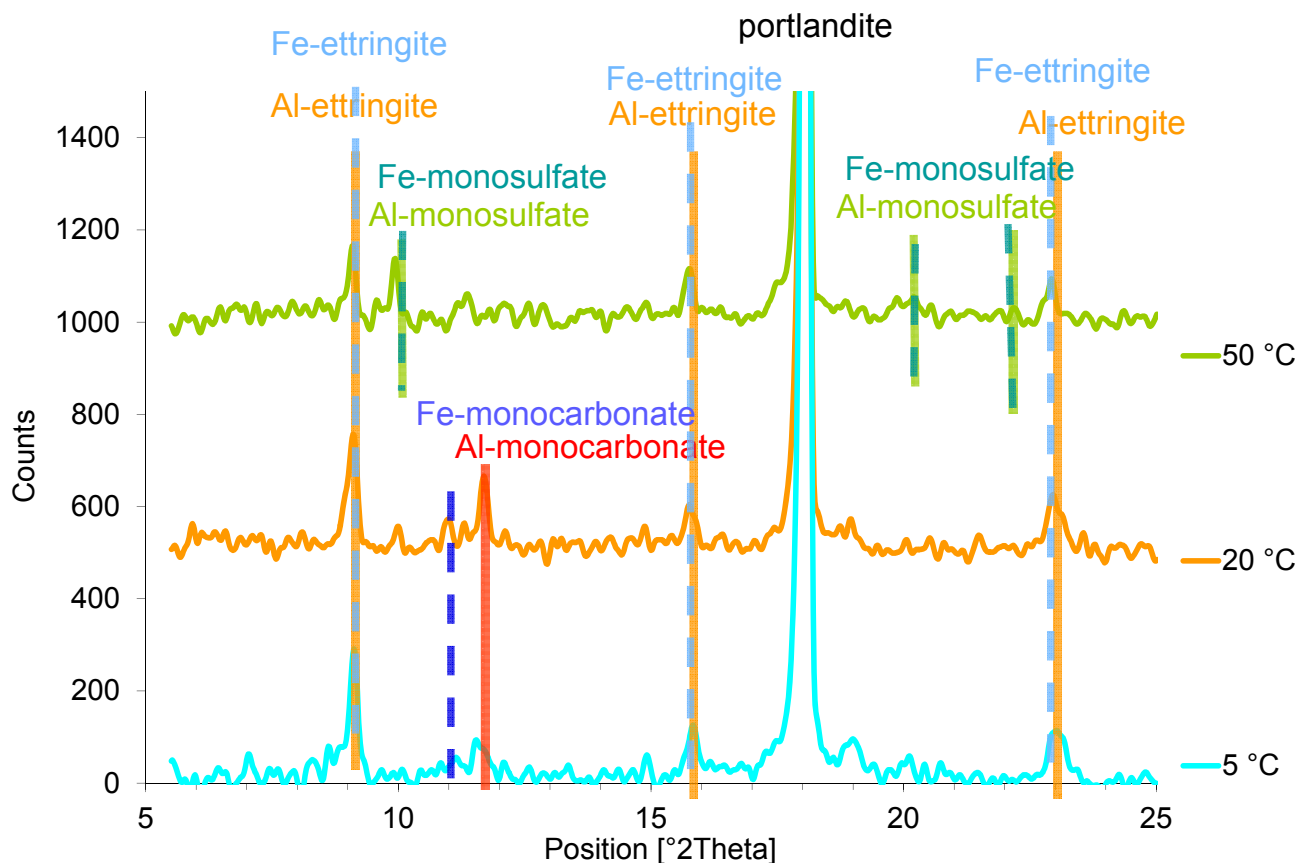
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Influence of temperature: 5% Cc





What happens with the iron?



Lothenbach ea 2007, CCR 37

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Stability of Fe and Al-hydrates at 25 °C

(Solubility products refer to Ca^{2+} , OH^- , $\text{Fe,Al}(\text{OH})_4^-$, HSiO_3^- , SO_4^{2-} , CO_3^{2-})

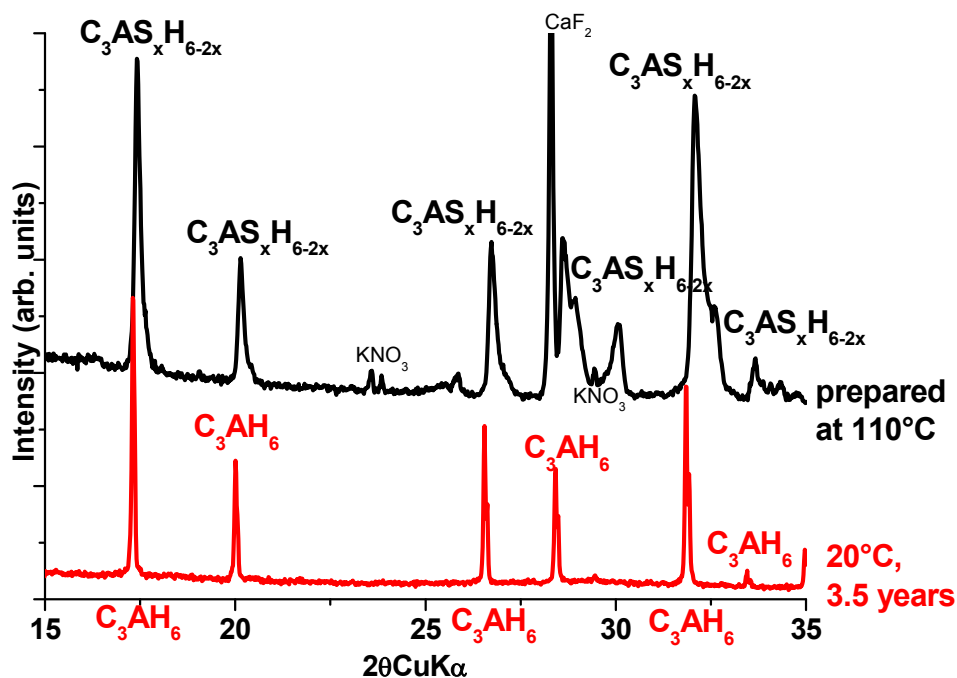
Fe-hydrates		Al-hydrates		Δ Al-Fe
FH	-11.2	-1.3	AH ₃	-10
C ₆ FsH ₃₂	-44.0	-45.0	C ₆ AsH ₃₂	1
C ₄ FsH ₁₂	-31.6	-29.3	C ₄ AsH ₁₂	-2
C ₄ FcH ₁₂	-34.6	-31.5	C ₄ AcH ₁₁	-3
C ₄ Fc _{0.5} H ₁₀	-30.8	-29.1	C ₄ Ac _{0.5} H ₁₀	-2
C ₃ FH ₆	-26.3	-20.5	C ₃ AH ₆	-6
C ₃ FS _{0.84} H _{4.32}	-34.2	-26.7	C ₃ AS _{0.84} H _{4.32}	-8

➡ Lower solubility product => higher stability

➡ **Stability Fe-ettringite < Fe-AFm < FH₃/Fe-siliceous hydrogarnet**

➡ **Formation of Al-containing siliceous hydrogarnet kinetically hindered at room temperature**

Al siliceous hydrogarnet



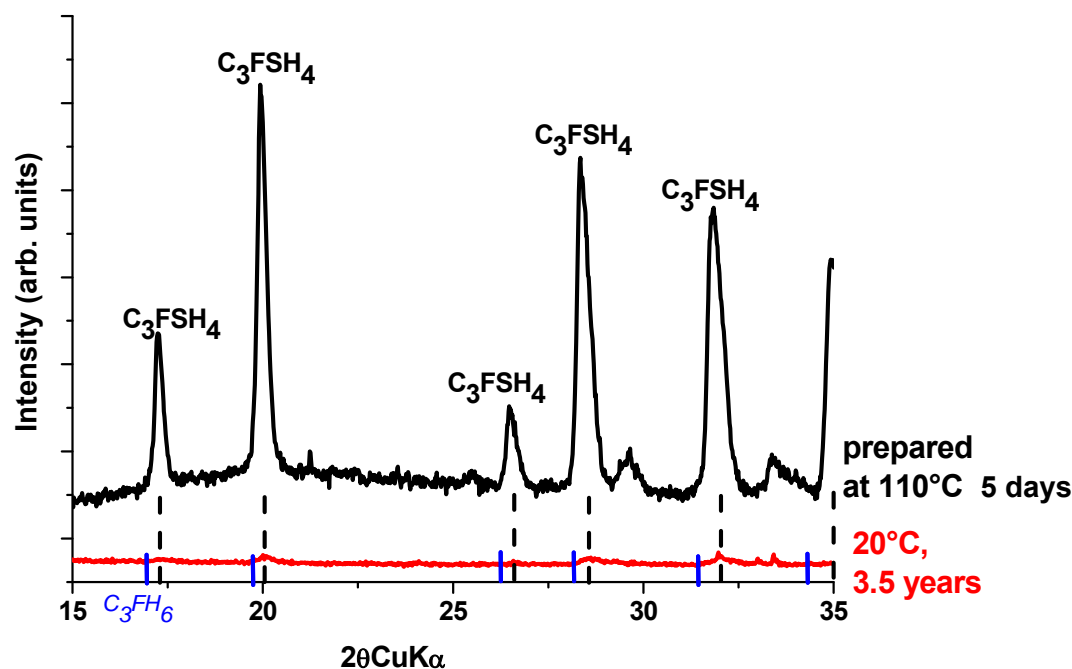
Room temperature: only C_3AH_6 + C-S-H forms;
 $C_3AS_xH_{6-2x}$ forms at 110 °C, but remains stable at 20 °C

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Fe siliceous hydrogarnet



Low temperature Fe-siliceous hydrogarnet poorly crystalline
 => difficult to detect by XRD

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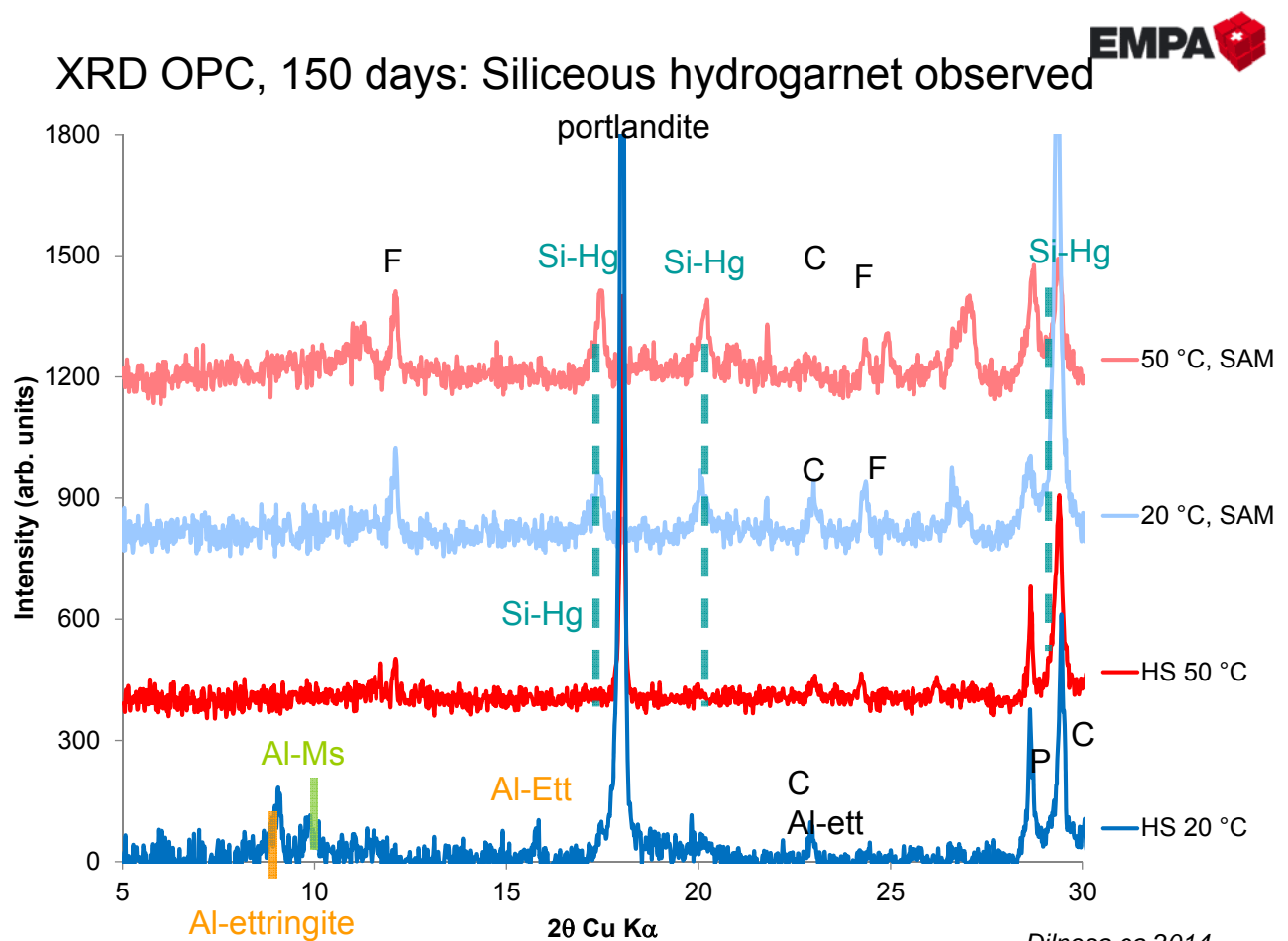
Selective Dissolution using SAM

Salicylic Acid/Methanol Extraction (SAM)

Better identification of minor phases

- Dissolves
 - alite, belite, lime
 - CH, C-S-H, AFt and AFm phases
- Not affected:
 - $C_2(A,F)$, periclase, calcite,
 - $C_3(A,F)SH_4$, hydrotalcite, ...

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EXAFS: Fe in siliceous hydrogarnet in the hydrated cement

At 20 °C								
Age	C ₂ (A,F)	Fe(OH) ₃	C ₃ FSH ₄	C ₃ (A,F)SH ₄	Fe-HtI	C ₄ FcH ₁₂	C ₆ FS ₃ H ₃₂	R-factor
Unhyd	1.00*	-				-	-	0.12
4 hrs	0.78(3)	0.20(3)	First hours			-	-	0.08
16 hrs	0.56(3)	0.44(3)	-	-	-	-	-	0.09
1 day	0.62(2)	-	-	0.38(2)	-	-	-	0.18
28 days	0.57(2)	-	-	0.43(2)	At ≥ 1 days		-	0.09
150 days	0.56(2)	-	-	0.44(2)	-	-	-	0.09
1 year	0.56(2)	-	-	0.44(2)	-	-	-	0.07
At 50 °C								
Age	C ₄ AF	Fe(OH) ₃	C ₃ FSH ₄	C ₃ (A,F)SH ₄	Fe-Ht	C ₄ FcH ₁₂	C ₆ FS ₃ H ₃₂	R-factor
Unhyd	1.00*							0.12
1 hrs	0.70(4)	0.30(4)	First hours					0.14
4 hrs	0.65(2)	0.35(2)						0.09
16 hrs	0.64(2)			0.36(2)				0.18
150 days	0.59(1)			0.41(1)	At ≥ 16 hours			0.09
1 year	0.58(2)			0.42(2)				0.07

20 °C

50 °C

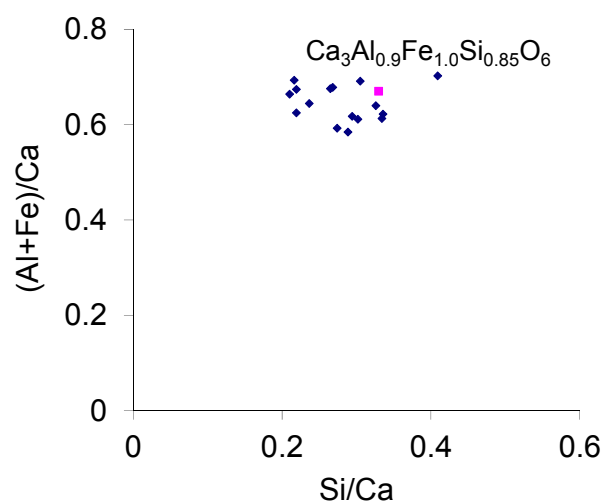
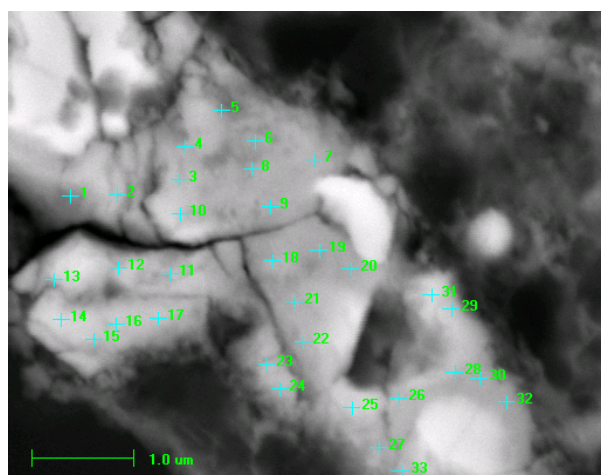
>1 day:

iron present only in Fe siliceous hydrogarnet $C_3(A,F)S_xH_{6-2x}$

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SEM/EDX analysis of OPC



- Siliceous hydrogarnet observed in all samples
- Mixed siliceous hydrogarnet $(C_3(A,F)S_{0.9}H_{4.2})$

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Conclusion: Fate of iron oxides

Thermodynamic modelling:

C_3FSH_4 stable from 1 to 60 °C

C_3ASH_4 stable but formation kinetically hindered (suppressed in calculations)

Experimental evidence:

XAFS spectroscopy => Fe associated with $C_3(A,F)S_xH_{6-2x}$

Similar amount of siliceous hydrogarnet at 20 and 50 °C

XRD, TGA, $C_3(A,F)SH_4$ present in hydrated cements
but difficult to detect; more crystalline at 50°C

SEM: Mixed Al/Fe siliceous hydrogarnet

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Phase/species	L	T	Amount (mol)	logSI/Activity	Concentration	A
⊕ a aq_gen	69	a	0.47421475	8.907e-10		
⊕ g gas_gen	5	g	0.0031148901	1.938e-10		
⊖ s C3(AF)S0.84H	2	s	0.011454257	-3.416e-09		
⊕ s C3AS0.84H4.32		I	0.005192054	0.453286	0.45328598	1
⊕ s C3FS0.84H4.32		I	0.0062622028	0.546714	0.54671402	1
⊕ s CSHQ	4	s	0.46350181	2.004e-09		
⊕ s SO4 OH AFm	2	s	0	-1		
⊕ s OH SO4 AFm	2	s	0	-1		
⊕ s SO4 CO3 AFt	2	s	0.018760835	-1.991e-09		
⊕ s CO3 SO4 AFt	2	s	3.9158123e-009	0.004993		
⊕ s hydrotalc-pyro	2	s	0	-8.645		
⊕ s Al(OH)3mic	1	s	0	-3.194		
⊕ s Gibbsite	1	s	0	-2.671		
⊕ s Kaolinite	1	s	0	-15.12		
⊕ s Graphite	1	s	0	-83.75		
⊕ s Mayenite	1	s	0	-145.1		
⊕ s Belite	1	s	0	-1.859		
⊕ s Aluminat	1	s	0	-38.92		
⊕ s Alite	1	s	0	-14.12		
⊕ s Ferrite	1	s	0	-36.89		
⊕ s CA	1	s	0	-13		
⊕ s CA2	1	s	0	-18.97		
⊕ s C2AH75	1	s	0	-4.164		
⊕ s C3AH6	1	s	0	-2.672		
⊕ s C4AH13	1	s	0	-3.238		
⊕ s C4AH19	1	s	0	-2.835		
⊕ s CAH10	1	s	0	-5.211		
⊕ s C2ASH8	1	s	0	-2.898		
⊕ s C4Ac0.5H12	1	s	0	-0.7393		
⊕ s C4AcH11	1	s	0.0188822	5.777e-09		
⊕ s Aragonite	1	s	0	-0.1441		
⊕ s Calcite	1	s	0.0247094	3.357e-09		
⊕ s C3FH6	1	s	0	-2.576		
⊕ s C4FH13	1	s	0	-2.731		
⊕ s C3FS0.84H4.32	1	s	0	-0.2622		
⊕ s C3FS1.34H3.32	1	s	0	-0.9075		
⊕ s C4Fc05H10	1	s	0	-5.017		
⊕ s C4FcH12	1	s	0	-2.688		
⊕ s lime	1	s	0	-9.957		

Solution
Hydrogarnet/hydroandradite
(C3(A,F)S0.84H4.32)
C-S-H
CH
Ettringite
Monocarbonate
hydrotalcite

Note $C_3AS_{0.42}H_{5.16}$:
not activated in database
=> suppressed during all
calculations as its formation not
observed at ambient conditions
(to include create an additional
Phase refering to
Dcomp: $C_3AS_{0.42}H_{5.16}$)

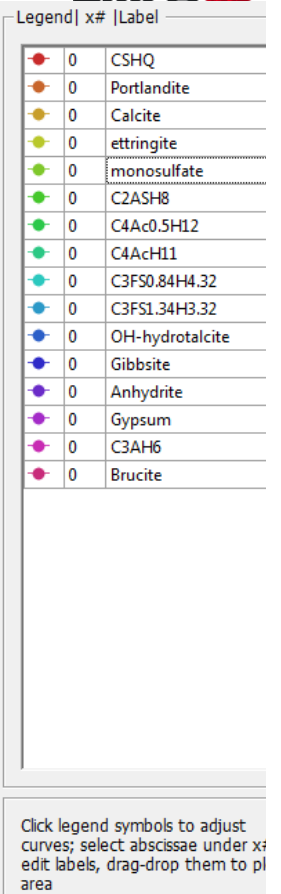
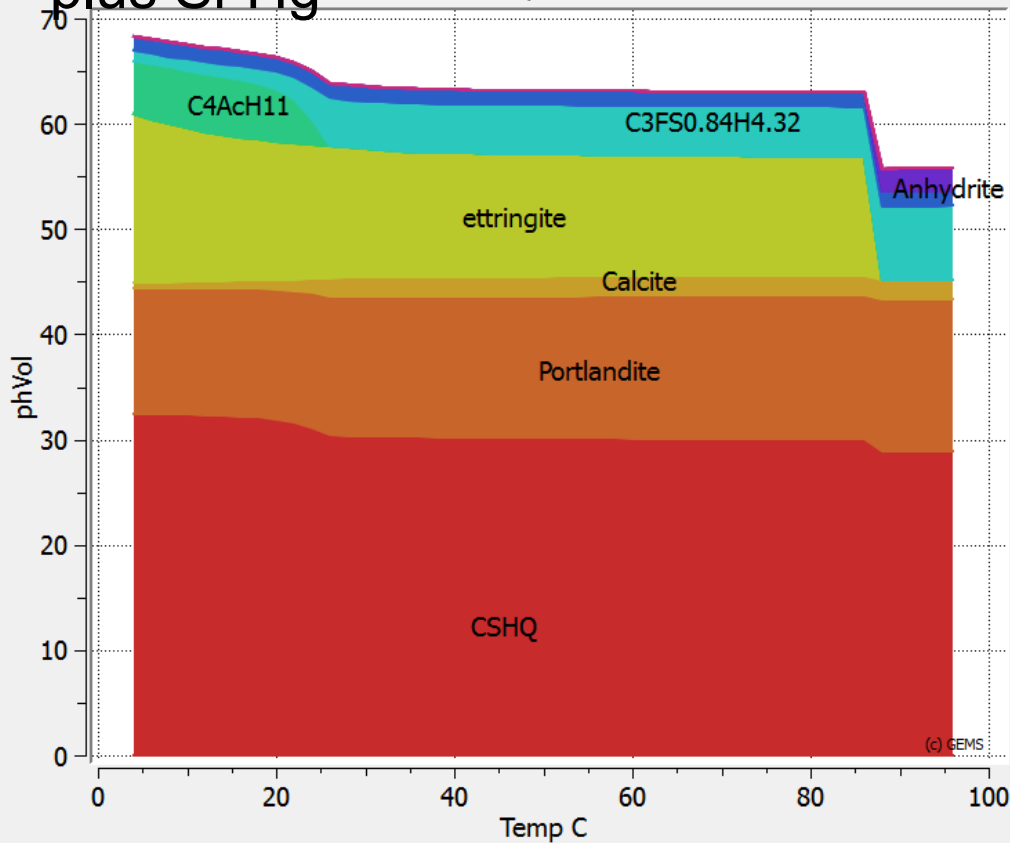
ystem: T = 293.15 K; P = 1.00 bar; V = 0.1506 L; Aqueous: built-in EDH(H); pH = 13.785; pe = 7.365; IS = 0.568 m

Influence of temperature: 5% Cc



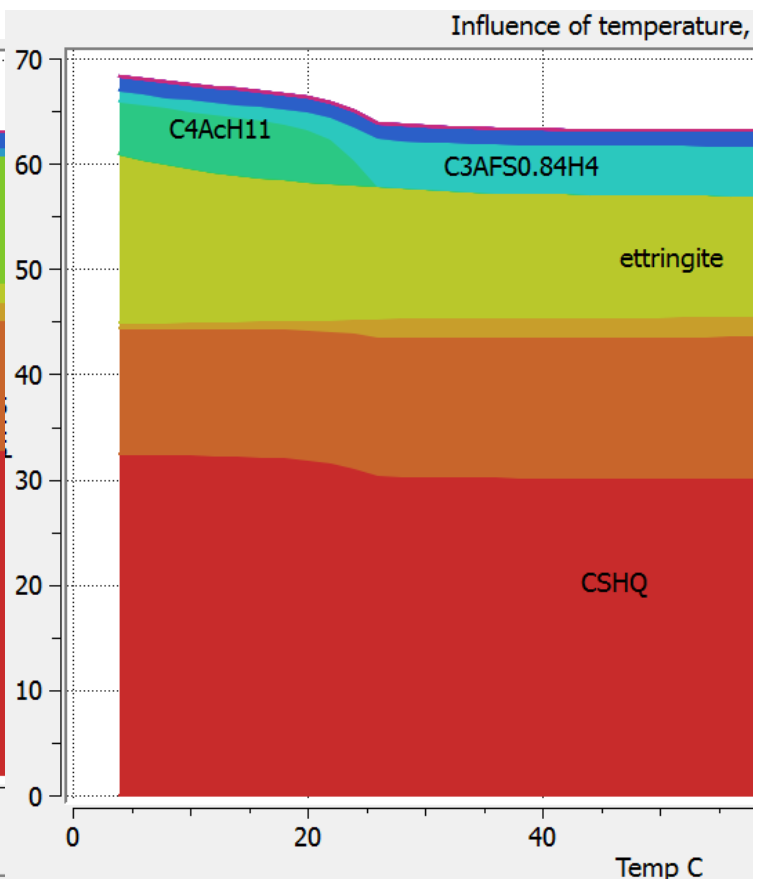
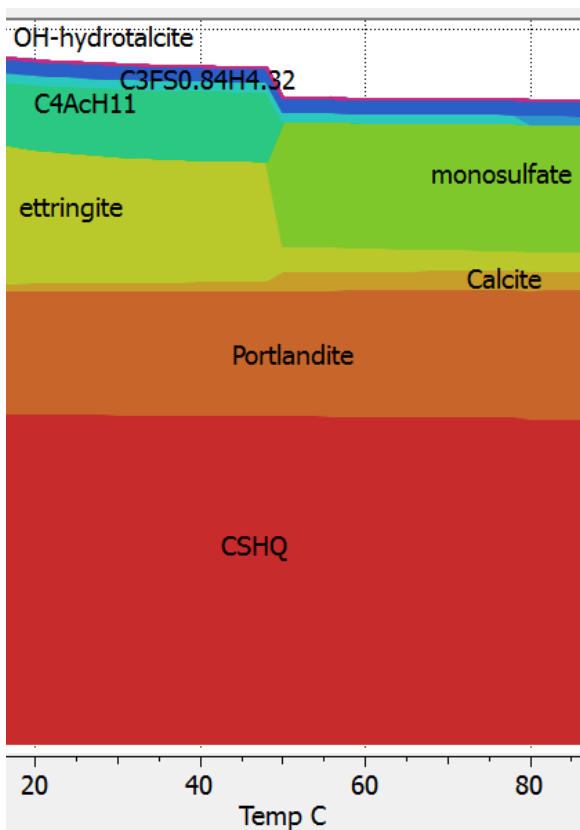
plus Si-Hg

Influence of temperature, PC with Cc

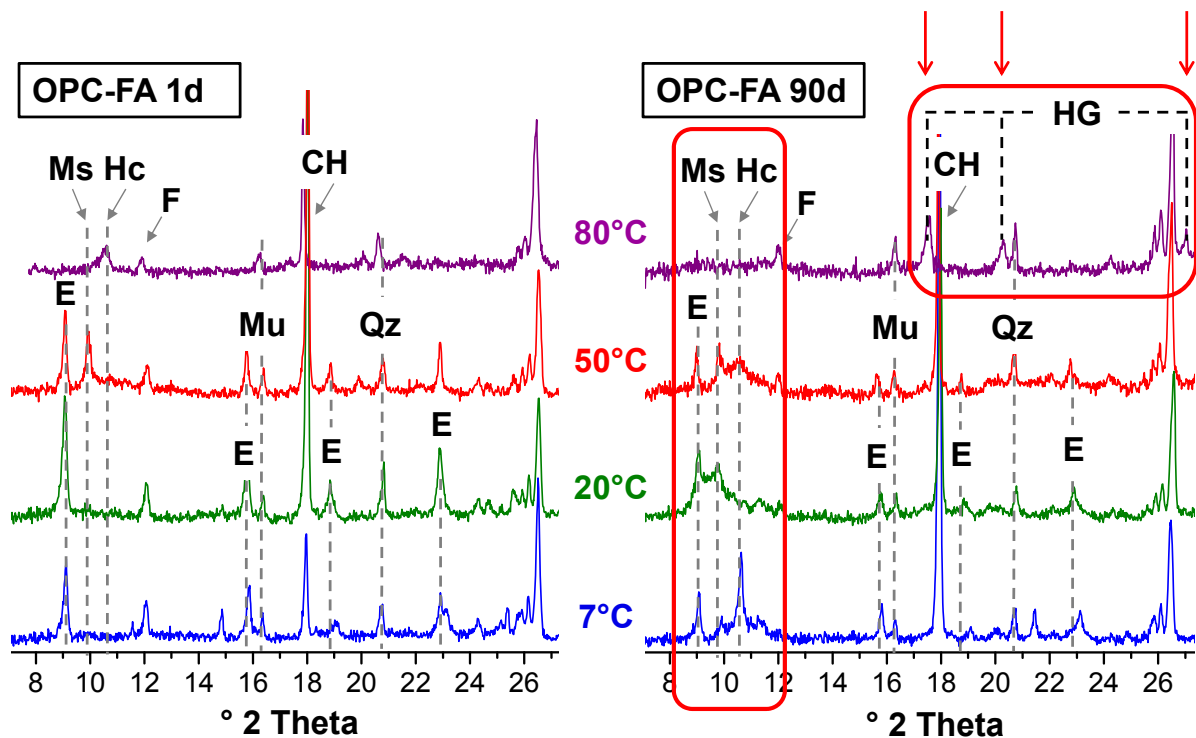


No $C_3AS_{0.84}H_{4.32}$

With $C_3AS_{0.84}H_{4.32}$



siliceous hydrogarnet in OPC blended with fly ash)

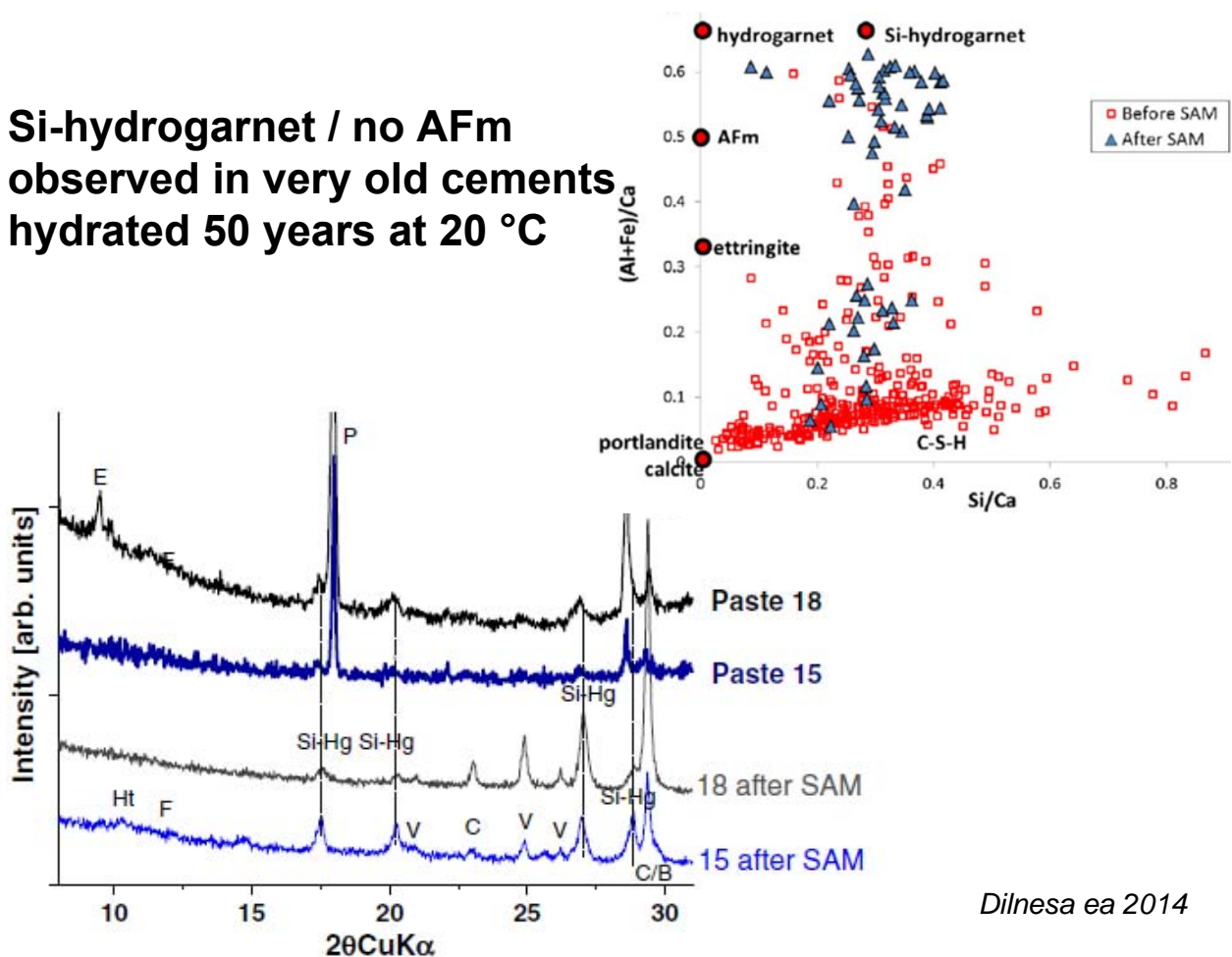


GEMS workshop, Dübendorf, May 19-21, 2014

Deschner et al, 2013

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**Si-hydrogarnet / no AFm
observed in very old cements
hydrated 50 years at 20 °C**



Dilnesa et al 2014

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Influence of temperature

Higher temperature:

→ faster kinetic of PC hydration and SiO_2 reaction:

OPC

→ **47 °C**: ettringite, monocarb. → monosulfate

→ volume decrease => decrease in strength

longterm

→ **Hydrogarnet-hydrogrossular instead of AFm**

In addition changes in CSH volume (water content);

Not captured in present CSH model (no gel water present)!