Oregon State University

Empa
Materials Science and Technology

Lecture 3
Hydrated Portland cement

Process calculations: Part 1

Frank Winnefeld

NTNU – Trondheim
Norwegian University of
Science and Technology

Software development/fitting
tools/kinetic:
Dmitrii Kulik
Dan Miron

PAUL SCHERRER INSTITUT
PSI

Tutorial – process: hydration of Portland cement

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Hydration of Portland cement

1) Hydration of PC - single system — Lecture 3

2) Influence of limestone on hydration of PC
   – process file
   a) Mass based output
   b) Volume based output
   c) Composition of aqueous phase

3) Influence of fly ash on hydration of PC
   – process file

— Lecture 4

Single file - hydration of Portland cement

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Hydration of a Portland cement

- The example will show the principle possibility to apply GEMS to simulate cement hydration.
- A cement composition from literature is used.
- 100% hydration with w/c = 0.50 at 20°C is assumed (other assumptions are possible).

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Single file - hydration of Portland cement

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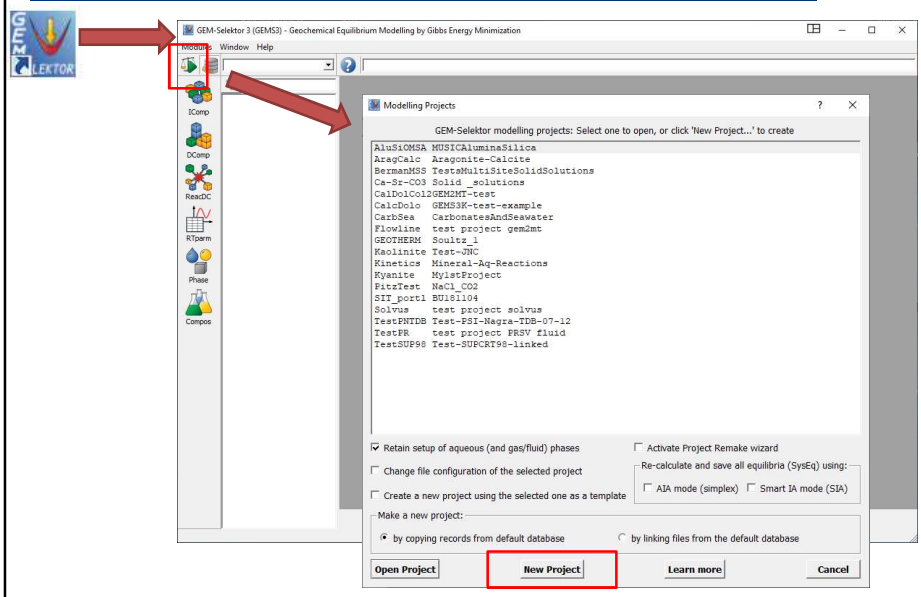

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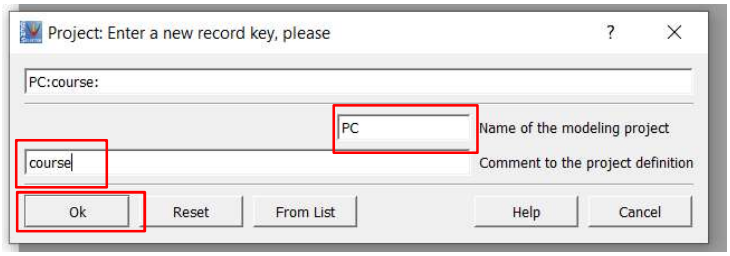
Single file - hydration of Portland cement



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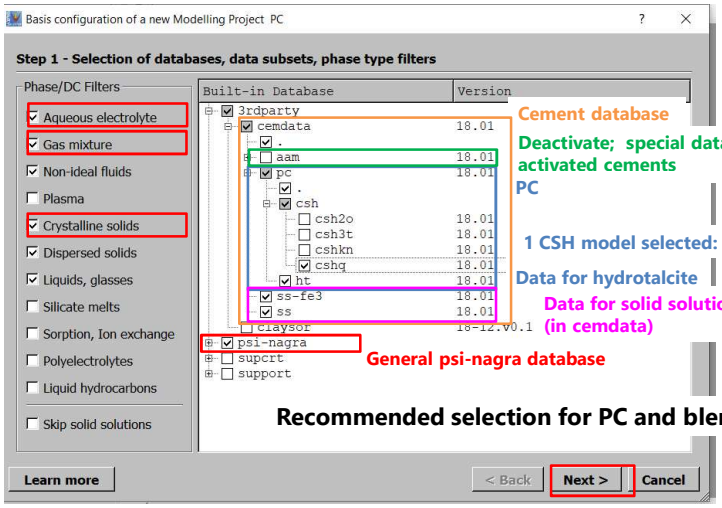
Single file - hydration of Portland cement

Select CEMDATA18 (3rd party data base)



Cement database

Deactivate; special data for alkali activated cements

PC

1 CSH model selected: «CSHQ»

Data for hydrotalcite

Data for solid solutions (in cemdata)

General psi-nagra database

Recommended selection for PC and blended cements

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Single file - hydration of Portland cement

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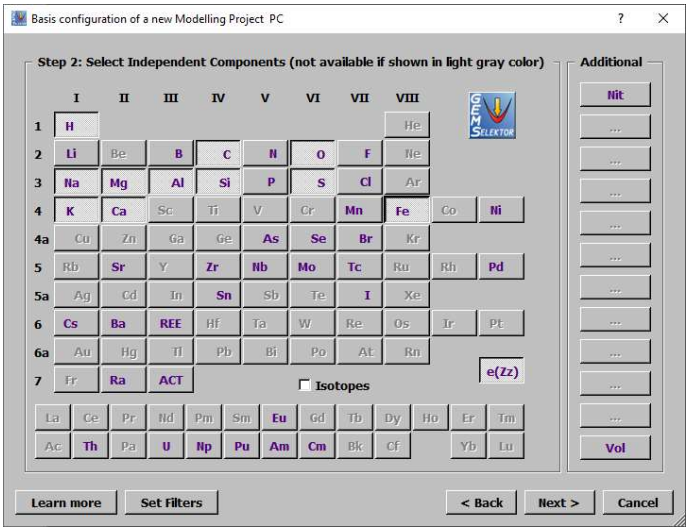
Select main elements present in PC



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Single file - hydration of Portland cement

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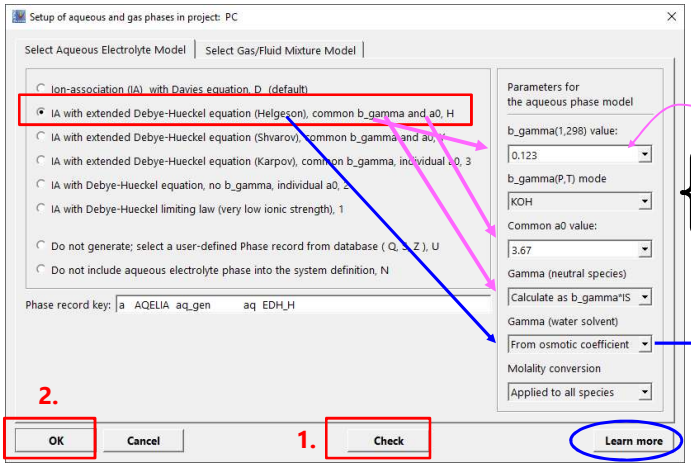
Select model for calculation of the aqueous phase



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Activity coefficients

Solubility product e. g. of gypsum
$K_{S0} = \{Ca^{2+}\}\cdot\{SO_4^{2-}\}\cdot\{H_2O\}^2/\{CaSO_4\cdot 2H_2O\}$
$K_{S0} = \{Ca^{2+}\}\cdot\{SO_4^{2-}\} = 10^{-4.58}$

{ } : activity; [ ]: concentration
$\{Ca^{2+}\} = [Ca^{2+}] \cdot \gamma_{Ca2+}$ ← Activity coefficicient

Correction of concentrations by activity coefficients, as the ions „feel" their neighbours (other ions, solvent).
Activity coefficients depend mainly on:

- ionic strength
- other ionic species
- temperature

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Activity vs. ionic strength – selecting the right aqueous electrolyte model

Debye-Hückel	$\log\gamma_{Ca^{2+}} = \frac{-AZ^2\sqrt{I}}{1+Ba\sqrt{I}}$	ionic strength	I < 0.1 M
Extended Debye-Hückel	$\log\gamma_{Ca^{2+}} = \frac{-AZ^2\sqrt{I}}{1+Ba\sqrt{I}} + bI$		
common a, common b (Helgeson)			I < 1-2 M
individual a, common b (Truesdell-Jones)			I < 1 M
individual a, no b			I < 0.3M
Davies	$\log\gamma_{Ca^{2+}} = -AZ^2(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.3I)$		0.1 < I <0. 5 M
SIT	$\log\gamma_{Ca^{2+}} = \frac{-AZ^2\sqrt{I}}{1+1.5\sqrt{I}} + \sum\varepsilon m_k$		I < 3 M

The calculation of activity coefficients is available as built-in function in the GEMS code.
For a detailed overview of different activity coefficients see:
C:\GEMS36\Gems3-app\Resources\doc\pdf\Activity-Coeffs.pdf and references therein

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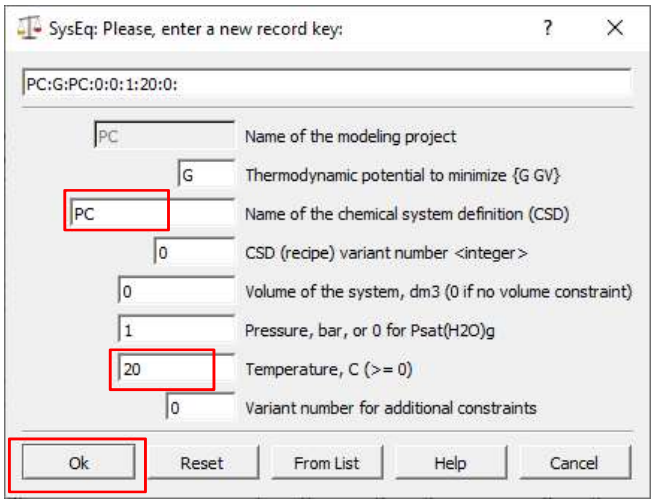
Single file - hydration of Portland cement



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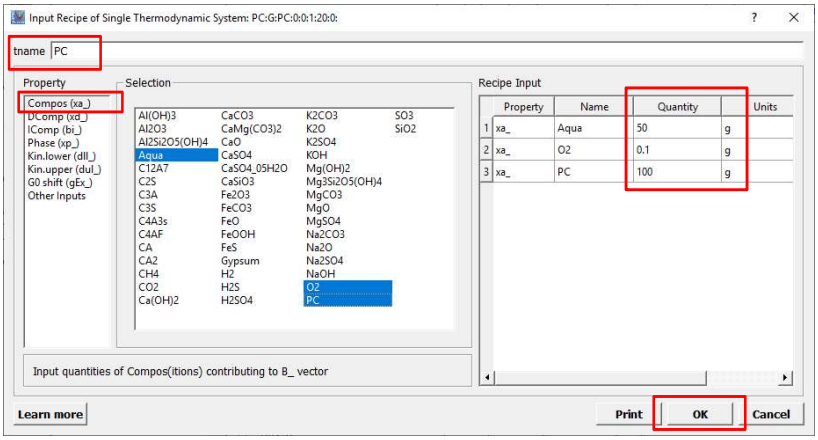
Single file - hydration of Portland cement

Use recipe wizard to enter PC composition



PC = predefined composition

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Composition of a PC without limestone addition *

Normative phase composition [g/100 g]

Alite [c]	66.5
Belite [c]	10.3
Aluminate [c]	7.5
Ferrite [c]	8.5
MgO(periclase) [c]	0.9
CaO (free) [d]	0.93
$CaCO_3$ [d]	0.6
$CaSO_4 \cdot 2H_2O$ [d]	3.1
K_2SO_4 [b]	1.3
Na_2SO_4 [b]	0.21

Present as solid solution in the clinker phases

K_2O [d]	0.054
Na_2O [d]	0.33
MgO [d]	0.94
SO_3 [d]	0.11

B. Lothenbach et al. / Cement and Concrete Research 38 (2008) 848–860

Compos :: Predefined composition objects (PCO)

Page 1 | Settings | 13/05/2019, 10:48

+ − + − − M | 10 | 0 | 9 | 1 | 10 | 0

Lothenbach_ea_b:2008:pap: | OPC composition

	formU	AUc	CA
0	CaO	g	63.9
1	SiO2	g	20.2
2	Al2O3	g	4.9
3	Fe2O3	g	3.2
4	MgO	g	1.8
5	K2O	g	0.78
6	Na2O	g	0.42
7	CO2	g	0.26
8	SO3	g	2.29

Available in CEMDATA18 as predefined composition «PC»

** Not completely without, as some $CaCO_3$ is present, mainly impurity of the calcium sulfate set regulator*

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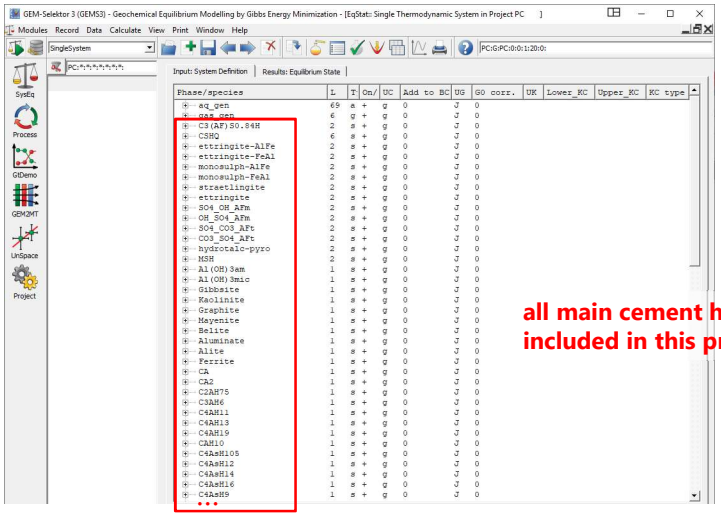

all main cement hydrates included in this project

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Single file - hydration of Portland cement

C-S-H is modeled as a solid solution of 6 different species:

Input: System Definition | Results: Equilibrium State

Phase/species	L	T	On/	UC	Add to BC	UG	G0 corr.	UK	Lower_KC	Upper_KC	KC type
aq_gen	69	a	+	g	0	J	0				
gas_gen	6	g	+	g	0	J	0				
C3(AF)S0.84H	2	s	+	g	0	J	0				
CSHQ	6	s	+	g	0	J	0				
CSHQ-JenD		I	+	M	0	J	0	M	0	1000000	B
CSHQ-JenH		I	+	M	0	J	0	M	0	1000000	B
CSHQ-TobD		I	+	M	0	J	0	M	0	1000000	B
CSHQ-TobH		I	+	M	0	J	0	M	0	1000000	B
KSiOH		I	+	M	0	J	0	M	0	1000000	B
NaSiOH		I	+	M	0	J	0	M	0	1000000	B

CSH-JenD = $(CaO)_{1.5}\cdot(SiO_2)_{0.6667}\cdot(H_2O)_{2.5}$

CSH-JenH = $(CaO)_{1.333}\cdot(SiO_2)_{1}\cdot(H_2O)_{2.1667}$

CSH-TobD = $[(CaO)_{1.25}\cdot(SiO_2)_{1}\cdot(H_2O)_{2.75}]_{0.6667}$

CSH-TobH = $(CaO)_{0.6667}\cdot(SiO_2)_{1}\cdot(H_2O)_{1.5}$ Kulik D.A., Cem. Concr. Res. 41 (2011), 477.

The 4 C-S-H species are in ss with (hypothetical) Na- and K-silicates to model alkali binding by C-S-H.

Lothenbach, B., Kulik, D., Matschei, T., Balonis, M., Baquerizo, L., Dilnesa, B.Z., Miron, D.G., Myers, R. (2019) Cemdata18: A chemical thermodynamic database for hydrated Portland cements and alkali-activated materials *Cement and Concrete Research*, 115, 472-506.

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Single file - hydration of Portland cement

Before calculation, deactivate the following phases:

- **Goethite, hematite, quartz,** …
  (form at high temperature after long times)
- C_3AH_6, **gibbsite** (depending on reaction time), …
- **Thaumasite** (formation fast at low temp. Very slow at ambient temp and above)
- others:
  Etttringite Al/Fe ss
  Monosulfate Al/Fe ss
  C_4AH_{13}, C_4AH_{19}

In general it is recommended:

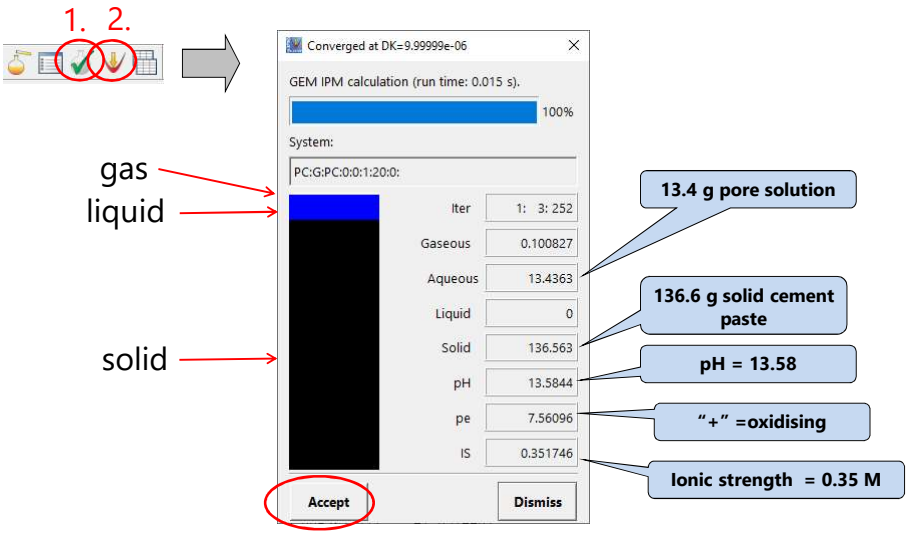
- Use either the pure phase or the ss (deactivate the other); in this case C_4AH_{13} & C_4AH_{19}
- **Look at the results, compare with experimental data !**

Input: System Definition | Results: Equilibrium State

Phase/species	L	T	On/	UC	Add to BC	UG
C4FH13	1	s	+	g	0	J
C3FS0.84H4.32	1	s	+	g	0	J
C3FS1.34H3.32	1	s	+	g	0	J
C4Fc05H10	1	s	+	g	0	J
C4FcH12	1	s	+	g	0	J
Dolomite-dis	1	s	+	g	0	J
Dolomite-ord	1	s	+	g	0	J
lime	1	s	+	g	0	J
Portlandite	1	s	+	g	0	J
Anhydrite	1	s	+	g	0	J
Gypsum	1	s	+	g	0	J
hemihydrate	1	s	+	g	0	J
thaumasite	1	s	+	g	0	J
Iron	1	s	+	g	0	J
Fe-carbonate	1	s	+	g	0	J
Siderite	1	s	+	g	0	J
Hematite	1	s	–	g	0	J
Magnetite	1	s	+	g	0	J
Ferrihydrite-am	1	s	+	g	0	J
Ferrihydrite-mc	1	s	+	g	0	J
Goethite	1	s	–	g	0	J
Pyrite	1	s	+	g	0	J
Troilite	1	s	+	g	0	J
Melanterite	1	s	+	g	0	J
arcanite	1	s	+	g	0	J
syngenite	1	s	+	g	0	J
K-oxide	1	s	+	g	0	J
OH-hydrotalcite	1	s	+	g	0	J
Magnesite	1	s	+	g	0	J
Brucite	1	s	+	g	0	J
thenardite	1	s	+	g	0	J
Natrolite	1	s	+	g	0	J
ZeoliteX	1	s	+	g	0	J
ZeoliteY	1	s	+	g	0	J
Na-oxide	1	s	+	g	0	J
Sulphur	1	s	+	g	0	J
Quartz	1	s	–	g	0	J

Single file - hydration of Portland cement

Experimental conditions: React 100 g PC with 50 g water (add 0.1 g air CO_2-free)



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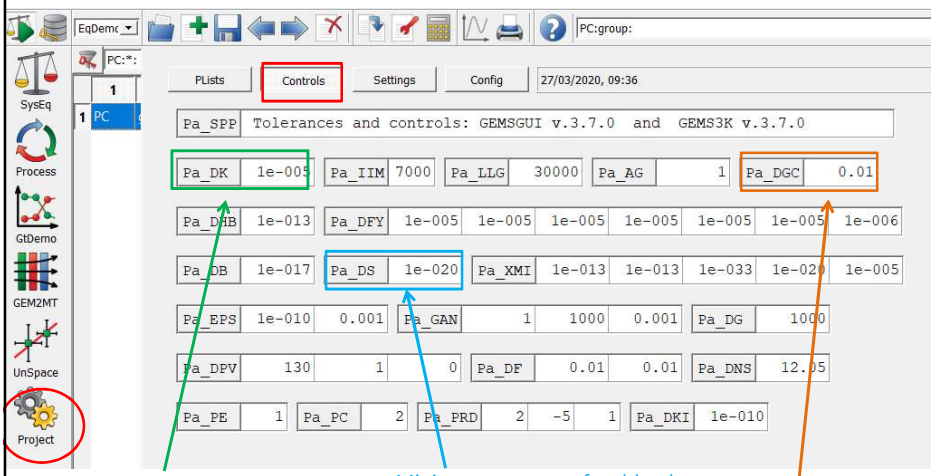
Convergence problem - workaround



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

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

Smoothing parameter:
use low positive value, e.g. 0.01

In case of problems
Do not touch the other values !!!

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Single file - hydration of Portland cement

Predicted stable phase assemblage

Si-Hydrogarnet
C-S-H
ettringite
hemicarbonate
monocarbonate
portlandite
hydrotalcite

Input: System Definition | Results: Equilibrium State

Phase/species	L	T	Amount (mol)	logSI/Activ
aq_gen	69	a	0.74137659	-7.24e-09
gas_gen	6	g	0.0031839841	8.458e-10
C3(AF)S0.84H	2	s	0.040769952	-1.116e-08
CSHQ	6	s	0.44660885	4.501e-09
straetlingite	2	s	0	-1.43
ettringite	2	s	0.0097500225	4.003e-10
SO4_OH_AFm	2	s	0	-1
OH_SO4_AFm	2	s	0	-1
SO4_CO3_AFt	2	s	0	-0.02332
CO3_SO4_AFt	2	s	0	-0.01936
C4Ac0.5H105	1	s	0	-1.807
C4Ac0.5H12	1	s	0.003353021	2.74e-07
C4Ac0.5H9	1	s	0	-4.902
C4AcH11	1	s	0.0043671711	-1.052e-07
C6AsH13	1	s	0	-29.53
lime	1	s	0	-9.961
Portlandite	1	s	0.46432155	-4.773e-09
Anhydrite	1	s	0	-3.615
K-oxide	1	s	0	-59.68
OH-hydrotalcite	1	s	0.01142203	1.975e-13
Magnesite	1	s	0	-9.084

limestone (0.6 M.-% in the system) fully reacted

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Single file - hydration of Portland cement

Composition of C-S-H

Input: System Definition | Results: Equilibrium State

Phase/species	L	T	Amount (mol)	logSI/Activity	Concentration	Activity coeff.
aq_gen	69	a	0.74137659	-7.24e-09		
gas_gen	6	g	0.0031839841	8.458e-10		
C3(AF)S0.84H	2	s	0.040769952	-1.116e-08		
CSHQ	6	s	0.44660885	4.501e-09		
CSHQ-JenD		I	0.1645959	0.368546	0.36854599	1
CSHQ-JenH		I	0.10337444	0.231465	0.23146527	1
CSHQ-TobD		I	0.12210382	0.273402	0.27340216	1
CSHQ-TobH		I	0.0048265056	0.010807	0.010807008	1
KSiOH		I	0.027356397	0.0612536	0.061253594	1
NaSiOH		I	0.024351788	0.054526	0.054525987	1
straetlingite	2	s	0	-1.43		

36.9 mol-% CSH-JenD = $(CaO)_{1.5}\cdot(SiO_2)_{0.6667}\cdot(H_2O)_{2.5}$
23.1 mol.-% CSH-JenH = $(CaO)_{1.333}\cdot(SiO_2)_1\cdot(H_2O)_{2.1667}$
27.3 mol.-% CSH-TobD = $[(CaO)_{1.25}\cdot(SiO_2)_1\cdot(H_2O)_{2.75}]_{0.6667}$
1.1 mol.-% CSH-TobH = $(CaO)_{0.6667}\cdot(SiO_2)_1\cdot(H_2O)_{1.5}$
6.1 mol.-% KSiOH = $[(KOH)_{2.5}\ SiO_2\ H_2O]_{0.2}$
5.5 mol.-% NaSiOH = $[(NaOH)_{2.5}\ SiO_2\ H_2O]_{0.2}$

Al-intake in C-S-H: In preparation

For alkali activated slag use CNASH_ss model:
See: Myers et al., Cem. Concr. Res. 66 (2014), 27-47.
(provided separately in CEMDATA18 as "aam")

C-S-H solid solution: 0.022 K_2O · 0.020 Na_2O · 1.580 CaO · 1 SiO_2 · 2.873 H_2O
=> Ca/Si = 1.58

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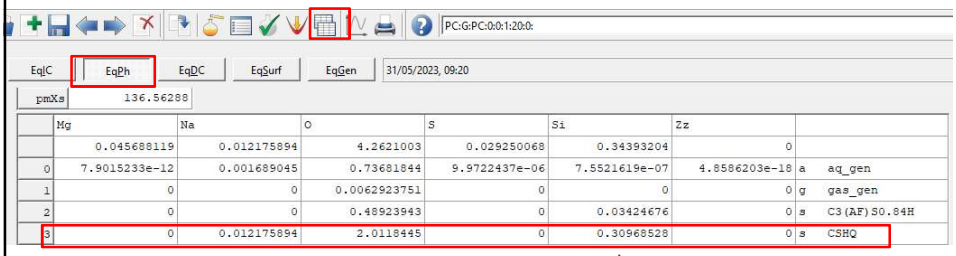
Composition of C-S-H *(scroll down, data in 2nd table)*



EqIC | EqPh | EqDC | EqSurf | EqGen | 31/05/2023, 09:20

pmXs 136.56288

	Mg	Na	O	S	Si	Zz		
	0.045688119	0.012175894	4.2621003	0.029250068	0.34393204	0		
0	7.9015233e-12	0.001689045	0.73681844	9.9722437e-06	7.5521619e-07	4.8586203e-18	a	aq_gen
1	0	0	0.0062923751	0	0	0	g	gas_gen
2	0	0	0.48923943	0	0.03424676	0	s	C3(AF)S0.84H
3	0	0.012175894	2.0118445	0	0.30968528	0	s	CSHQ

bXa[{CSHQ}][{Na}]

bXa[{CSHQ}][{Si}]

Syntax for use in process calculations

Summary C-S-H solid solution :

C-S-H solid solution: 0.022 K_2O · 0.020 Na_2O · 1.580 CaO · 1 SiO_2 · 2.873 H_2O
Ca/Si = 1.58, K/Si = 0.044, Na/Si = 0.039 (K/Ca = 0.028, Na/Ca = 0.025)

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Presence of hydrogarnet

Input: System Definition | Results: Equilibrium State

Phase/species	L	T	Amount (mol)	logSI/Activity	Concentration	Activity coeff.
a aq_gen	69	a	0.74137659	-7.24e-09		
g gas_gen	6	g	0.0031839841	8.458e-10		
s C3(AF)S0.84H	2	s	0.040769952	-1.116e-08		
C3AFS0.84H4.32		I	0.040539289	0.994342	0.99434233	1
C3FS0.84H4.32		I	0.00023066309	0.0056577	0.0056576738	1
s CSHQ	6	s	0.44660885	4.501e-09		

Iron-containing siliceous hydrogarnet is modelled as a solid solution with the following end members:

$C_3\mathbf{A_{0.5}F_{0.5}}S_{0.84}H_{4.32}$ and $C_3FS_{0.84}H_{4.32}$ **=> Al/Fe ≈ 1**

Al/Fe ratios > 1 are not considered due to experimental findings on hydrated cement pastes with «normal» curing times (up to a few years).

The data for $C_3AS_{0.42}H_{5.16}$ and $C_3AS_{0.84}H_{4.32}$ are deactivated but would be available in the database.

B.Z. Dilnesa, B. Lothenbach, G. Renaudin, A. Wichser, D. Kulik, Synthesis and characterization of hydrogarnet $Ca_3(Al_xFe_{1-x})_2(SiO_4)_y(OH)_{4(3-y)}$, Cem Concr Res 59 (2014) 96-111.
B.Z. Dilnesa, E. Wieland, B. Lothenbach, R. Dähn, K. Scrivener, Fe-containing phases in hydrated cements, Cem. Concr. Res. 58 (2014) 45–55.

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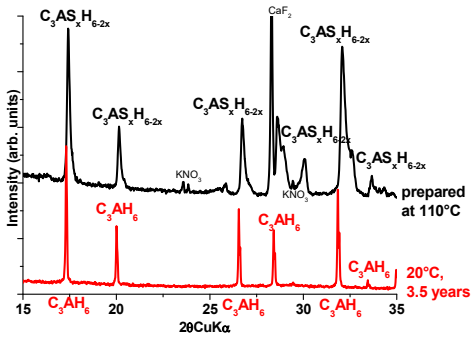
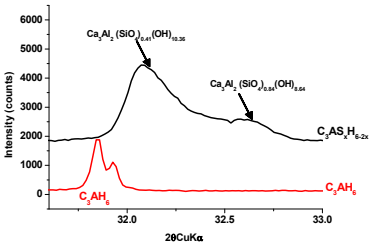
Presence of hydrogarnet





Room temperature: only C_3AH_6 and $C_3FS_xH_{6-2x}$ forms, *but no $C_3AS_xH_{6-2x}$*
$C_3AS_xH_{6-2x}$ forms only at 110 C°, altough stable at 20 °C

However, mixed $C_3A_{0.5}F_{0.5}S_xH_{6-2x}$ form

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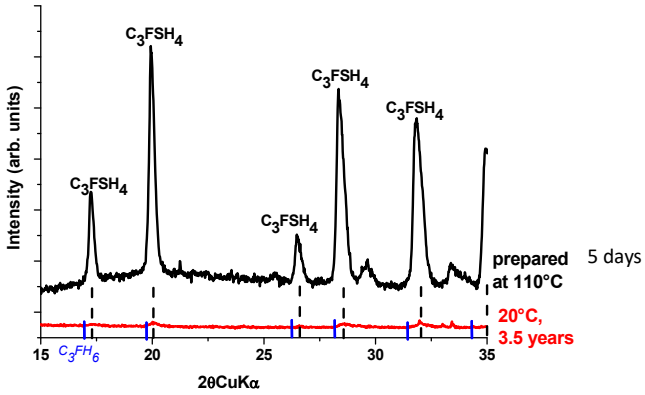
Fe- siliceous hydrogarnet in hydrated PC



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

Dilnesa ea 2014

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Single file - hydration of Portland cement

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Si-hydrogarnet in hydrated PC

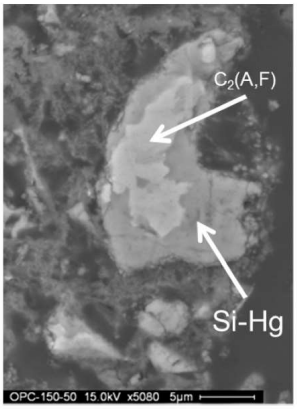
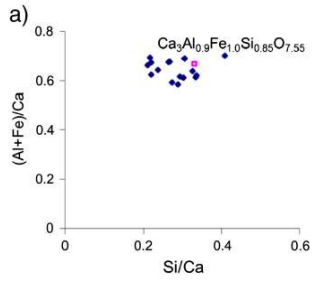


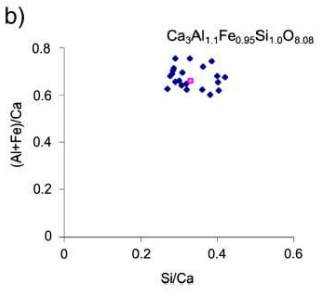
Fig. 8. SEM of ferrite clinker surrounded by hydration products after selective extraction.

B.Z. Dilnesa, E. Wieland, B. Lothenbach, R. Dähn, K. Scrivener, Fe-containing phases in hydrated cements, Cem. Concr. Res. 58 (2014) 45–55.

20°C



50°C



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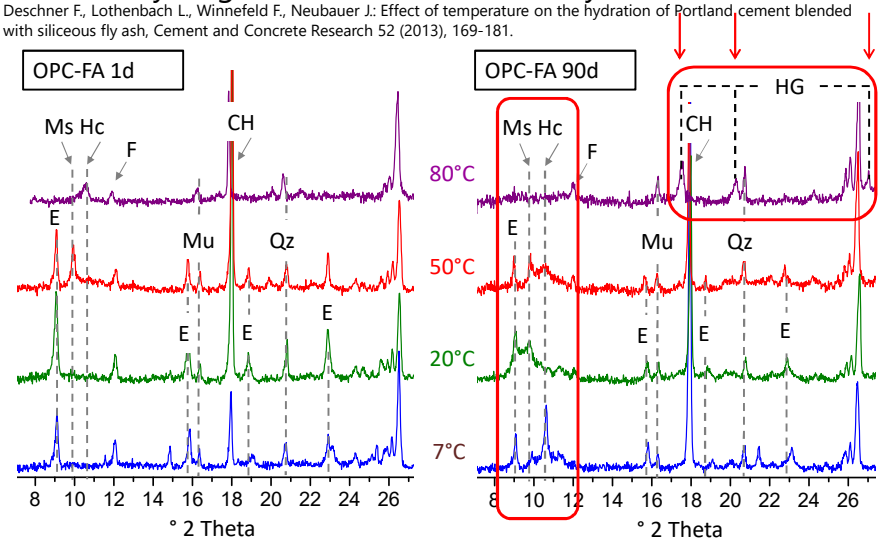
Siliceous hydrogarnet (PC blended with fly ash)

Deschner F., Lothenbach L., Winnefeld F., Neubauer J.: Effect of temperature on the hydration of Portland cement blended with siliceous fly ash, Cement and Concrete Research 52 (2013), 169-181.



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Single file - hydration of Portland cement

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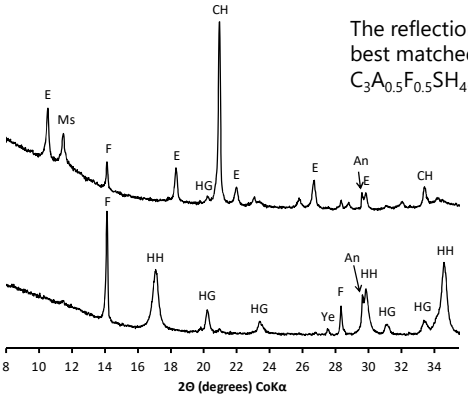
Si-hydrogarnet in hydrated ACSA



The reflections of the siliceous hydrogarnet (HG) were best matched by a hydrogarnet of the composition $C_3A_{0.5}F_{0.5}SH_4$.

before selective extraction

After selective extraction

Chitvoranund N., Winnefeld F., Hargis C.W., Sinthupinyo S., Lothenbach B.: Synthesis and hydration of alite-calcium sulfoaluminate cement, Advances in Cement Research 29 (2017), 101-111.

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Single file - hydration of Portland cement

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Hydrated cement composition – summary

- possibility to apply GEMS to simulate hydrated cement
- use metastability constraints (e.g. goethite suppressed)
- use either oxide composition or phase composition as input
- iron and alkalis present in real "PC"
  thus to improve accuracy of the calculation one has to consider:
  - Iron containing phases (mainly hydrogarent important
    (Möschner et al. Geoch. Cosm. Acta 2007, Dilnesa et al. CCR 2014a+b
    included in the cement database)
  - Sorption of alkalis on C-S-H , good proxy, not perfect
    (*experimental data:* Hong and Glasser CCR 1999, included in the database)
  - Sorption of sulfate on C-S-H
    (*experimental data:* Divet et al. CCR 1998, Barbarulo et al. 2002, Skapa PhD Thesis U. Aberdeen, 2009) not included
  - Substitution of alumina (Richardson CCR 1994, Chen et al. ICCC 2007, Pardal et al. CCR 2009 & Inorg. Chem. 2012, ongoing work based on CASH I+II projects at Empa, for alkali activated slags use CNASH_ss model by Myers et al., CCR 2014, provided separately as aam for GEMS)
- kinetics can be taken into account as function of clinker reactivity over time
  (e.g. Lothenbach et al. CCR 2006 & 2008)

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