

## Lecture 3 Hydrated Portland cement



### Process calculations: Part 1

Frank Winnefeld

## Tutorial – process: hydration of Portland cement

### 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

Lecture 4

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

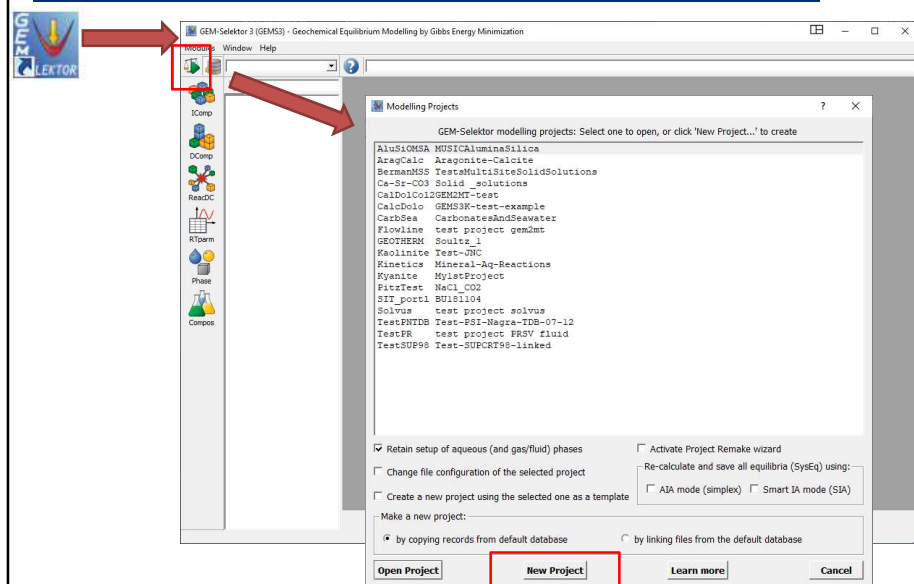
## Single file - hydration of Portland cement

### 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  $20^{\circ}\text{C}$  is assumed (other assumptions are possible).

3

## Single file - hydration of Portland cement



4

## Single file - hydration of Portland cement

Project: Enter a new record key, please

PC:course:

course

PC

Name of the modeling project

Comment to the project definition

Ok Reset From List Help Cancel

5

## Single file - hydration of Portland cement

### Select CEMDATA18 (3<sup>rd</sup> party data base)

Basis configuration of a new Modelling Project PC

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

Database	Version
3rdparty	
<input checked="" type="checkbox"/> cemdata	18.01
<input type="checkbox"/> aam	18.01
<input checked="" type="checkbox"/> pc	18.01
<input checked="" type="checkbox"/> csh	18.01
<input type="checkbox"/> csh2o	18.01
<input type="checkbox"/> csh3t	18.01
<input type="checkbox"/> cshkn	18.01
<input checked="" type="checkbox"/> cshq	18.01
<input checked="" type="checkbox"/> ht	18.01
<input checked="" type="checkbox"/> ss-fe3	18.01
<input checked="" type="checkbox"/> ss	18.01
<input checked="" type="checkbox"/> claysol	18-12.v0.1
<input checked="" type="checkbox"/> psi-nagra	18-12.v0.1
<input type="checkbox"/> supcrt	
<input type="checkbox"/> support	

Learn more

< Back Next > Cancel

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

6

## Single file - hydration of Portland cement

### Select main elements present in PC

7

## Single file - hydration of Portland cement

### Select model for calculation of the aqueous phase

1) constant,  
-> select at 298 K  
2) f(pressure, temp)  
-> electrolyte  
a0=3.67 for KOH

Calculates  
activity of water

More details

8

## 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

$$\{Ca^{2+}\} = [Ca^{2+}] \cdot \gamma_{Ca^{2+}} \longleftarrow \text{Activity coefficient}$$

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

9

## 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  $I < 0.1 \text{ M}$

Extended Debye-Hückel  $\log \gamma_{Ca^{2+}} = \frac{-AZ^2\sqrt{I}}{1 + Ba\sqrt{I}} + bI$

common a, common b (Helgeson)

$I < 1-2 \text{ M}$

individual a, common b (Truesdell-Jones)

$I < 1 \text{ M}$

individual a, no b

$I < 0.3 \text{ M}$

Davies  $\log \gamma_{Ca^{2+}} = -AZ^2 \left( \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right)$   $0.1 < I < 0.5 \text{ M}$

SIT  $\log \gamma_{Ca^{2+}} = \frac{-AZ^2\sqrt{I}}{1 + 1.5\sqrt{I}} + \sum \varepsilon m_k$   $I < 3 \text{ M}$

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

10

## Single file - hydration of Portland cement

SysEq: Please, enter a new record key:

PC:G:PC:0:0:1:20:0:

PC Name of the modeling project

G Thermodynamic potential to minimize {G GV}

PC Name of the chemical system definition (CSD)

0 CSD (recipe) variant number <integer>

0 Volume of the system, dm3 (0 if no volume constraint)

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

20 Temperature, C (>= 0)

0 Variant number for additional constraints

Ok Reset From List Help Cancel

11

## Single file - hydration of Portland cement

Use recipe wizard to enter PC composition

Input Recipe of Single Thermodynamic System: PC:G:PC:0:0:1:20:0:

fname PC

Property Selection

Compos (x<sub>a</sub>)

Al(OH)<sub>3</sub> CaCO<sub>3</sub> K<sub>2</sub>CO<sub>3</sub> SO<sub>3</sub>

Al<sub>2</sub>O<sub>3</sub> CaMg(CO<sub>3</sub>)<sub>2</sub> K<sub>2</sub>O SiO<sub>2</sub>

Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub> CaO K<sub>2</sub>SO<sub>4</sub>

Aqua CaSO<sub>4</sub> KOH

C12A7 CaSO<sub>4</sub>·0.5H<sub>2</sub>O Mg(OH)<sub>2</sub>

C<sub>2</sub>S CaSiO<sub>3</sub> Mg<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>

C<sub>3</sub>A Fe<sub>2</sub>O<sub>3</sub> MgCO<sub>3</sub>

C<sub>3</sub>S FeCO<sub>3</sub> MgO

C<sub>4</sub>A<sub>3</sub>S FeO MgSO<sub>4</sub>

C<sub>4</sub>AF Fe(OH) Na<sub>2</sub>CO<sub>3</sub>

CA FeS Na<sub>2</sub>O

CA<sub>2</sub> Gypsum Na<sub>2</sub>SO<sub>4</sub>

CH<sub>4</sub> H<sub>2</sub> NaOH

CO<sub>2</sub> H<sub>2</sub>S O<sub>2</sub>

Ca(OH)<sub>2</sub> H<sub>2</sub>SO<sub>4</sub> PC

Recipe Input

	Property	Name	Quantity	Units
1	x <sub>a</sub>	Aqua	50	g
2	x <sub>a</sub>	O <sub>2</sub>	0.1	g
3	x <sub>a</sub>	PC	100	g

Input quantities of Compos(tions) contributing to B<sub>-</sub> vector

Learn more Print OK Cancel

PC = predefined composition

12

## Single file - hydration of Portland cement

### Composition of a PC without limestone addition \*

Normative phase composition [g/100 g]

Alite <sup>c</sup>	66.5
Belite <sup>c</sup>	10.3
Aluminate <sup>c</sup>	7.5
Ferrite <sup>c</sup>	8.5
MgO(periclar) <sup>c</sup>	0.9
CaO (free) <sup>d</sup>	0.93
CaCO <sub>3</sub> <sup>d</sup>	0.6
CaSO <sub>4</sub> · 2H <sub>2</sub> O <sup>d</sup>	3.1
K <sub>2</sub> SO <sub>4</sub> <sup>b</sup>	1.3
Na <sub>2</sub> SO <sub>4</sub> <sup>b</sup>	0.21

Present as solid solution in the clinker phases

K <sub>2</sub> O <sup>d</sup>	0.054
Na <sub>2</sub> O <sup>d</sup>	0.33
MgO <sup>d</sup>	0.94
SO <sub>3</sub> <sup>d</sup>	0.11

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: OFC composition

formU	AUC	CA
0	CaO	g 63.9
1	SiO <sub>2</sub>	g 20.2
2	Al <sub>2</sub> O <sub>3</sub>	g 4.9
3	Fe <sub>2</sub> O <sub>3</sub>	g 3.2
4	MgO	g 1.8
5	K <sub>2</sub> O	g 0.78
6	Na <sub>2</sub> O	g 0.42
7	CO <sub>2</sub>	g 0.26
8	SO <sub>3</sub>	g 2.29

Available in CEMDATA18 as predefined composition «PC»

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

\* Not completely without, as some CaCO<sub>3</sub> is present, mainly impurity of the calcium sulfate set regulator

13

## Single file - hydration of Portland cement

GEM-Selector 3 (GEM3) - Geochemical Equilibrium Modeling by Gibbs Energy Minimization - [EqSet: Single Thermodynamic System in Project PC]

Modules Record Data Calculate View Print Window Help

SingleSystem

Input: System Definition Results: Equilibrium State

Phase/species	L	T	On/	UC	Add to BC	UG	Go corr.	UK	Lower_KC	Upper_KC	KC type
aq_gen	69	a	+	g	0	J	0				
clinker	6	g	+	g	0	J	0				
C3 (AF) SO <sub>3</sub> 84R	2	s	+	g	0	J	0				
CSH	6	s	+	g	0	J	0				
ettringite-AlFe	2	s	+	g	0	J	0				
ettringite-FeAl	2	s	+	g	0	J	0				
monosulph-AlFe	2	s	+	g	0	J	0				
monosulph-FeAl	2	s	+	g	0	J	0				
ettringite	2	s	+	g	0	J	0				
SO <sub>4</sub> OH 3Am	2	s	+	g	0	J	0				
OH SO <sub>4</sub> 3Am	2	s	+	g	0	J	0				
SO <sub>4</sub> CO <sub>3</sub> AFt	2	s	+	g	0	J	0				
CO <sub>3</sub> SO <sub>4</sub> AFt	2	s	+	g	0	J	0				
hydrotalcite-pyro	2	s	+	g	0	J	0				
NSS	2	s	+	g	0	J	0				
Al (OH) 3Am	1	s	+	g	0	J	0				
Al (OH) 3mic	1	s	+	g	0	J	0				
Gibbsite	1	s	+	g	0	J	0				
Kaolinite	1	s	+	g	0	J	0				
Graphite	1	s	+	g	0	J	0				
Haynesite	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				
C2AH7	1	s	+	g	0	J	0				
C3AH6	1	s	+	g	0	J	0				
C4AH11	1	s	+	g	0	J	0				
C4AH13	1	s	+	g	0	J	0				
C4AH19	1	s	+	g	0	J	0				
C4AH10	1	s	+	g	0	J	0				
C4AH10S	1	s	+	g	0	J	0				
C4AH12	1	s	+	g	0	J	0				
C4AH14	1	s	+	g	0	J	0				
C4AH16	1	s	+	g	0	J	0				
C4AH9	1	s	+	g	0	J	0				

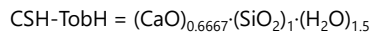
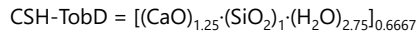
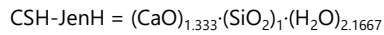
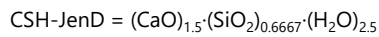
all main cement hydrates included in this project

14

## 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



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.

15

## Single file - hydration of Portland cement

Before calculation, deactivate the following phases:

- Goethite, hematite, quartz, ...  
(form at high temperature after long times)
- $\text{C}_3\text{AH}_6$ , gibbsite (depending on reaction time), ...
- Thaumasite (formation fast at low temp. Very slow at ambient temp and above)
- others:  
Ettringite Al/Fe ss  
Monosulfate Al/Fe ss  
 $\text{C}_4\text{AH}_{13}$ ,  $\text{C}_4\text{AH}_{19}$

In general it is recommended:

- Use either the pure phase or the ss (deactivate the other); in this case  $\text{C}_4\text{AH}_{13}$  &  $\text{C}_4\text{AH}_{19}$
- Look at the results, compare with experimental data !

Input: System Definition		Results: Equilibrium State									
Phase/species	L	T	On/UC	Add to BC	UG	G0 corr.	UK	Lower_KC	Upper_KC	KC type	
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				
Fe-sulfate	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-mc	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				
arcanite	1	s	+	g	0	J	0				
syngenite	1	s	+	g	0	J	0				
K-oxide	1	s	+	g	0	J	0				
OH-hydroxalite	1	s	+	g	0	J	0				
Magnesite	1	s	+	g	0	J	0				
Brucite	1	s	+	g	0	J	0				
thenardite	1	s	+	g	0	J	0				
Na-silicate	1	s	+	g	0	J	0				
ZeoliteX	1	s	+	g	0	J	0				
ZeoliteY	1	s	+	g	0	J	0				
Na-oxide	1	s	+	g	0	J	0				
Sulphur	1	s	+	g	0	J	0				
Quartz	1	s	+	g	0	J	0				



## Single file - hydration of Portland cement

**Experimental conditions:** React 100 g PC with 50 g water (add 0.1 g air CO<sub>2</sub>-free)

1. 2.

gas  
liquid  
solid

Converged at DK=9.99999e-06  
GEM IPM calculation (run time: 0.015 s).  
100%

System:  
PC:G:PC:0:0:1:20:0:

	Iter	1:	3:	252
Gaseous		0.100827		
Aqueous		13.4363		
Liquid		0		
Solid		136.563		
pH		13.5844		
pe		7.56096		
IS		0.351746		

Accept Dismiss

13.4 g pore solution  
136.6 g solid cement paste  
pH = 13.58  
" + " = oxidising  
Ionic strength = 0.35 M

17

## Convergence problem - workaround

EqDem PC: group: 27/03/2020, 09:36

Pa\_SPP Tolerances and controls: GEMSGUI v.3.7.0 and GEMS3K v.3.7.0

Pa_DK	1e-003	Pa_IIM	7000	Pa_LLG	30000	Pa_AG	1	Pa_DGC	0.01
Pa_DAB	1e-013	Pa_DFY	1e-005	1e-005	1e-005	1e-005	1e-005	1e-005	1e-006
Pa_DB	1e-017	Pa_DS	1e-020	Pa_XMI	1e-013	1e-013	1e-033	1e-020	1e-005
Pa_EPS	1e-010	0.001	Pa_GAN	1	1000	0.001	Pa_DG	1000	
Pa_DPV	130	1	0	Pa_DF	0.01	0.01	Pa_DNS	12.05	
Pa_PE	1	Pa_PC	2	Pa_PRD	2	-5	1	Pa_DKI	1e-010

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

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

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

18

## Single file - hydration of Portland cement

### Predicted stable phase assemblage

Si-Hydrogarnet

C-S-H

ettringite

hem carbonate

mon carbonate

portlandite

hydrotalcite

Input: System Definition		Results: Equilibrium State			
Phase/species	L	T	Amount (mol)	logSI/Activity	
aq_gen	69	a	0.74137659	-7.24e-09	
gas_gen	6	g	0.0031839841	8.458e-10	
C3(A,F)S0.84H	2	s	0.040769952	-1.116e-08	
CSHQ	6	s	0.44660885	4.501e-09	
ettringite	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**

19

## 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(A,F)S0.84H	2	s	0.040769952	-1.116e-08		
CSHQ	6	s	0.44660885	4.501e-09		
CSHQ-JenD	I	I	0.1645959	0.368546	0.36854599	1
CSHQ-JenH	I	I	0.10337444	0.231465	0.23146527	1
CSHQ-TobD	I	I	0.12210382	0.273402	0.27340216	1
CSHQ-TobH	I	I	0.0048265056	0.010807	0.010807008	1
KSIOH	I	I	0.027356397	0.0612536	0.061253594	1
NaSiOH	I	I	0.024351788	0.054526	0.054525987	1
ettringite	2	s	0	-1.43		

36.9 mol.-% CSH-JenD =  $(\text{CaO})_{1.5}(\text{SiO}_2)_{0.6667}(\text{H}_2\text{O})_{2.5}$

23.1 mol.-% CSH-JenH =  $(\text{CaO})_{1.333}(\text{SiO}_2)_{1.1}(\text{H}_2\text{O})_{2.1667}$

27.3 mol.-% CSH-TobD =  $[(\text{CaO})_{1.25}(\text{SiO}_2)_{1.1}(\text{H}_2\text{O})_{2.75}]_{0.6667}$

1.1 mol.-% CSH-TobH =  $(\text{CaO})_{0.6667}(\text{SiO}_2)_{1.1}(\text{H}_2\text{O})_{1.5}$

6.1 mol.-% KSIOH =  $[(\text{KOH})_{2.5} \text{SiO}_2 \text{H}_2\text{O}]_{0.2}$

5.5 mol.-% NaSiOH =  $[(\text{NaOH})_{2.5} \text{SiO}_2 \text{H}_2\text{O}]_{0.2}$

**AI-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<sub>2</sub>O · 0.020 Na<sub>2</sub>O · 1.580 CaO · 1 SiO<sub>2</sub> · 2.873 H<sub>2</sub>O  
=> Ca/Si = 1.58**

20

## Single file - hydration of Portland cement

Composition of C-S-H (scroll down, data in 2<sup>nd</sup> table)

PC:G:PC:0.0:1:20:0:

EqC	EqPh	EqDC	EqSurf	EqGen	31/05/2023, 09:20
pmXa	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
1	0	0	0.0062923751	0	0
2	0	0	0.48923943	0	0.03424676
3	0	0.012175894	2.0118445	0	0.30968528

**bXa[{CSHQ}][{Na}]**

Syntax for use in process calculations

**bXa[{CSHQ}][{Si}]**

### Summary C-S-H solid solution :

**C-S-H solid solution: 0.022 K<sub>2</sub>O · 0.020 Na<sub>2</sub>O · 1.580 CaO · 1 SiO<sub>2</sub> · 2.873 H<sub>2</sub>O**  
**Ca/Si = 1.58, K/Si = 0.044, Na/Si = 0.039 (K/Ca = 0.028, Na/Ca = 0.025)**

21

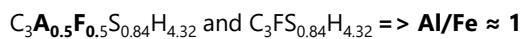
## Single file - hydration of Portland cement

### 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	I	0.040539289	0.994342	0.99434233	1
C3FS0.84H4.32	I	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:



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

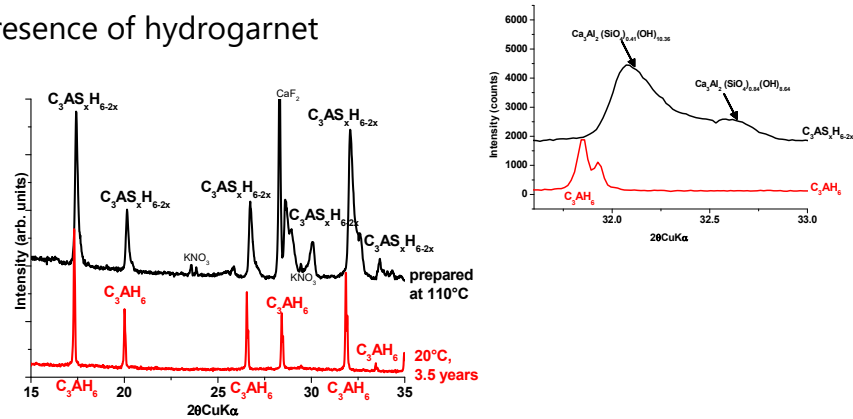
$Ca_3(Al,Fe_{1-x})_2(SiO_2)_x(OH)_{4(3-y)}$  Cem Concr Res 59 (2014) 96-111.

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

22

## Single file - hydration of Portland cement

### Presence of hydrogarnet



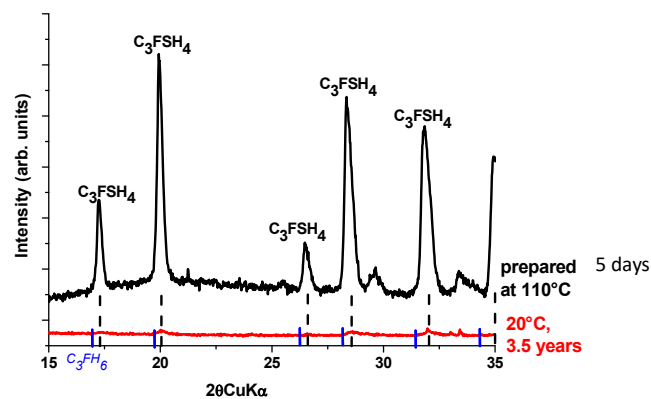
Room temperature: only  $C_3AH_6$  and  $C_3FS_xH_{6-2x}$  forms, but no  $C_3AS_xH_{6-2x}$   
 $C_3AS_xH_{6-2x}$  forms only at 110 °C, although stable at 20 °C

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

23

## Single file - hydration of Portland cement

### Fe- siliceous hydrogarnet in hydrated PC



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

Dilnesa et al 2014

24

## Single file - hydration of Portland cement

### Si-hydrogarnet in hydrated PC

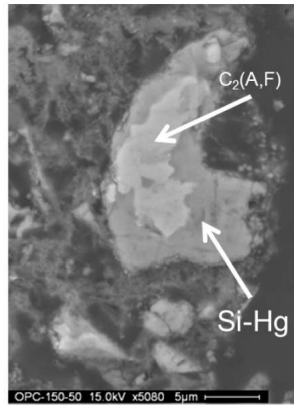
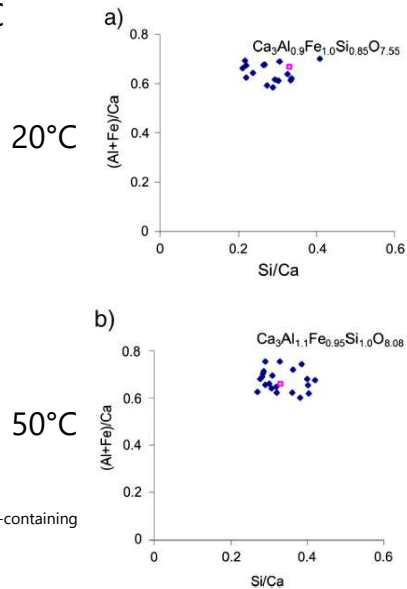


Fig. 8. SEM of ferrite clinker surrounded by hydration products after selective extraction.

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

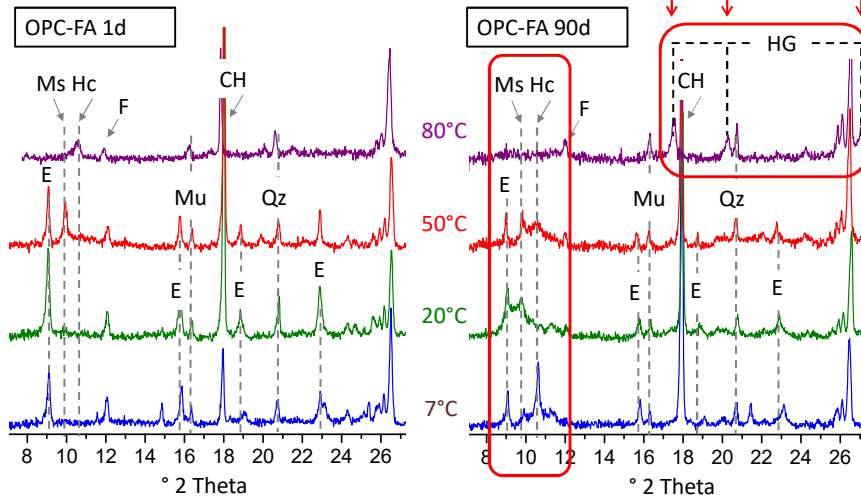


25

## Single file - hydration of Portland cement

### Siliceous hydrogarnet (PC blended with fly ash)

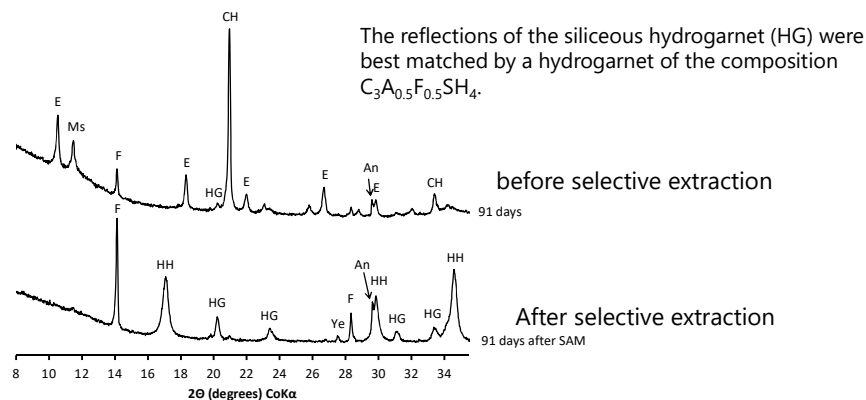
Deschner F, Lothenbach L, Winnefeld F, Neubauer J.: Effect of temperature on the hydration of Portland cement blended with siliceous fly ash, Cement and Concrete Research 52 (2013), 169–181.



26

## Single file - hydration of Portland cement

### Si-hydrogarnet in hydrated ACSA



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.

27

## Single file - hydration of Portland cement

### 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 hydrogarnet 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)

28