Empa GEMS workshop 2014

Tutorial:

Influence of limestone on the hydration of calcium sulfoaluminate cements

F. Winnefeld

Thanks to: Barbara Lothenbach, Laure Pelletier-Chaignat & Lukas Martin

GEMS V.3.2 2482.930, CEMDATA14 (version April 14, 2014)

Outline

Influence of limestone on the hydration of calcium sulfoaluminate cements

1. Introduction
2. Hydrates in the system C_4A_3s – Cs – H_2O
3. Hydrates in the system C_4A_3s – Cc – H_2O
4. Hydrates in the system C_4A_3s – Cs – Cc – H_2O
5. Hydration products of a commercial CSA clinker in the presence of anhydrite and limestone
6. Appendix: occurrence of CAH_{10}

1. Introduction: CSA cements

EMPA

Calcium sulfoaluminate cement (CSA)

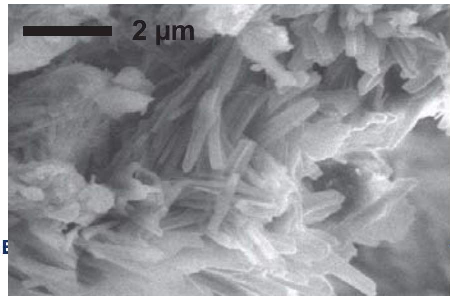
≈ 75-85% CSA clinker

- made from mixtures of calcite, clay and anhydrite (rotary kiln, ≈ 1250°C)
- main phase: ye'elimite = $4CaO{\cdot}3Al_2O_3{\cdot}SO_3$
- minor phases: belite, ferrite, calcium aluminates, perovskite, gehlenite, calcium sulfosilicate, …

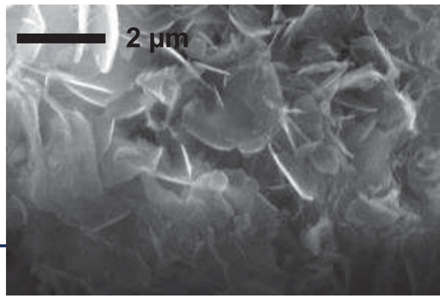
≈ 15-25% calcium sulfate (gypsum, anhydrite)

Main hydration products:

- ettringite, $3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$



- monosulfate, $3CaO{\cdot}Al_2O_3{\cdot}CaSO_4{\cdot}12H_2O$



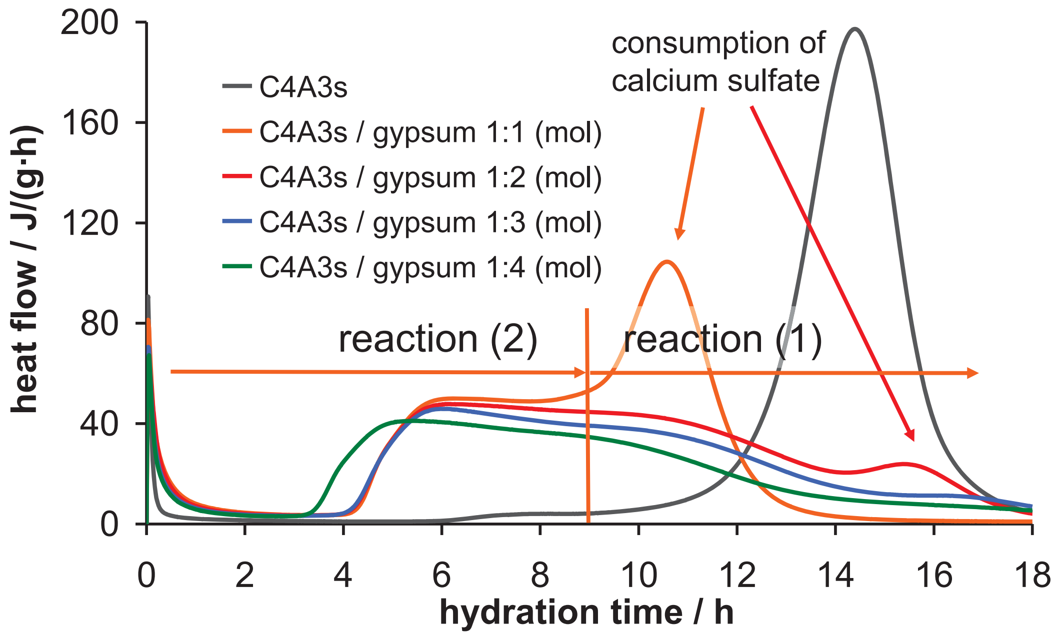
1. Introduction: Hydration of ye'elimite

EMPA

(1) $C_4A_3s + 18\,H \longrightarrow C_3A{\cdot}CsH_{12} + 2\,AH_3$ **(monosulfate)**

(2) $C_4A_3s + 2\,CsH_2 + 24\,H \longrightarrow C_3A{\cdot}3CsH_{32} + 2\,AH_3$ **(ettringite)**

(3) $C_4A_3s + 6\,CH + 8\,CsH_2 + 74\,H \longrightarrow 3\,C_3A{\cdot}3CsH_{32}$



Winnefeld F., Barlag S.: J. Therm. Anal. Calorim. 101 (2010), 949.

2. Hydrates in the system C_4A_3s – Cs – H_2O

EMPA

Hydration of ye'elimite at 20°C

- variable amounts of anhydrite
- water/cement ratio of 1.00 (100 g solid and 100 g water)
- assumption of 100% hydration
- exclusion of CO_2
- single (parent file)
- process file for variable anhydrite additions
- comparison to experimental data

=> open GEMS project "Yeelimite"

2. Hydrates in the system C_4A_3s – Cs – H_2O

EMPA

open single file „Ye_anh":

hydration of a mixture of 90 g C_4A_3s + 10 g Cs + 100 g water + 1 g O_2

Input: System Definition | Results: Equilibrium State

Phase/species	L	T	On/	UC	Add to BC	UG	G0 corr.
aq_gen	29	a	+	g	0	J	0
gas_gen	5	g	+	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
Al(OH)3mic	1	s	+	g	0	J	0
Gibbsite	1	s	-	g	0	J	0
Graphite	1	s	-	g	0	J	0
Mayenite	1	s	+	g	0	J	0
Aluminate	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
C4AH19	1	s	+	g	0	J	0
CAH10	1	s	+	g	0	J	0
C4AsH12	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
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
Sulphur	1	s	+	g	0	J	0

SO_4/CO_3-AFt ss deactivated

gibbsite deactivated (does not form at ambient temperature and „normal" hydration times)

we use the ss instead

all carbon containing phases deactivated

2. Hydrates in the system C_4A_3s – Cs – H_2O

EMPA

Compos | DComp | Phase | IComp | Surfaces | Config | 21/04/2014, 13

Yeelimite:G:Ye_anh:0:

Hydration of ye'elimite + anhydrite
GEMS 2014

Masses	0	1	1	1	0.201	21.1376
Volums	1	1	Procs	0	0	0

	AC	CCvp			xa
0	+	Al(OH)3	MIN Aluminum-hydroxide...	g	0
1	+	Al2O3	MIN Aluminum-oxide_1M_	g	0
2	+	Aqua	AQ 1_mole_H2O_	g	100
3	+	C12A7	MIN Mayenite_1M_	g	0
4	+	C3A	MIN Tricalcium_alumina...	g	0
5	+	C4A3s	MIN Yeelimite_1M_	g	90
6	+	CA	MIN Calcium_aluminate_...	g	0
7	+	CA2	MIN Calcium_dialuminat...	g	0
8	*	CH4	GA Methane_1M_	g	0
9	*	CO2	GA Carbon-dioxide_1M_	g	0
10	+	Ca(OH)2	MIN Calcium-hydroxide_...	g	0
11	*	CaCO3	MIN Calcium-carbonate_...	g	0
12	+	CaO	MIN Calcium-oxide_1M_	g	0
13	+	CaSO4	MIN Calcium-sulfate_1M_	g	10
14	+	CaSO4_05H2O	MIN hemihydrate_1M_	g	0
15	+	Gypsum	MIN Ca-sulfate-2H2O-1M_	g	0
16	+	H2	GA Hydrogen_1M_	g	0
17	+	H2S	GA Hydrogen-sulfide_1...	g	0
18	+	H2SO4	AQ Sulfuric-acid_1M_	g	0
19	+	O2	GA Oxygen_1M_	g	1
20	+	SO3	MIN Sulfur-trioxide_1M_	g	0

hydration of a mixture of 90 g C_4A_3s + 10 g Cs + 100 g water + 1 g O_2

=> calculate phase assemblage

2. Hydrates in the system C_4A_3s – Cs – H_2O

EMPA

Result: hydration of a mixture of 90 g C_4A_3s + 10 g Cs + 100 g water + 1 g O_2

Input: System Definition | Results: Equilibrium State

	Phase/species	L	T	Amount (mol)	logSI/Activity	Concentration
a	aq_gen	23	a	2.1481191	1.75e-09	
g	gas_gen	3	g	0.03119591	2.369e-10	
s	SO4_OH_AFm	2	s	0.10938991	3.174e-09	
	C4AH13		J	0.0012490694	0.00134535	0.011418506
	monosulphate		M	0.10814084	0.987658	0.98858149
s	OH_SO4_AFm	2	s	2.8306647e-007	3.174e-09	
	C4AH13		M	3.2321935e-009	0.00134535	0.011418496
	monosulphate		J	2.7983428e-007	0.987658	0.9885815
s	Al(OH)3mic	1	s	0.59081956	-3.845e-10	
s	Mayenite	1	s	0	-118.9	
s	Aluminate	1	s	0	-37.14	
s	CA	1	s	0	-8.171	
s	CA2	1	s	0	-7.78	
s	C2AH75	1	s	0	-0.7903	
s	C3AH6	1	s	0	-0.8406	
s	C4AH19	1	s	0	-2.413	
s	CAH10	1	s	0	-0.2867	
s	ettringite	1	s	0.037596495	-5.961e-09	
s	lime	1	s	0	-11.49	
s	Portlandite	1	s	0	-1.519	
s	Anhydrite	1	s	0	-3.756	
s	Gypsum	1	s	0	-3.482	
s	hemihydrate	1	s	0	-4.529	
s	Sulphur	1	s	0	-120.5	

solid solution SO_4/OH-AFm

microcrystalline AH_3

ettringite

=> we will now look at the process file

2. Hydrates in the system C_4A_3s – Cs – H_2O

open process file„Ye_anh_pr“:
hydration of a mixture of
100 g (C_4A_3s + Cs; various C_4A_3s/Cs ratios) + 100 g water + 1 g O_2

Input

Controls | Sampling | Results | Config | 21/04/2014, 15:51

Addition of anhydrite to ye'elimite
GEMS 2014

101 single systems

creates numbers 0 … 50 in steps of 0.5 = % Cs in the system)

	iTm	iV	iP	iTC	iNv	iTau	ipXi	iNu	ipH	ipe
0	1000	0	1	20	0	0	0	0	0	0
1	1100	0	1	20	0	0	0	50	0	0
2	1	0	0	0	0	0	0	0.5	0	0
cTm	1100	0	1	20	0	0	0	50	0	0

```
$ hydration of 100 g solid with 100 g water and 1 g oxygen added
xa_[{Aqua}] =: 100;
xa_[{O2}] =: 1;
$ amount of calcium sulfate is taken from iNu
xa_[{CaSO4}] =: cNu;
$
$ calculation of the amount of ye'elimite
xa_[{C4A3s}] =: 100-cNu;
```


2. Hydrates in the system C_4A_3s – Cs – H_2O

Sampling

Controls | Sampling | Results | Config | 21/04/2014, 15:51

NeIt	9999 101	Next	0	I	0	J	100
Jp	100						
pSTkey	Yeelimite:G:Ye_anh:0:0:1:20:0:	cTm	1100	cNV	0		
cTau	0	cpXi	0	cXi	1	cNu	50
cpH	0	cpe	0	cEh	0	cT	293.15

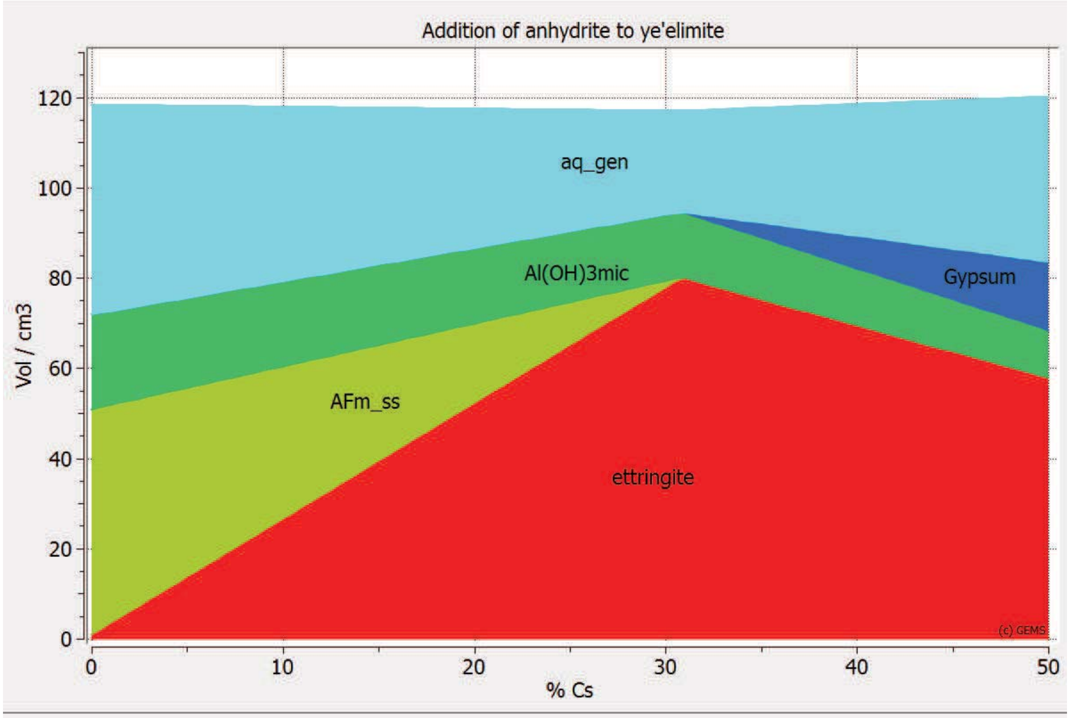
```
$ x-axis: amount of anhydrite added
xp[J] =: cNu;
$ y-axis: phase volumes
yp[J][0] =: phVol[{ettringite}];
yp[J][1] =: phVol[{SO4_OH_AFm}]+phVol[{OH_SO4_AFm}];
yp[J][2] =: phVol[{Al(OH)3mic}];
yp[J][3] =: phVol[{Gypsum}];
yp[J][4] =: phVol[{aq_gen}];
```

we need both solid solutions

=> calculate systems using the process file and display results graph

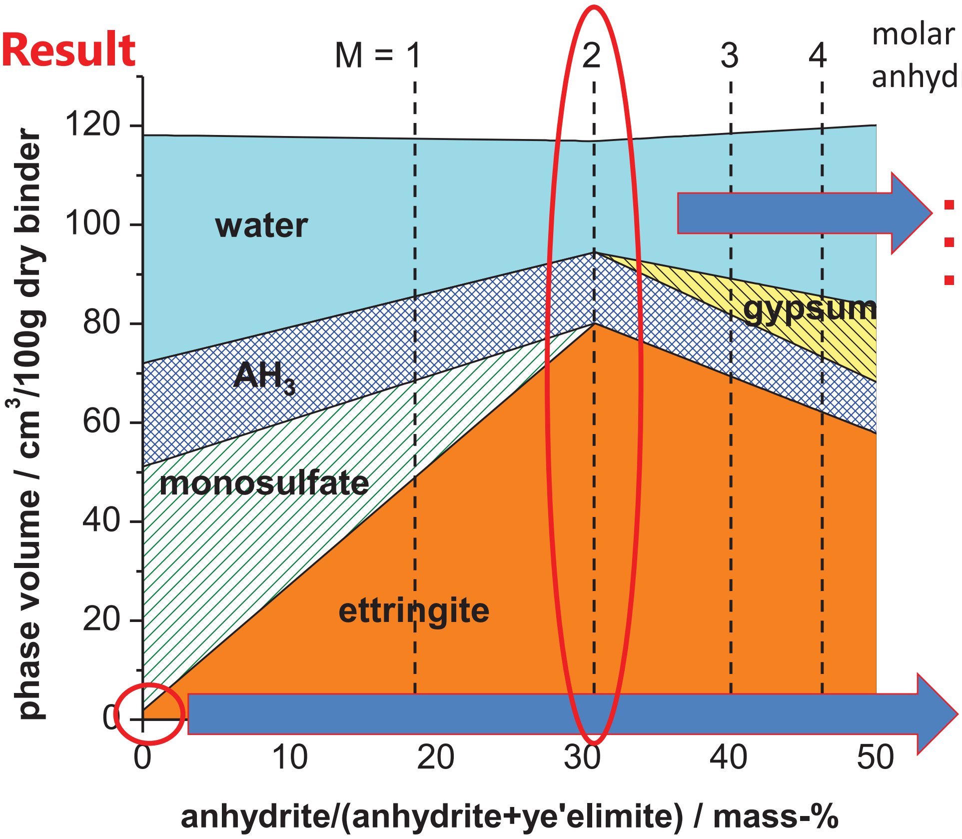
2. Hydrates in the system $C_4A_3s – Cs – H_2O$

Result



2. Hydrates in the system $C_4A_3s – Cs – H_2O$

Result



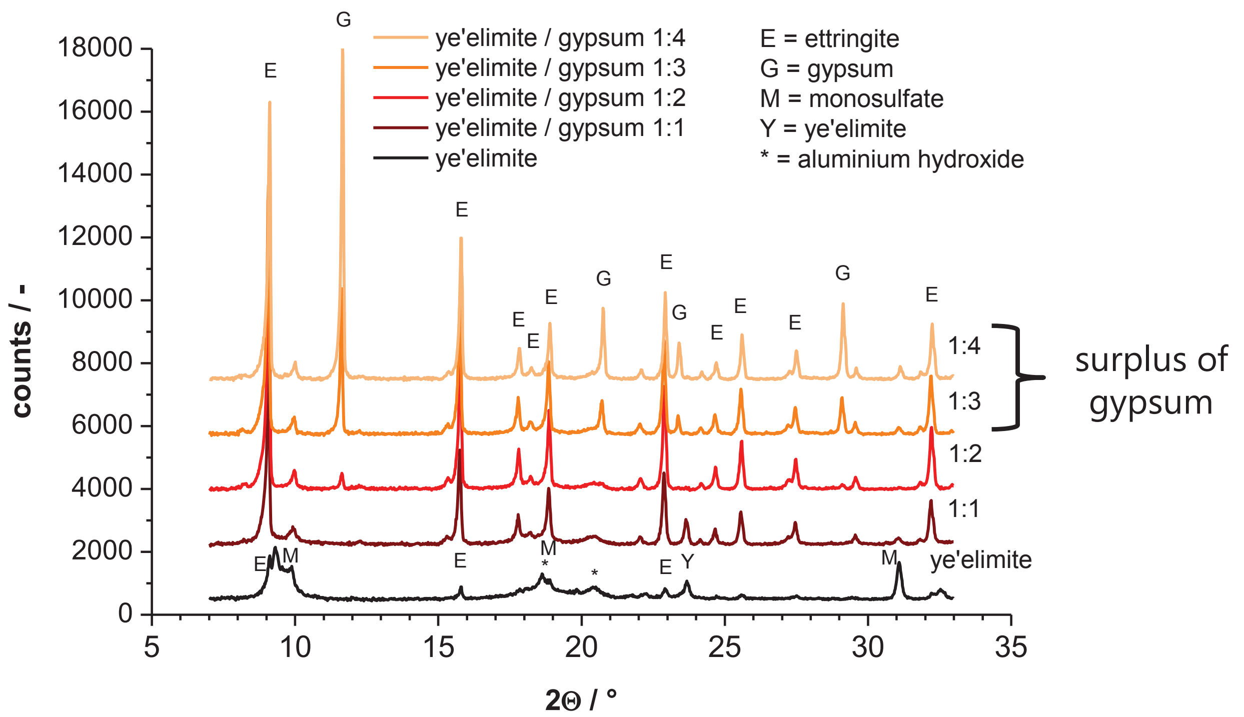
- max. bound water
- max. vol. of hydrates
- lowest total volume
  => max. chemical shrinkage

Formation of some ettringite due to incorporation of OH^- in monosulfate (solid solution)

2. Hydrates in the system C_4A_3s – Cs – H_2O

EMPA

Experiment: XRD after 18 h of hydration at water/solid = 2



Winnefeld F., Barlag S.: J. Therm. Anal. Calorim. 101 (2010), 949.

3. Hydrates in the system C_4A_3s – Cc – H_2O

EMPA

Hydration of ye'elimite at 20°C

- variable amounts of calcite
- water/cement ratio of 1.00 (100 g solid and 100 g water)
- assumption of 100% hydration
- exclusion of CO_2
- single (parent file)
- process file for variable calcite additions
- comparison to experimental data

=> open single file "Ye_cal" in GEMS project "Yeelimite"

3. Hydrates in the system C_4A_3s – Cc – H_2O

EMPA

Result

Input: System Definition | Results: Equilibrium State

	Phase/species	L	T	Amount (mol)	logSI/Activity	Concentration
a	aq_gen	29	a	1.9949533	9.829e-10	
g	gas_gen	5	g	0.031199785	-1.343e-09	
s	SO4_OH_AFm	2	s	0	-0.6997	
s	OH_SO4_AFm	2	s	0	-0.6997	
s	SO4_CO3_AFt	2	s	0.049981584	3.211e-08	
	tricarboalu		J	0.00082269489	0.000580702	0.01645996
	ettringite		M	0.049158889	0.981119	0.98354004
s	CO3_SO4_AFt	2	s	4.1696143e-007	3.211e-08	
	tricarboalu		M	6.8631924e-009	0.000580702	0.016460018
	ettringite		J	4.1009824e-007	0.981119	0.98353998
s	Al(OH)3mic	1	s	0.58996332	5.526e-10	
s	Graphite	1	s	0	-82.72	
s	Mayenite	1	s	0	-123.1	
s	Aluminate	1	s	0	-38.18	
s	CA	1	s	0	-8.517	
s	CA2	1	s	0	-8.126	
s	C2AH75	1	s	0	-1.483	
s	C3AH6	1	s	0	-1.88	
s	C4AH13	1	s	0	-4.256	
s	C4AH19	1	s	0	-3.798	
s	CAH10	1	s	0	-0.6328	
s	C4AsH12	1	s	0	-0.7009	
s	C4Ac0_5H12	1	s	0	-1.248	
s	C4AcH11	1	s	0.097444931	-5.071e-09	

solid solution SO_4/CO_3-AFt

microcrystalline AH_3

monocarbonate

=> we will now look at the process file

3. Hydrates in the system C_4A_3s – Cc – H_2O

EMPA

open process file„Ye_cal_pr“:

hydration of a mixture of 100 g (C_4A_3s + Cc; various C_4A_3s/Cc ratios) + 100 g water + 1 g O_2

similar structure than previous file

Input

```
$ hydration of 100 g solid with 100 g water and 1 g oxygen added
xa_[{Aqua}] =: 100;
xa_[{O2}] =: 1;
$ amount of calcium carbonate is taken from iNu
xa_[{CaCO3}] =: cNu;
$
$ calculation of the amount of ye'elimite
xa_[{C4A3s}] =: 100-cNu;
```

Output

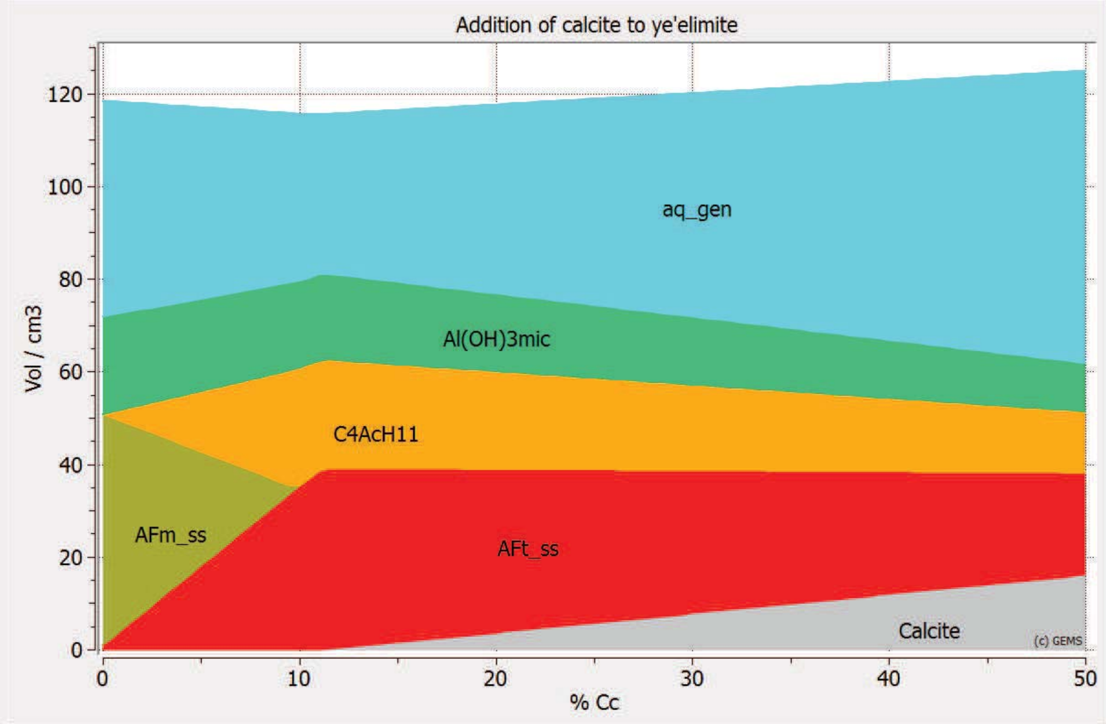
```
$ x-axis: amount of calcite added
xp[J] =: cNu;
$ y-axis: phase volumes
yp[J][0] =: phVol[{Calcite}];
yp[J][1] =: phVol[{SO4_CO3_AFt}]+phVol[{CO3_SO4_AFt}];
yp[J][2] =: phVol[{SO4_OH_AFm}]+phVol[{OH_SO4_AFm}];
yp[J][3] =: phVol[{C4AcH11}];
yp[J][4] =: phVol[{Al(OH)3mic}];
yp[J][5] =: phVol[{aq_gen}];
```

=> calculate systems using the process file and display results graph

3. Hydrates in the system C_4A_3s – Cc – H_2O

EMPA

Result



3. Hydrates in the system C_4A_3s – Cc – H_2O

EMPA

open single file „Ye_cal":

hydration of a mixture of 90 g C_4A_3s + 10 g Cc + 100 g water + 1 g O_2

Input: System Definition | Results: Equilibrium State

Phase/species	L	T	On/	UC
aq_gen	29	a	+	g
gas_gen	5	g	+	g
SO4_OH_AFm	2	s	+	g
OH_SO4_AFm	2	s	+	g
SO4_CO3_AFt	2	s	+	g
CO3_SO4_AFt	2	s	+	g
Al(OH)3mic	1	s	+	g
Gibbsite	1	s	-	g
Graphite	1	s	+	g
Mayenite	1	s	+	g
Aluminate	1	s	+	g
CA	1	s	+	g
CA2	1	s	+	g
C2AH75	1	s	+	g
C3AH6	1	s	+	g
C4AH13	1	s	-	g
C4AH19	1	s	+	g
CAH10	1	s	+	g
C4AsH12	1	s	-	g
C4Ac0.5H12	1	s	+	g
C4AcH11	1	s	+	g
ettringite	1	s	-	g
Aragonite	1	s	+	g
Calcite	1	s	+	g
lime	1	s	+	g
Portlandite	1	s	+	g
Anhydrite	1	s	+	g
Gypsum	1	s	+	g
hemihydrate	1	s	+	g
Sulphur	1	s	+	g

deactivated (metastability constraint)

deactivated (use of ss instead)

Compos | DComp | Phase | IComp | Surfaces | Config | 21/04/2014, 12:

Hydration of ye'elimite + calcite
GEMS 2014

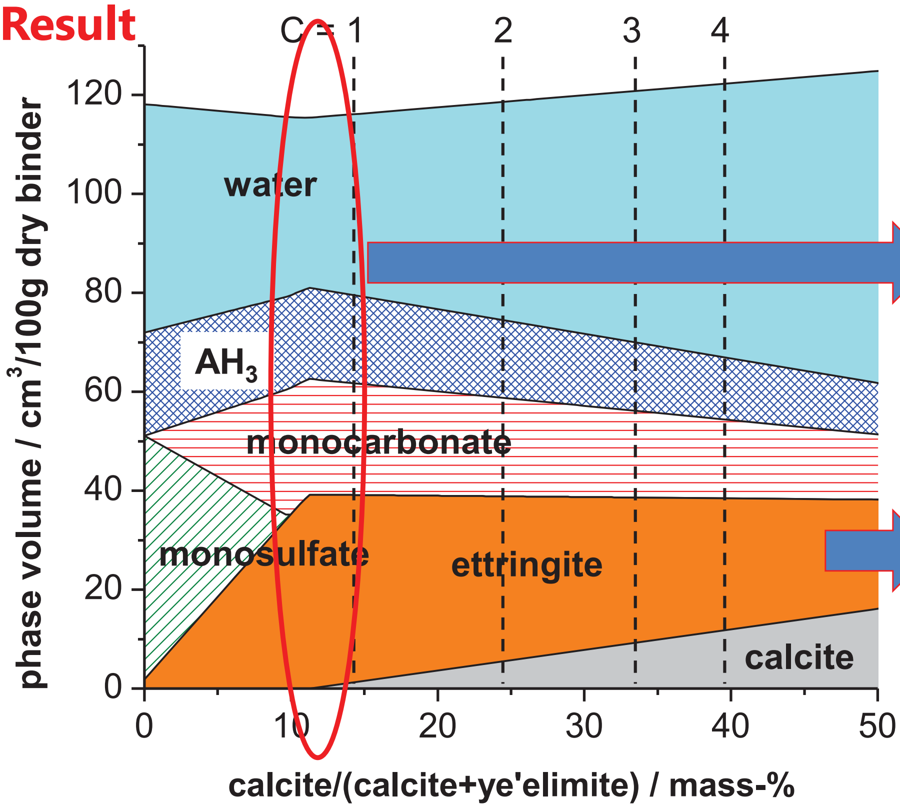
Masses	0	1	1	1	0.201	21.1965
Volums	1	1	Procs	0	0	0

	AC	CCvp			xa
0	*	Al(OH)3	MIN Aluminum-hydroxide…	g	0
1	*	Al2O3	MIN Aluminum-oxide_1M_	g	0
2	+	Aqua	AQ 1_mole_H2O_	g	100
3	*	C12A7	MIN Mayenite_1M_	g	0
4	*	C3A	MIN Tricalcium_alumina…	g	0
5	+	C4A3s	MIN Yeelimite_1M_	g	90
6	*	CA	MIN Calcium_aluminate_…	g	0
7	*	CA2	MIN Calcium_dialuminat…	g	0
8	*	CH4	GA Methane_1M_	g	0
9	*	CO2	GA Carbon-dioxide_1M_	g	0
10	*	Ca(OH)2	MIN Calcium-hydroxide_…	g	0
11	+	CaCO3	MIN Calcium-carbonate_…	g	10
12	*	CaO	MIN Calcium-oxide_1M_	g	0
13	*	CaSO4	MIN Calcium-sulfate_1M_	g	0
14	*	CaSO4_05H2O	MIN hemihydrate_1M_	g	0
15	*	Gypsum	MIN Ca-sulfate-2H2O-1M_	g	0
16	*	H2	GA Hydrogen_1M_	g	0
17	*	H2S	GA Hydrogen-sulfide_1…	g	0
18	*	H2SO4	AQ Sulfuric-acid_1M_	g	0
19	+	O2	GA Oxygen_1M_	g	1
20	*	SO3	MIN Sulfur-trioxide_1M_	g	0

=> calculate phase assemblage

3. Hydrates in the system $C_4A_3s – Cc – H_2O$

Result



- max. bound water
- max. vol. of hydrates
- lowest total volume
  => max. chemical shrinkage

Formation of ettringite without addition of calcium sulfate !

we will compare later with experimental data

$$3\ C_4A_3s\ +\ 2\ Cc\ +\ 72\ H\ \rightarrow$$
$$C_3A{\cdot}3Cs{\cdot}32H\ +\ 2\ C_3A{\cdot}Cc{\cdot}11H\ +\ 6\ AH_3$$

4. Hydrates in the system $C_4A_3s – Cs – Cc – H_2O$

Hydration of ye'elimite at 20°C

- variable amounts of anhydrite and calcite
- water/cement ratio of 1.00 (100 g solid and 100 g water)
- assumption of 100% hydration
- exclusion of CO_2
- 2 process files for variable calcite or anhydrite additions
- comparison to experimental data

=> open single file "Ye_anh_cal_1" in GEMS project "Yeelimite": constant calcite, varying anhydrite
(Ye_anh_cal_2: vice versa, not further discussed in this presentation)

4. Hydrates in the system C_4A_3s – Cs – Cc – H_2O

open process file„Ye_anh_cal_1“:

hydration of a mixture of 100 g (84 g C_4A_3s + 16 g Cc = 1:1 per mol; varying C_4A_3s/Cs ratios) + 100 g water + 1 g O_2

(process file Ye_anh_cal_2 does the same vice versa)

Input

```
$ hydration of 100 g solid with 100 g water and 1 g oxygen added
xa_[{Aqua}] =: 100;
xa_[{O2}] =: 1;
$
$ amount of calcium carbonate in g to be changed below
xa_[{CaCO3}] =: 14;
$
$ amount of calcium sulfate is taken from iNu
xa_[{CaSO4}] =: cNu;
$
$ calculation of the amount of ye'elimite
xa_[{C4A3s}] =: 100-xa_[{CaCO3}]-cNu;
```

change here if amount of calcite should be varied

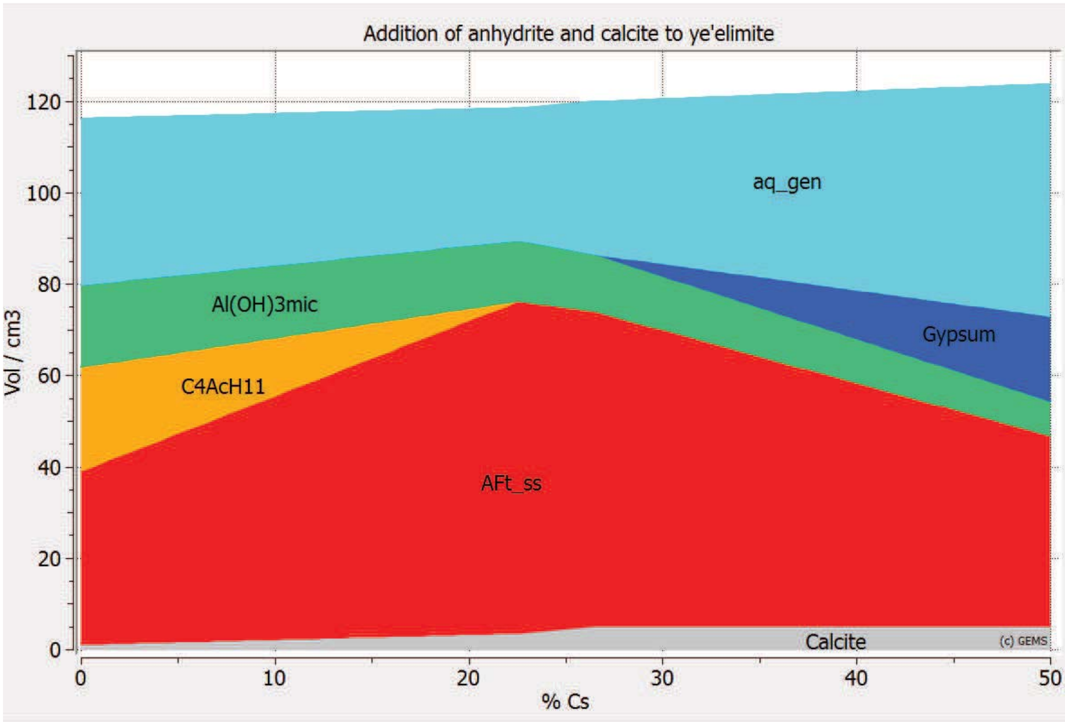
Output

```
$ x-axis: amount of anhydrite added
xp[J] =: cNu;
$ y-axis: phase volumes
yp[J][0] =: phVol[{Calcite}];
yp[J][1] =: phVol[{SO4_CO3_AFt}]+phVol[{CO3_SO4_AFt}];
yp[J][2] =: phVol[{SO4_OH_AFm}]+phVol[{OH_SO4_AFm}];
yp[J][3] =: phVol[{C4AcH11}];
yp[J][4] =: phVol[{Al(OH)3mic}];
yp[J][5] =: phVol[{Gypsum}];
yp[J][6] =: phVol[{aq_gen}];
```

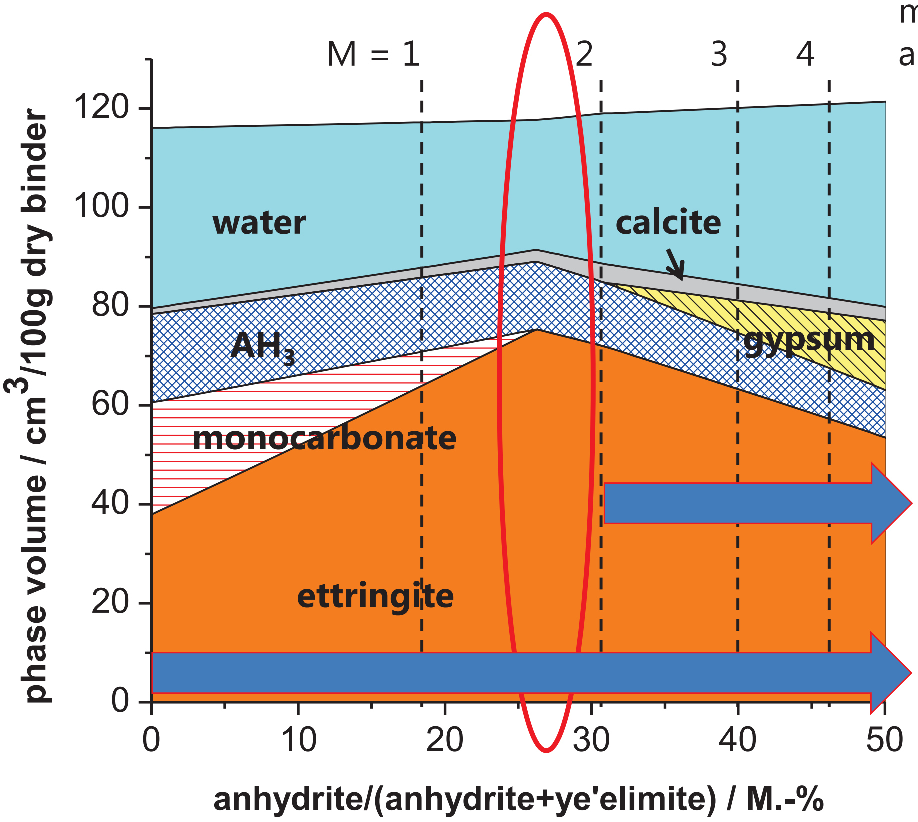
=> calculate systems using the process file and display results graph

4. Hydrates in the system C_4A_3s – Cs – Cc – H_2O

Result



4. Hydrates in the system $C_4A_3s – Cs – Cc – H_2O$



molar ratio anhydrite/ye'elimite

molar ratio C_4A_3s / calcite = 1:1 (86:14 by mass)

Formation of ettringite without addition of calcium sulfate !

- max. bound water
- max. volume of hydrates

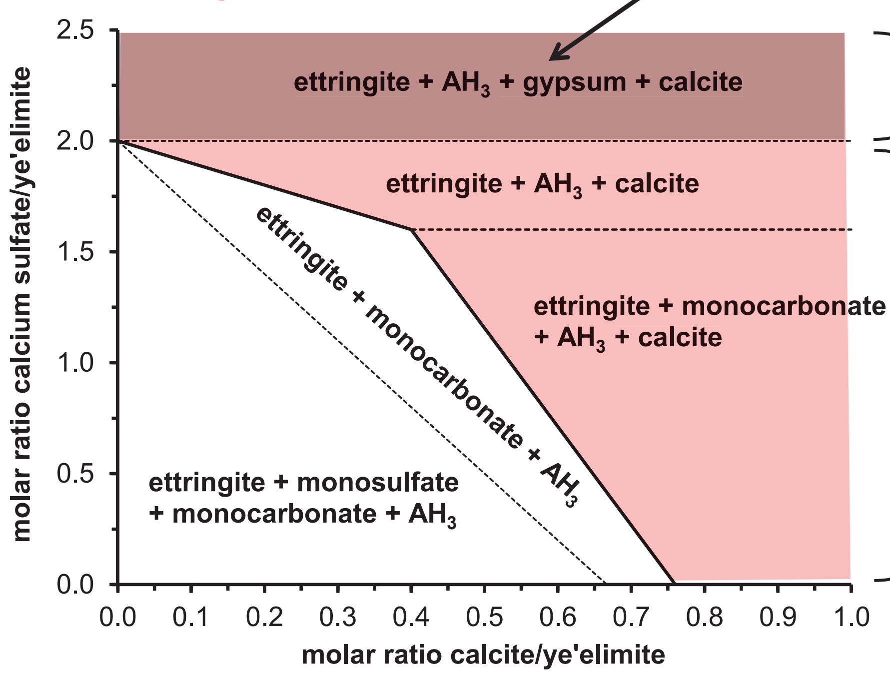
=> already at M < 2

- max. chemical shrinkage

4. Hydrates in the system $C_4A_3s – Cs – Cc – H_2O$

Phase diagram

calcite does not take part in reactions



excess calcite+gypsum

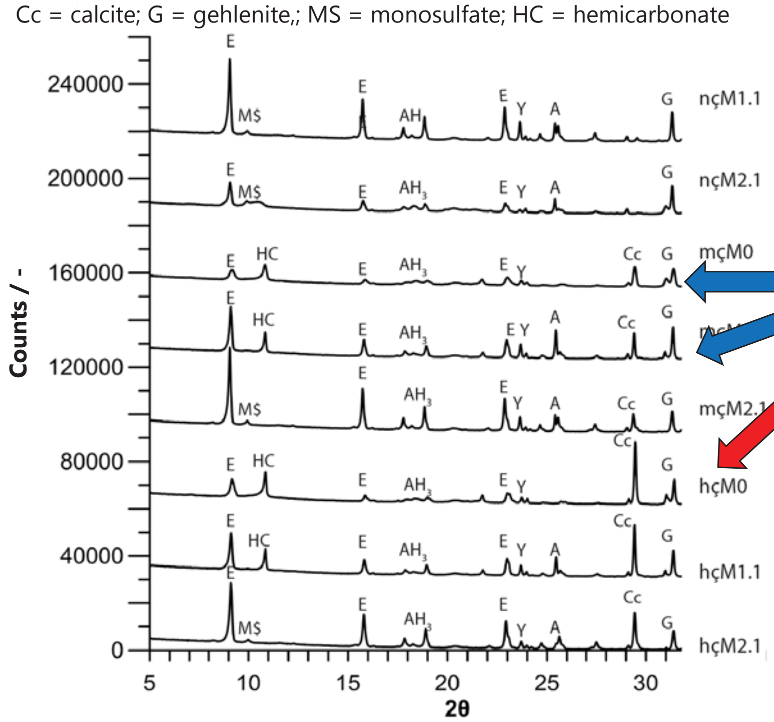
excess calcite

- calcite participates only in the reactions, when ratio Cs / C_4A_3s < 2
- no hemicarbonate (only stable in presence of portlandite => OPC)

4. Hydrates in the system C_4A_3s – Cs – Cc – H_2O

Experiment: XRD after 90 d of hydration (commercial CSA cement)

E = ettringite; AH_3 = aluminium hydroxide; Y = ye'elimite; A = anhydrite;
Cc = calcite; G = gehlenite,; MS = monosulfate; HC = hemicarbonate



Binder composition

Anhydrite	Calcite
Low	-
High	-

- Participation of calcite without anhydrite (formation of ettringite) or when low&medium amounts of anhydrite are added
- Formation of hemicarbonate instead of monocarbonate (metastability)

Low	**high**
High	**high**

Martin L.H.J, Winnefeld F., Müller C.J., Lothenbach B.: 1st International Conference on Sulphoaluminate Cement: Materials and Engineering Technology, Wuhan, China, October 23-24, 2013, 229.

5. Commercial CSA clinker + anhydrite + limestone

Hydration of a commercial CSA clinker at 20°C

- variable amounts of anhydrite and calcite
- water/cement ratio of 1.00 (100 g solid and 100 g water)
- assumption of 100% hydration
- exclusion of CO_2
- 2 process files for variable calcite or anhydrite additions
- reactive part of the CSA clinker as predefined composition in GEMS

5. Commercial CSA clinker + anhydrite + limestone

EMPA

Composition of the CSA clinker

needs to be recalculated (reactive part only) in mol per 100 g referred to the elements

rough assumption:
inert phases contain no minor elements

XRF

	CSA clinker
SiO_2	5.41
Al_2O_3	42.61
Fe_2O_3	1.55
Cr_2O_3	0.032
MnO	0.023
TiO_2	2.100
P_2O_5	0.113
CaO	35.87
MgO	1.01
K_2O	0.53
Na_2O	0.03
SO_3	8.52
L.O.I.	1.98
Total	**99.75**
Density (g/cm^3)	2.75
Blaine (cm^2/g)	5080
CaO_{free} (wt%)	0.06

QXRD

	CSA clinker
$C_4A_3\bar{S}$	68.1
CA	3.2
CA_2	0.7
$C_{12}A_7$	1.4
C_2AS	19.4
C_2S	1.7
CT	3.9
M	0.6
MA	1.1

inert:
24.4%

[1] Martin L.H.J., Winnefeld F., Müller C.J., Lothenbach B.: 1st International Conference on Sulphoaluminate Cement: Materials and Engineering Technology, Wuhan, China, October 23-24, 2013, 229.

5. Commercial CSA clinker + anhydrite + limestone

EMPA

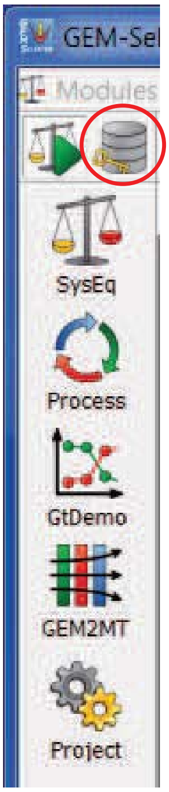
Calculation of the composition of the reactive part

Predefined composition									
CSA				nonreactive	reactive	normalized	Elements		
	XRD / M.-%		XRF / M.-%	M.-%	M.-%	M.-%		g/100g	mol/100g
C4A3s	68.10	SiO2	5.41	4.25	1.16	1.58263034	Si	0.73977669	0.02634016
CA	3.20	Al2O3	42.61	8.00	34.61	47.2587898	Al	25.0117477	0.92699485
CA2	0.70	Fe2O3	1.55	0.19	1.36	1.85591639	Fe	1.29808923	0.02324367
C2AS *	19.40	CaO	35.87	9.54	26.33	35.9497673	Ca	25.6929668	0.64107408
CT * **	3.90	Na2O	0.03		0.03	0.04096665	Na	0.03039141	0.00132195
MA *	1.10	K2O	0.53		0.53	0.72374413	K	0.60081458	0.01536677
M	0.60	MgO	1.01	0.31	0.70	0.95365699	Mg	0.5750894	0.02366136
C12A7	1.40	SO3	8.52		8.52	11.6345283	S	4.65967044	0.14531499
C2S	1.70	TiO2	2.1	2.10	0.00	0	Ti	0	0
		H2O			0.00	0	H	0	0
							O	41.3914538	2.58706287

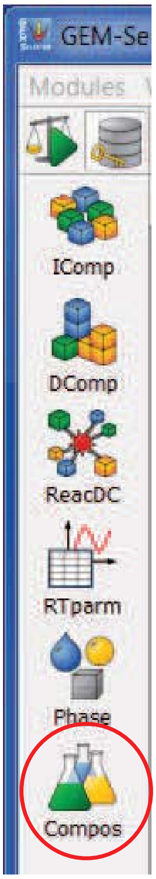
75.6% is reactive, 24.4% is inert.

=> open now GEMS project “CSA”

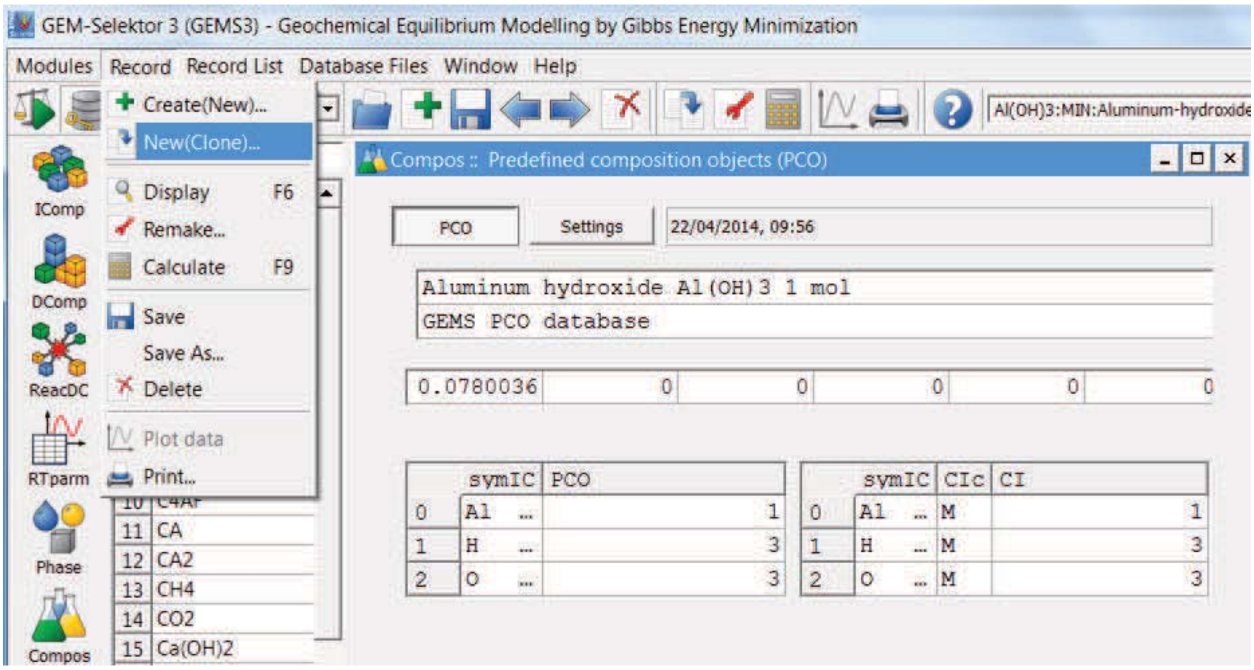
5. Commercial CSA clinker + anhydrite + limestone



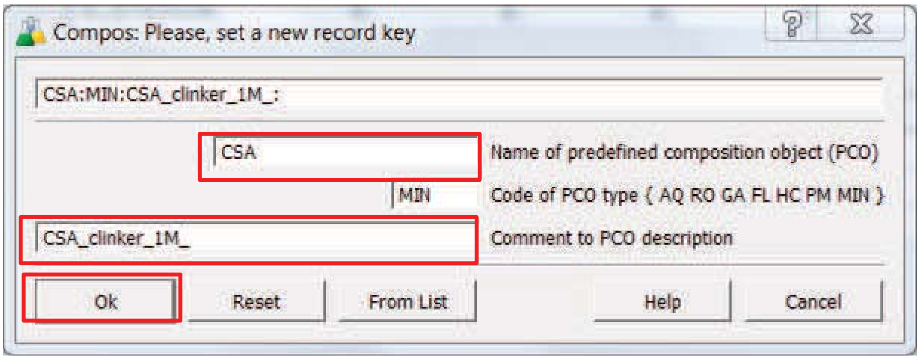
access database



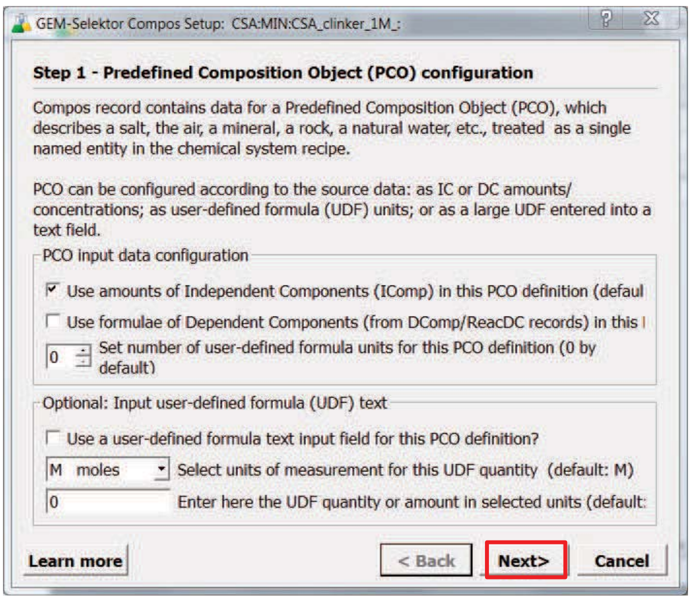
5. Commercial CSA clinker + anhydrite + limestone

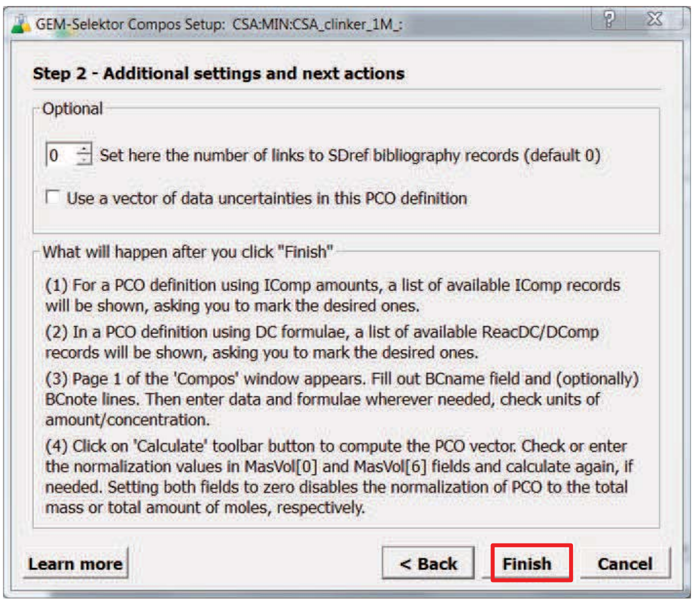


5. Commercial CSA clinker + anhydrite + limestone



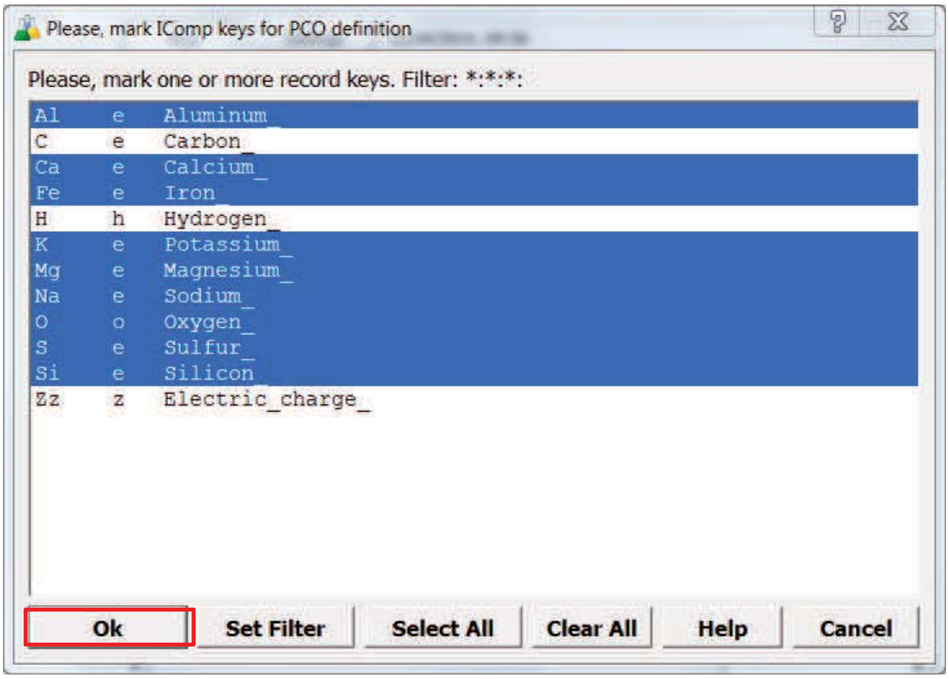
5. Commercial CSA clinker + anhydrite + limestone





5. Commercial CSA clinker + anhydrite + limestone

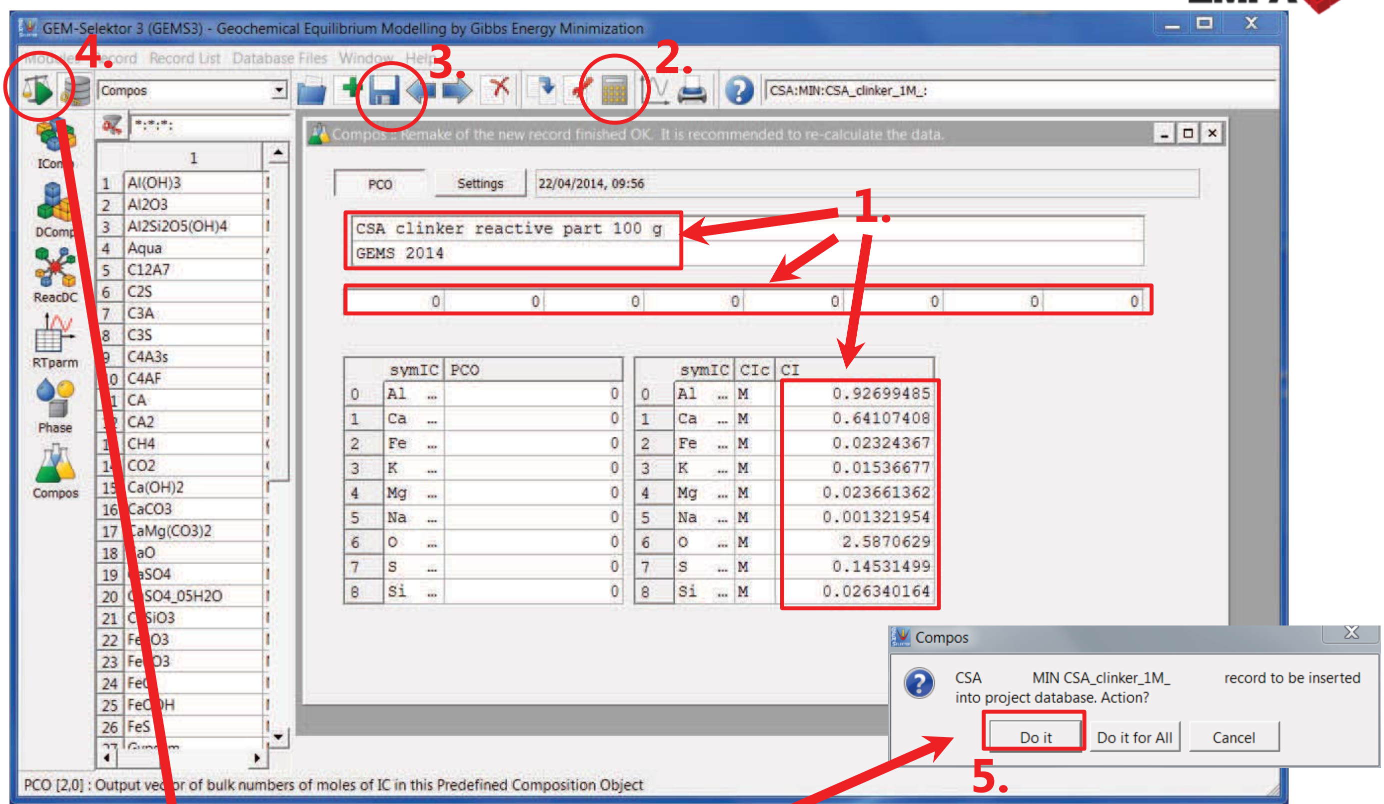
EMPA



select elements

5. Commercial CSA clinker + anhydrite + limestone

EMPA



load the project afterwards, your predefined composition will be inserted

5. Commercial CSA clinker + anhydrite + limestone

Open process file CSA_Cs_Cc_1
Input:

CSA:G:CSA_parent:0:0:1:20:0:CSA_Cs_Cc_1:S:

Controls | Sampling | Results | Config | 22/04/2014, 11:10

CSA clinker + anhydrite + calcite
GEMS 2014#

	iTm	iV	iP	iTC	iNv	iTau	ipXi	iNu	ipH	ipe
0	1000	0	1	20	0	0	0	0	0	0
1	1100	0	1	20	0	0	0	50	0	0
2	1	0	0	0	0	0	0	0.5	0	0
cTm	1100	0	1	20	0	0	0	50	0	0

```
$ hydration of 100 g solid with 100 g water and 1 g oxygen added
xa_[{Aqua}] =: 100;
xa_[{O2}] =: 1;
$
$ amount of calcium carbonate in g
xa_[{CaCO3}] =: 10;
$
$ amount of calcium sulfate is taken from iNu
xa_[{CaSO4}] =: cNu;
$
$ calculation of the amount of CSA
xa_[{CSA}] =: (100-xa_[{CaCO3}]-cNu)*0.756;
```

consideration of inert part

calculates with fixed $CaCO_3$ (here: 10 g) and varying $CaSO_4$
(process file CSA_Cs_Cc_2 does it vice versa)

5. Commercial CSA clinker + anhydrite + limestone

Open process file CSA_Cs_Cc_1
Output:

Controls | Sampling | Results | Config | 22/04/2014, 11:10

NeIt	9999	101	Next	0	I	0	J	100	Jp	100	

pSTkey	CSA:G:CSA_parent:0:0:1:20:0:	cTm	1100	cNV	0

cTau	0	cpXi	0	cXi	1	cNu	50
cpH	0	cpe	0	cEh	0	cT	293.15

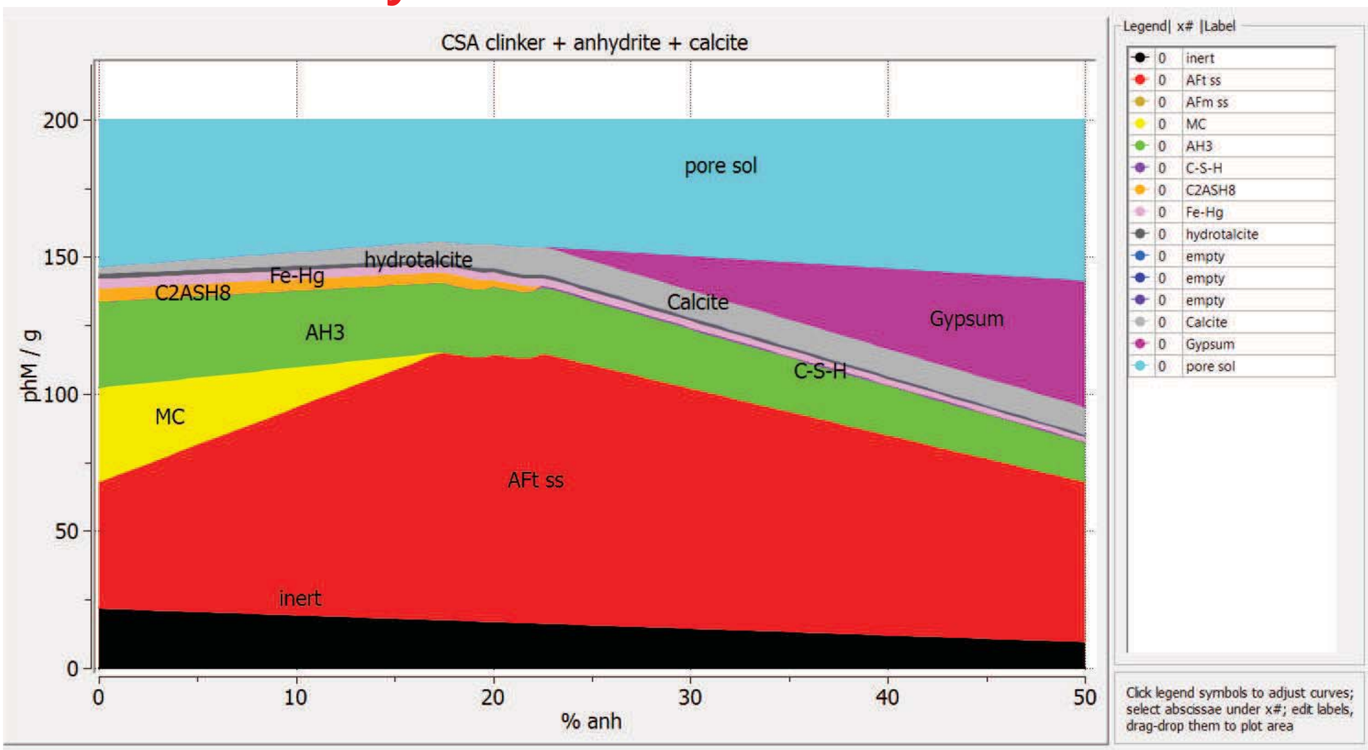
```
$ x-axis: amount of anhydrite added
xp[J] =: cNu;
$ y-axis: phase masses
yp[J][0] =: (100-xa_[{CaCO3}]-cNu)*0.244;
yp[J][1] =: phM[{ettringite-Al}]+phM[{ettringite-Fe}]+phM[{SO4_CO3_AFt}]
+phM[{CO3_SO4_AFt}];
yp[J][2] =: phM[{monosulphate-Al}]+phM[{monosulphate-Fe}]
+phM[{SO4_OH_AFm}]+phM[{OH_SO4_AFm}];
yp[J][3] =: phM[{C4AcH11}];
yp[J][4] =: phM[{Al(OH)3mic}];
yp[J][5] =: phM[{CSHQ}];
yp[J][6] =: phM[{C2ASH8}];
yp[J][7] =: phM[{C3FS0.84H4.32}]+phM[{C3FS1.34H3.32}];
yp[J][8] =: phM[{OH-hydrotalcite}];
yp[J][9] =: 0;
yp[J][10] =: 0;
yp[J][11] =: 0;
yp[J][12] =: phM[{Calcite}];
yp[J][13] =: phM[{Gypsum}];
yp[J][14] =: phM[{aq_gen}];
```

consideration of inert part

5. Commercial CSA clinker + anhydrite + limestone

EMPA

Result: blend of CSA/calcite 90/10 + variable amounts of anhydrite



5. Commercial CSA clinker + anhydrite + limestone

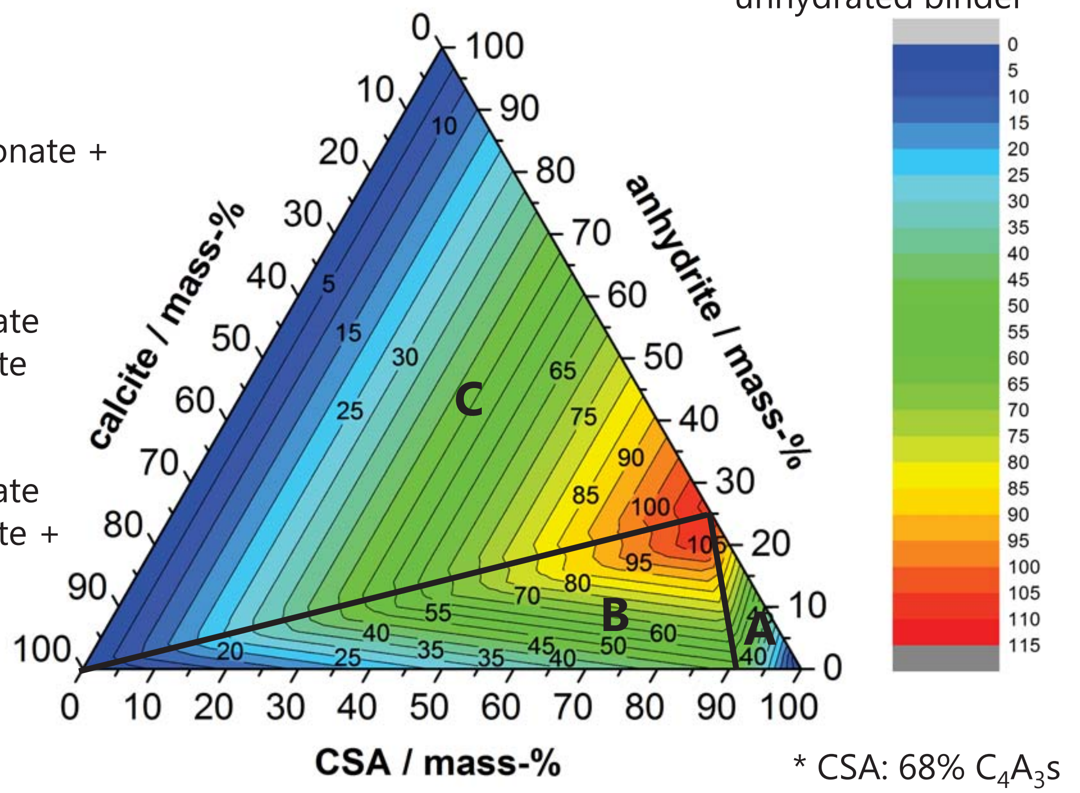
EMPA

Phase diagram (commercial CSA*)

A: ettringite + monosulfate + monocarbonate + AH_3

B: ettringite + monocarbonate + AH_3 + calcite

C: ettringite + monocarbonate + AH_3 + calcite + gypsum



* CSA: 68% C_4A_3s

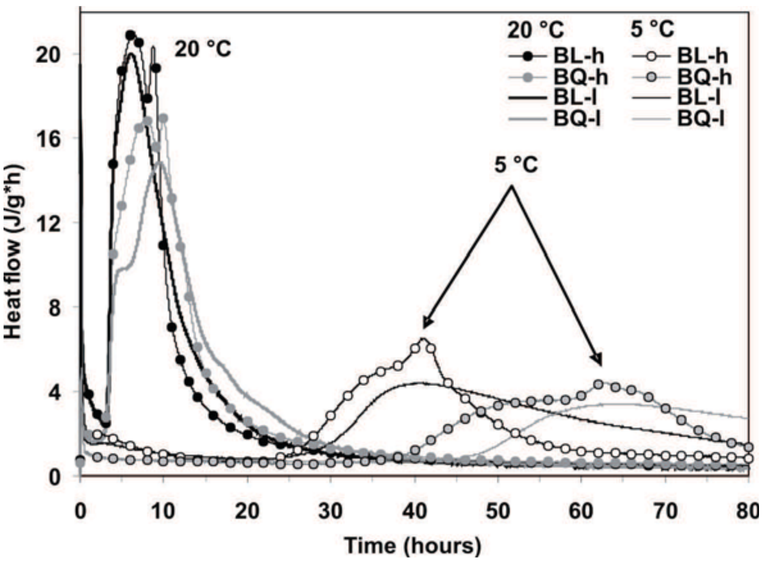
5. Commercial CSA clinker + anhydrite + limestone

EMPA

Conduction calorimetry

5 & 20°C, w/c = 0.80,
cement/filler ≈ 1:1

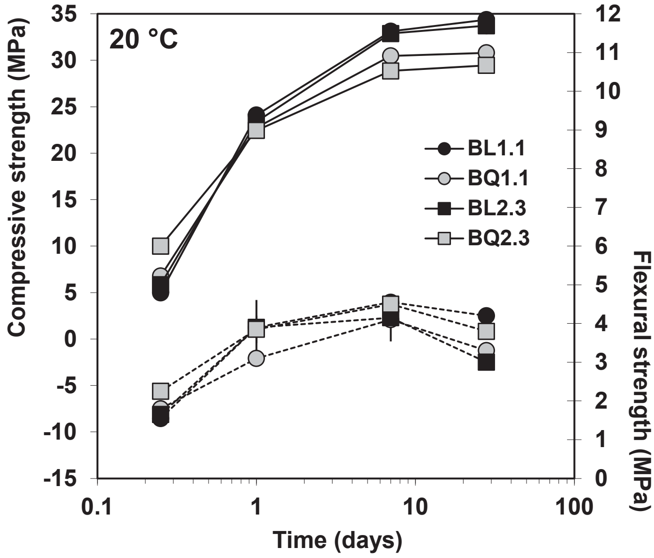
Limestone powder
Quartz powder



Compressive & flexural strength

20°C, w/c = 0.80
cement/filler/sand ≈ 1:1:2

L = Limestone powder
Q = Quartz powder

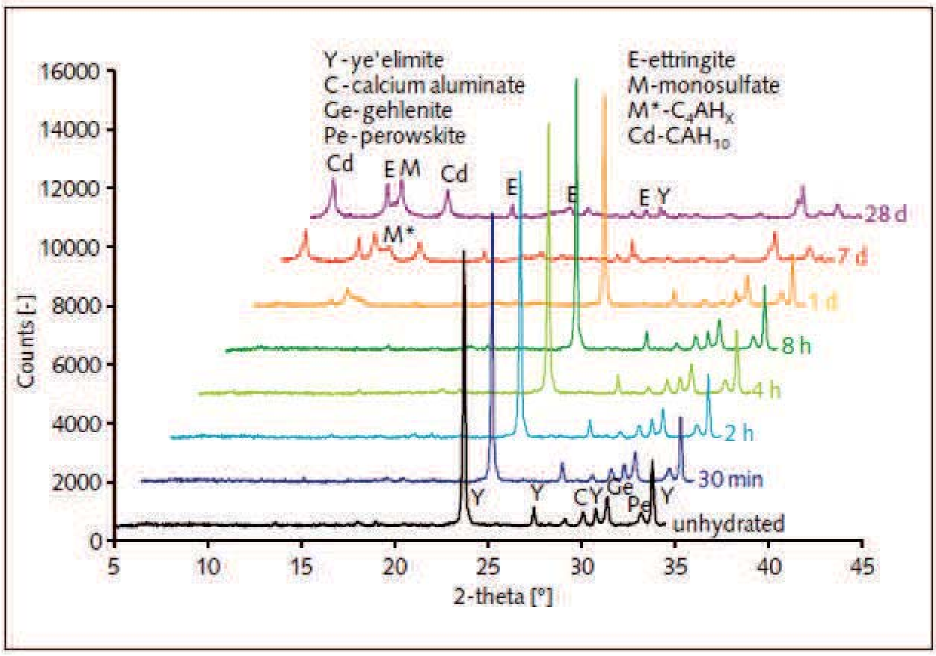


[1] Pelletier-Chaignat, Winnefeld, Lothenbach, Müller: Constr. Build. Mater. 26 (2012), 619.

6. Appendix: occurrence of CAH_{10}

EMPA

CAH_{10} may occur as hydration product in CSA clinkers or CSA cements very low in calcium sulfate



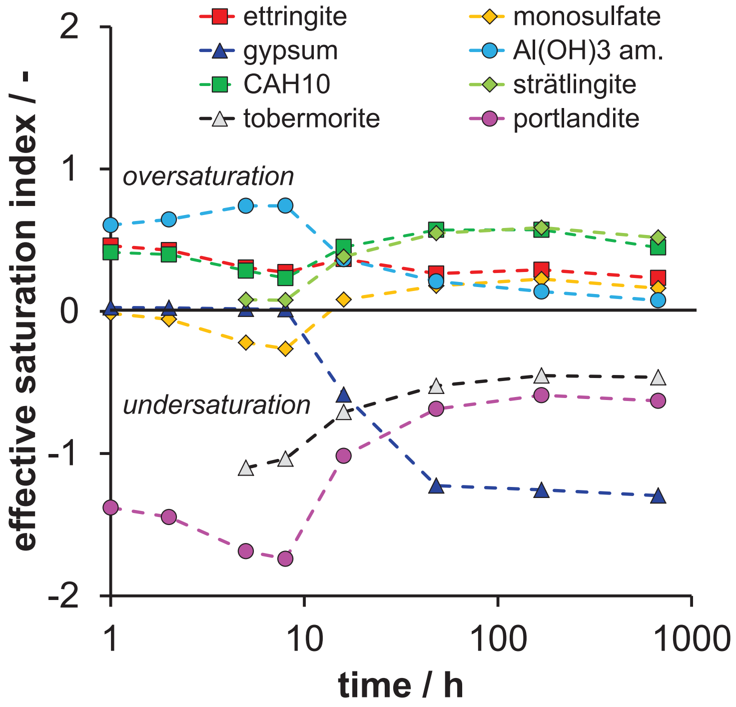
[1] Winnefeld F., Barlag S.: ZKG International 62 (2009), 42.

6. Appendix: occurrence of CAH_{10}

pore solution of CSA cements may be oversaturated with respect to CAH_{10}

The presence of CAH_{10} is linked to the solubility of AH_3.

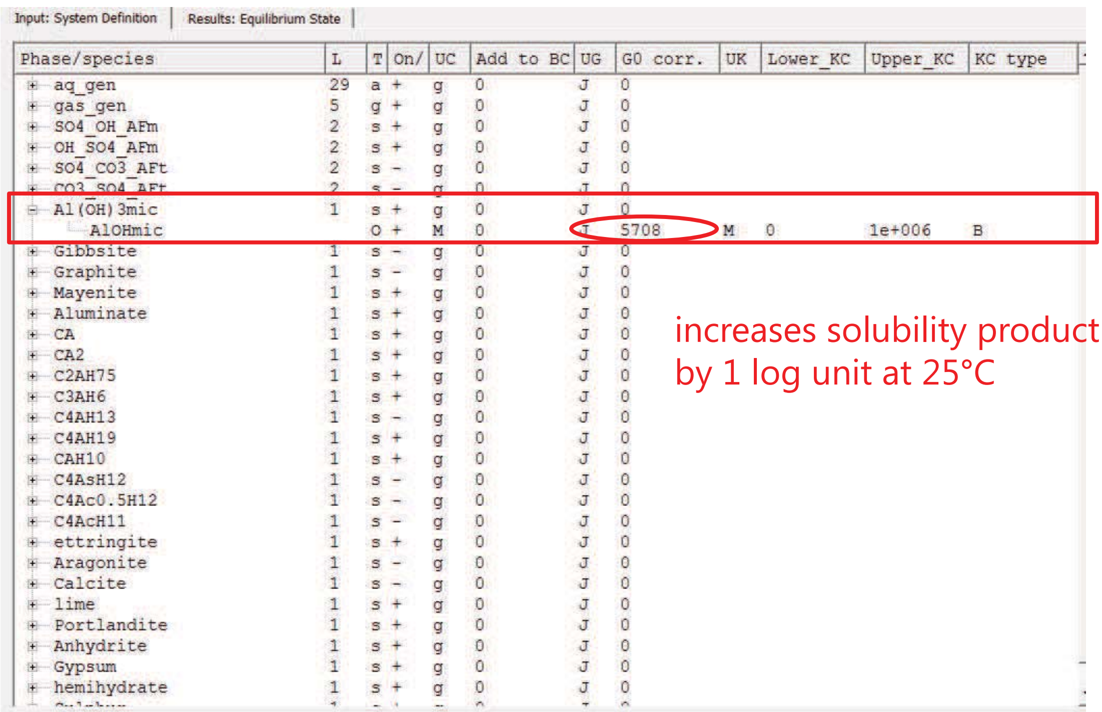
AH_3 with high solubility:
=> CAH_{10} may form (as predicted by GEMS)



[1] Winnefeld, Lothenbach: Cem. Concr. Res. 40 (2010), 1239.

6. Appendix: occurrence of CAH_{10}

project „Yeelimite“, single file „ye_anh“



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	29	a	+	g	0	J	0				
gas_gen	5	g	+	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				
Al(OH)3mic	1	s	+	g	0	J	0				
AlOHmic		O	+	M	0	J	5708	M	0	1e+006	B
Gibbsite	1	s	–	g	0	J	0				
Graphite	1	s	–	g	0	J	0				
Mayenite	1	s	+	g	0	J	0				
Aluminate	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				
C4AH19	1	s	+	g	0	J	0				
CAH10	1	s	+	g	0	J	0				
C4AsH12	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				
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				

increases solubility product by 1 log unit at 25°C

6. Appendix: occurrence of CAH_{10}

Result: change of phase assemblage CAH_{10} instead of AFm

Input: System Definition | Results: Equilibrium State

Phase/species		L	T	Amount (mol)
a	aq_gen	23	a	2.1481191
g	gas_gen	3	g	0.03119591
s	SO4_OH_AFm	2	s	0.10938991
s	OH_SO4_AFm	2	s	2.8306647e-007
s	Al(OH)3mic	1	s	0.59081956
s	Mayenite	1	s	0
s	Aluminate	1	s	0
s	CA	1	s	0
s	CA2	1	s	0
s	C2AH75	1	s	0
s	C3AH6	1	s	0
s	C4AH19	1	s	0
s	CAH10	1	s	0
s	ettringite	1	s	0.037596495
s	lime	1	s	0
s	Portlandite	1	s	0
s	Anhydrite	1	s	0
s	Gypsum	1	s	0
s	hemihydrate	1	s	0
s	Sulphur	1	s	0

Input: System Definition | Results: Equilibrium State

Phase/species		L	T	Amount (mol)
a	aq_gen	23	a	0.53765046
g	gas_gen	3	g	0.031237305
s	SO4_OH_AFm	2	s	0
s	OH_SO4_AFm	2	s	0
s	Al(OH)3mic	1	s	0.29458899
s	Mayenite	1	s	0
s	Aluminate	1	s	0
s	CA	1	s	0
s	CA2	1	s	0
s	C2AH75	1	s	0
s	C3AH6	1	s	0
s	C4AH19	1	s	0
s	CAH10	1	s	0.22148015
s	ettringite	1	s	0.073643289
s	lime	1	s	0
s	Portlandite	1	s	0
s	Anhydrite	1	s	0
s	Gypsum	1	s	0
s	hemihydrate	1	s	0
s	Sulphur	1	s	0

References

- Winnefeld F., Barlag S.: ZKG International 62 (2009), 42.
- Winnefeld F., Barlag S.: J. Therm. Anal. Calorim. 101 (2010), 949.
- Winnefeld F., Lothenbach, B.: Cem. Concr. Res. 40 (2010), 1239.
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