Thermodynamic modeling
and ternary blends (CSA-OPC-C$)

4th GEMS Workshop: Thermodynamic Modeling of Cementitious Systems

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Outline

Introduction

1. Method

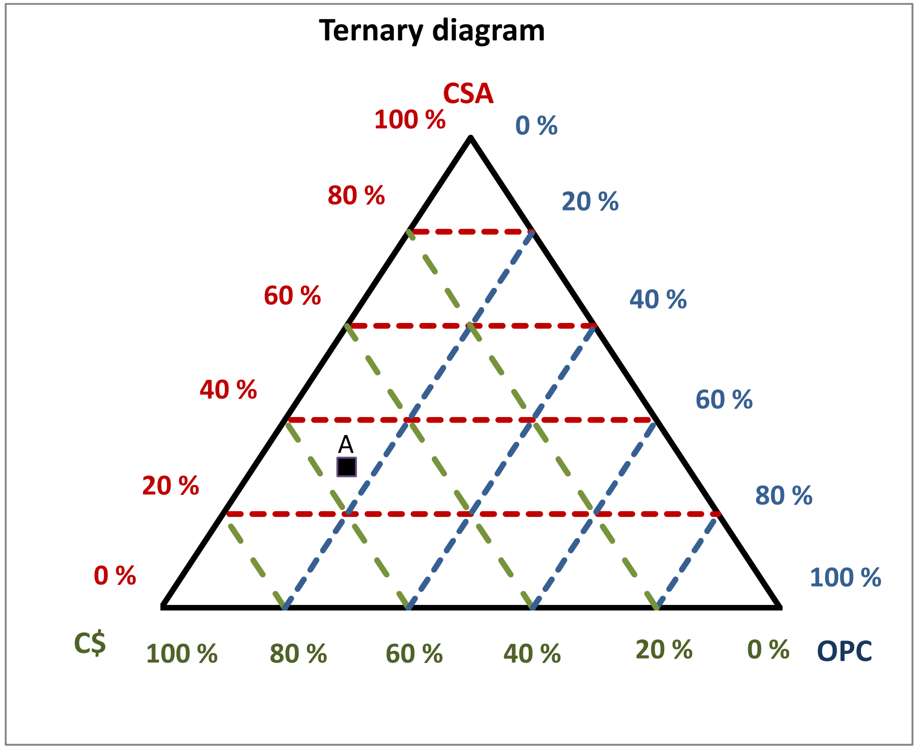
2. Modeling

3. Results and applications

Conclusion

Introduction

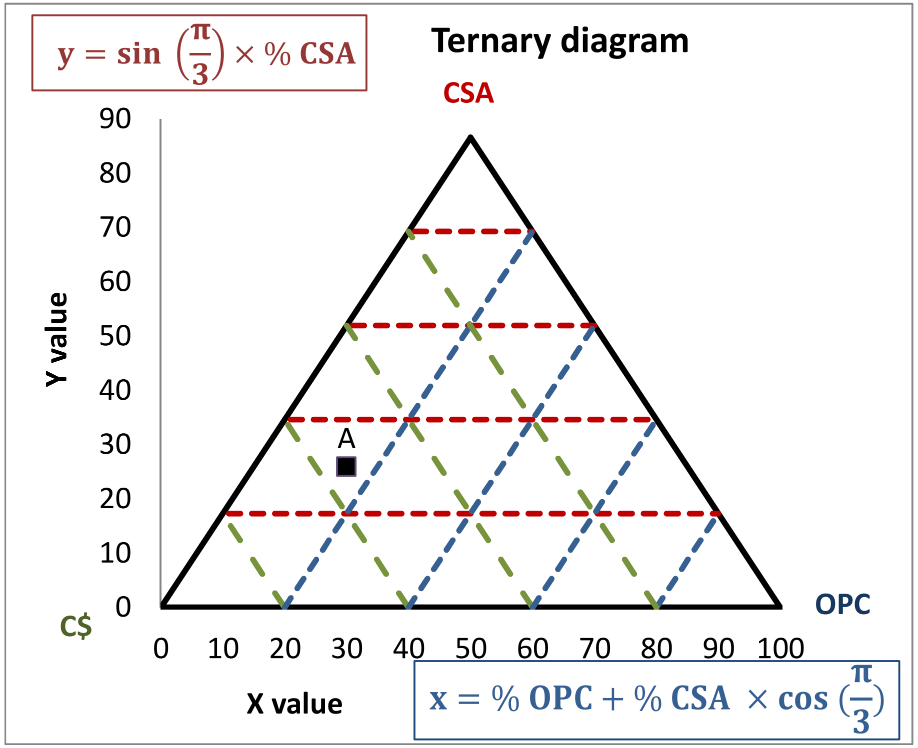
All the possible blends with three components (CSA, OPC and C$ for example) can be represented in a ternary diagram (an equilateral triangle):



Point A: 55% of anhydrite,
30% of CSA clinker,
15% of OPC.

Introduction

The points in this diagram can also be described by a X and a Y value:

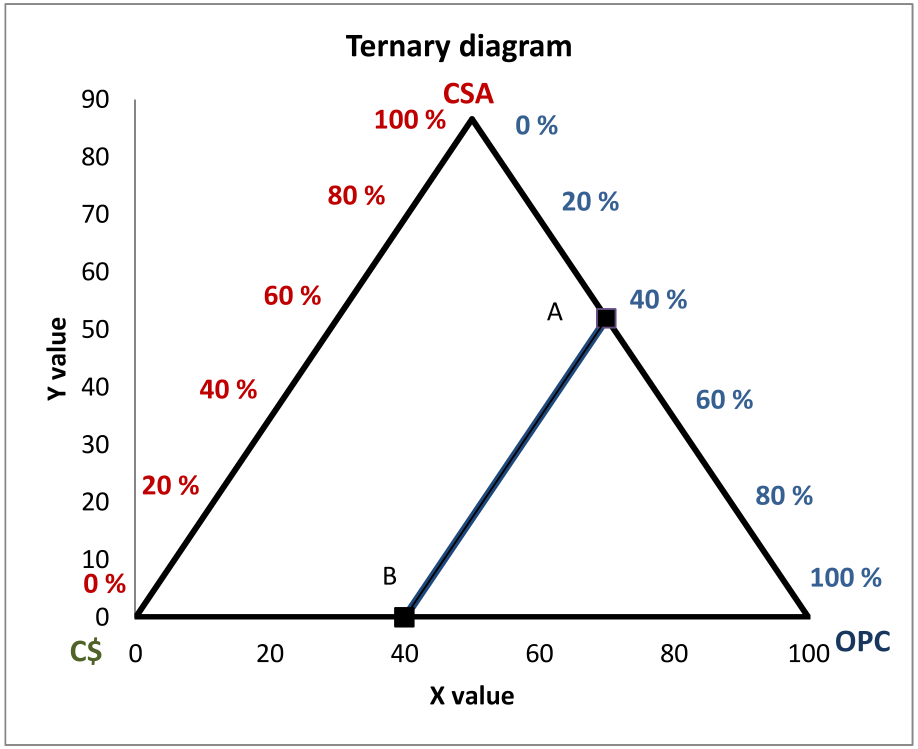


Point A: X = %OPC + %CSA x 0.5 = 15 + 30 x 0.5 = 30.

Y = %CSA x $\sqrt{3}/2$ = 26.

Introduction

In the following example, the blue line corresponds to blends with 40% of OPC and variable proportions of CSA and anhydrite (C$).



From point A to point B, the quantity of anhydrite varies from 0% to 60%.

We will model the effect of the anhydrite-CSA proportions in this ternary blend containing 40% of OPC.

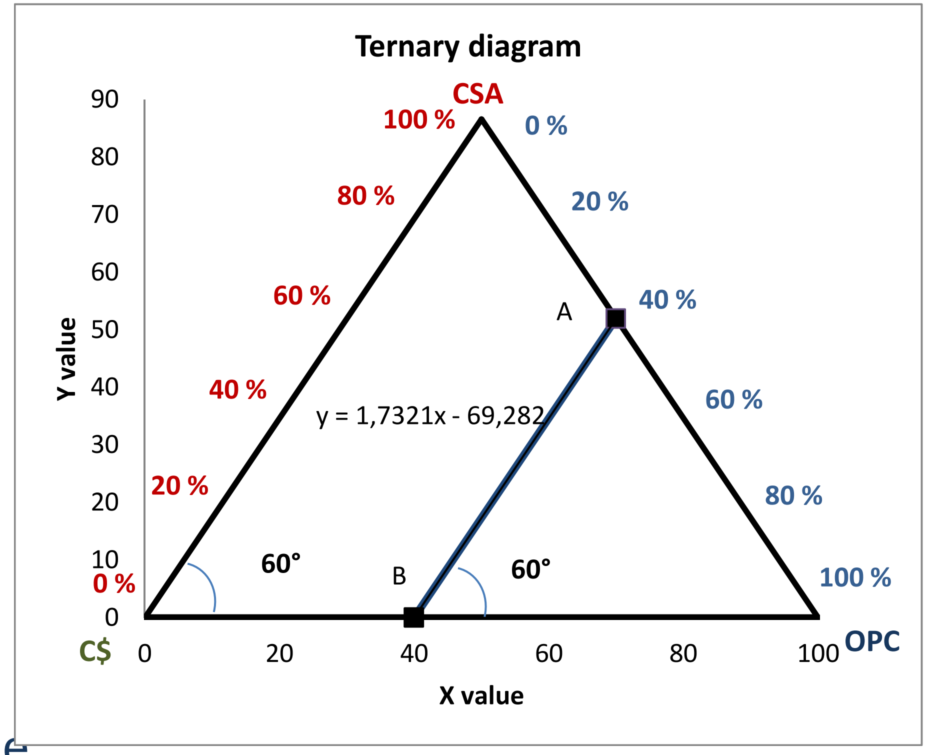
1. Method

The phenomenon (anhydrite and CSA % variation) has to be described by an equation :

$Y = 2 \times \sin(\Pi/3) \times X - (2 \times \sin(\Pi/3)) \times 40$

$Y = \sqrt{3} \times X - 40\sqrt{3}$

X value varies from 40 (point B) to 70 (point A).



Each step during GEMS modeling (cNu) will be associated with the value of X.

101 points (it's enough!) will describe the blue line ($0 \leq cNu \leq 100$, 101 steps)

→ X = proportion of OPC + (100- proportion of OPC)/200 x cNu
= 40 + 0.3 x cNu

1. Method

For each modeling step (cNu value), the OPC, CSA and C$ proportions can be calculated :

- $X = 40 + 0.3 \times cNu$,
- $Y = \sqrt{3} \times X - 40\sqrt{3}$,
- CSA % $= Y \times \frac{2}{\sqrt{3}} = 2 \times X - 80 = 2 \times (40 + 0.3 \times cNu) - 80$
  $= 0.6 \times cNu$,
- OPC % $= X$ - CSA % $\times 0.5 = 40 + 0{,}3 \times cNu - (0.6 \times cNu) \times 0.5$
  $= 40$,
- C$ % = 100 - CSA % - OPC % = 100 – 40 – 0.6 x cNu
  = 60 – 0.6 x cNu.

Therefore, if the composition of the raw materials is known, we can indicate the composition of the blends for each modeling step (X value from 40 to 70) .

For example :

$$\% \text{ anhydrite}_{\text{in the blend}} = \% \text{ OPC} \times \% \text{ anhydrite}_{\text{OPC}} + \% \text{ CSA} \times \% \text{ anhydrite}_{\text{CSA}} + \% \text{ anhydrite} \times \% \text{ anhydrite}_{\text{natural anhydrite}}$$

$$= 40 \times \% \text{ anhydrite}_{\text{OPC}} + 0.6 \times cNu \times \% \text{ anhydrite}_{\text{CSA}} + (60 - 0.6 * cNu) \times \% \text{ anhydrite}_{\text{natural anhydrite}}$$

1. Method

Cement composition:

Component	OPC	CSA	Natural anhydrite
C_3S	62	0	0
C_2S	15	10	0
$C_4A_3\$$	0	66	0
$C\$$	0	4	87
$C\$H_2$	3	0	0
C_3A	6	0	0
C_4AF	11	0	0
Considered as unreactive (M, CT, CMc, etc.)	3	20	13

2. Modeling

SysEq

You can open the modeling project.

Input recipe:

Ternary blends
CSA-OPC-C$

Masses	0	1	1	1	0.107	16.9683
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	*	Al2Si2O5(OH)4	MIN	Kaolinite_1M_	g	0
3	+	Aqua	AQ	1_mole_H2O_	g	100
4	*	C12A7	MIN	Mayenite_1M_	g	0
5	+	C2S	MIN	Dicalcium_silicate…	g	1
6	+	C3A	MIN	Tricalcium_alumina…	g	1
7	+	C3S	MIN	Tricalcium_silicat…	g	1
8	+	C4A3s	MIN	Yeelimite_1M_	g	1
9	+	C4AF	MIN	Ferrite_1M_	g	1
10	*	CA	MIN	Calcium_aluminate_…	g	0
11	*	CA2	MIN	Calcium_dialuminat…	g	0
12	*	Ca(OH)2	MIN	Calcium-hydroxide_…	g	0
13	*	CaO	MIN	Calcium-oxide_1M_	g	0
14	+	CaSO4	MIN	Calcium-sulfate_1M_	g	1
15	*	CaSO4 0.5H2O	MIN	hemihydrate_1M_	g	0
16	*	CaSiO3	MIN	Calcium-silicate_1…	g	0
17	*	Fe2O3	MIN	Iron-oxide-(hemati…	g	0
18	*	FeO	MIN	Iron-oxide_1M_	g	0
19	*	FeOOH	MIN	Iron-hydroxide_1M_	g	0
20	*	FeS	MIN	Iron-sulfide_1M_	g	0
21	+	Gypsum	MIN	Ca-sulfate-2H2O-1M_	g	1
22	*	H2	GA	Hydrogen_1M_	g	0
23	*	H2S	GA	Hydrogen-sulfide_1…	g	0
24	*	H2SO4	AQ	Sulfuric-acid_1M_	g	0
25	*	O2	GA	Oxygen_1M_	g	0
26	*	SO3	MIN	Sulfur-trioxide_1M_	g	0
27	*	SiO2	MIN	Silicon-dioxide_1M_	g	0

Water : 100g

Presence of C_3S, C_2S, C_4A_3\$, C\$, C\$$H_2$, C_3A and C_4AF in the blends

2. Modeling

SysEq

Input recipe:

Input: System Definition | Results: Equilibrium State

Phase/species	L	T	On/	UC	Add to BC	UG	G0 c
aq_gen	47	a	+	g	0	J	0
gas_gen	4	g	+	g	0	J	0
C3(AF)S0.84H	2	s	-	g	0	J	0
CSHQ	4	s	+	g	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
Al(OH)3mic	1	s	+	g	0	J	0
Gibbsite	1	s	+	g	0	J	0
Kaolinite	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
CAH10	1	s	+	g	0	J	0
C4AsH12	1	s	-	g	0	J	0
C2ASH8	1	s	+	g	0	J	0
ettringite	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
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
Iron	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
Sulphur	1	s	+	g	0	J	0
Quartz	1	s	-	g	0	J	0
Silica-amorph	1	s	+	g	0	J	0

Not formed components due to:
- kinetic reasons (not experimentally observed)
- modeling stability.

2. Modeling

Process:

Input :

cNu value = modeling step

```
Ternary blends : 40% of OPC
CSA-OPC-C$
```

	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	100	0	0
2	1	0	0	0	0	0	0	1	0	0
cTm	1100	0	1	20	0	0	0	100	0	0

OPC, CSA and anhydrite composition

```
$ Blend composition:

xa_[{C3S}] =: 0.01*(modC[0][0]*40+0.60*cNu*modC[0]
[1]+(60-0.6*cNu)*modC[0][2]);

xa_[{C2S}] =: 0.01*(modC[1][0]*40+0.60*cNu*modC[1]
[1]+(60-0.6*cNu)*modC[1][2]);

xa_[{C4A3s}] =: 0.01*(modC[2][0]*40+0.60*cNu*modC[2]
[1]+(60-0.6*cNu)*modC[2][2]);

xa_[{CaSO4}] =: 0.01*(modC[3][0]*40+0.60*cNu*modC[3]
[1]+(60-0.6*cNu)*modC[3][2]);

xa_[{Gypsum}] =: 0.01*(modC[4][0]*40+0.60*cNu*modC[4]
[1]+(60-0.6*cNu)*modC[4][2]);

xa_[{C3A}] =: 0.01*(modC[5][0]*40+0.60*cNu*modC[5]
[1]+(60-0.6*cNu)*modC[5][2]);

xa_[{C4AF}] =: 0.01*(modC[6][0]*40+0.60*cNu*modC[6]
[1]+(60-0.6*cNu)*modC[6][2]);
```

	modC[0]	modC[1]	modC[2]
0	65	0	0
1	12	10	0
2	0	66	0
3	0	4	87
4	3	0	0
5	6	0	0
6	11	0	0
7	3	20	13
8	0	0	0
9	0	0	0
10	0	0	0
11	0	0	0
12	0	0	0
13	0	0	0
14	0	0	0
15	0	0	0
16	0	0	0
17	0	0	0
18	0	0	0
19	0	0	0

Inert phases

2. Modeling

Output :

Controls | Sampling | Results | Config | 14/04/2014, 18:11

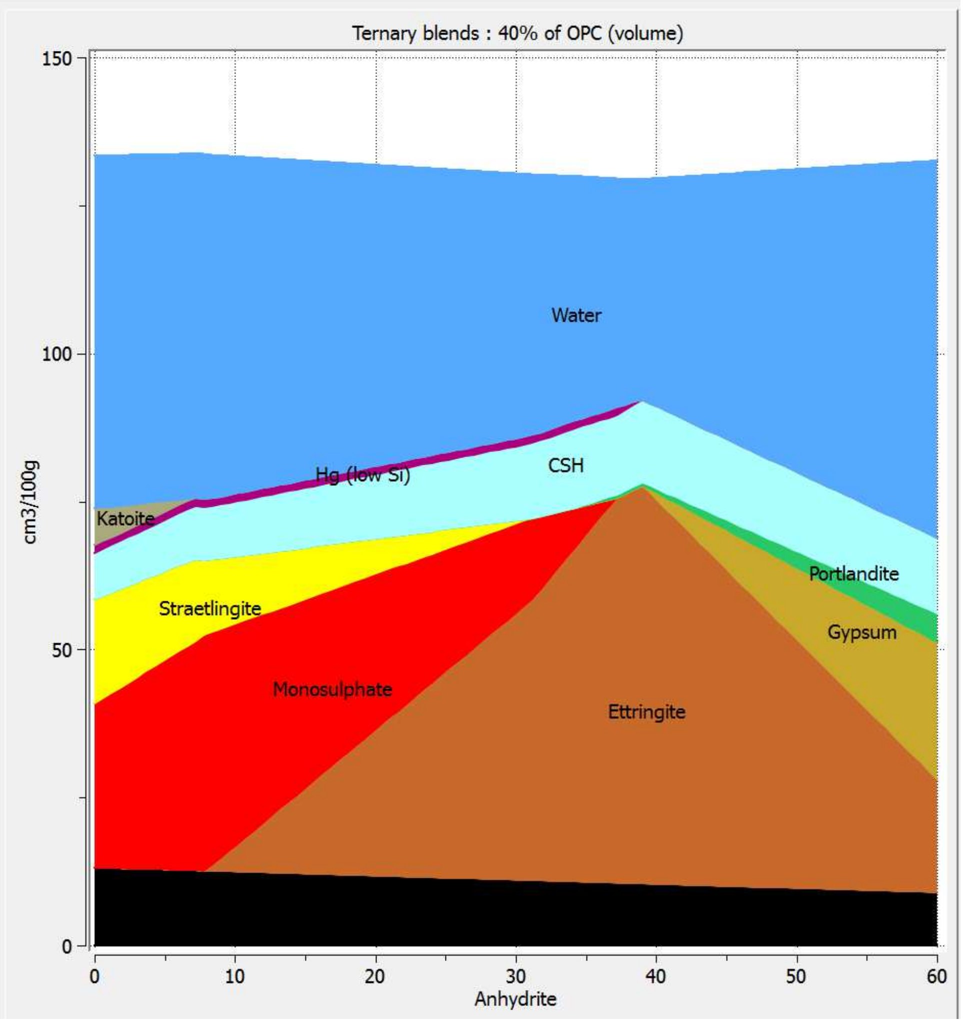
NeIt	9999	101	Next	0	I	0	J	100	Jp	100

pSTkey	GEMS2014:G:CSA-OPC-C$:0:0:1:20:0:	cTm	1100	cNV	0

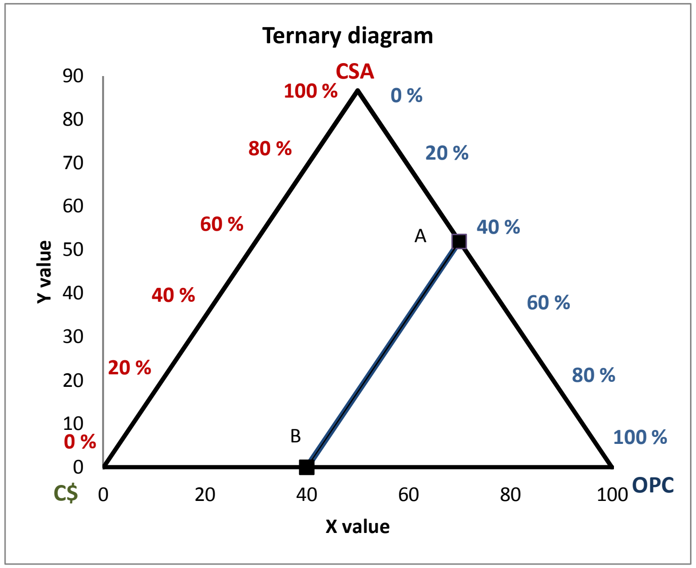
cTau	0	cpXi	0	cXi	1	cNu	100
cpH	0	cpe	0	cEh	0	cT	293.15

```
$ x-axis : step = anhydrite percentage
xp[J] =: 60-0.60*cNu;

$ y-axis composition : unreacted phases
yp[J][0] =: 0.01*(modC[7][0]*40+0.6*cNu*modC[7][1]+(60-0.6*cNu)*modC[7]
[2]);

$ y-axis composition : hydration product
yp[J][1] =: phM[{ettringite-Fe}]+phM[{ettringite-Al}];
yp[J][2] =: phM[{Gypsum}];
yp[J][3] =: phM[{Al(OH)3mic}];
yp[J][4] =: phM[{monosulphate-Al}]+phM[{monosulphate-Fe}];
yp[J][5] =: phM[{C2ASH8}];
yp[J][6] =: phM[{Portlandite}];
yp[J][7] =: phM[{CSHQ}];
yp[J][8] =: phM[{C3FS0.84H4.32}];
yp[J][9] =: phM[{C3AH6}];
yp[J][10] =: phM[{aq_gen}];
$ End
```

Results (volume):



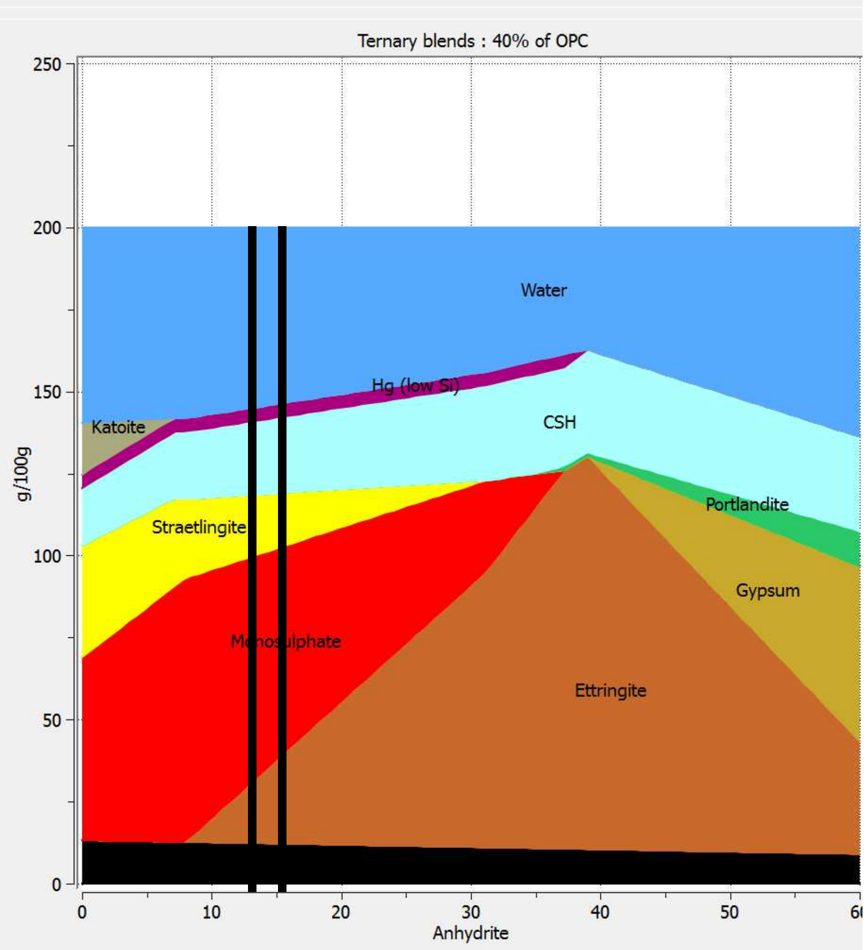
Point A Point B

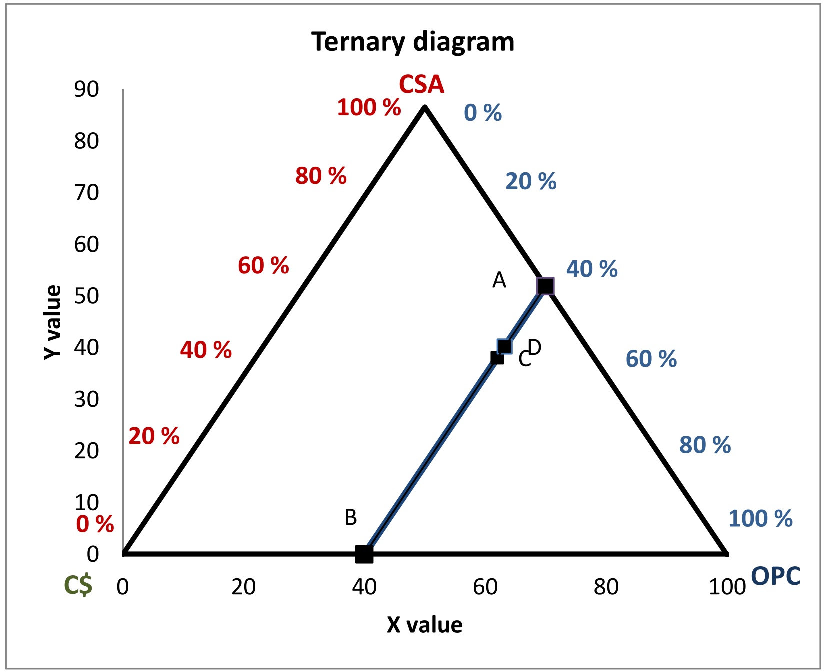


In OPC-CSA blends, ettringite proportion can induce stability issues :

(40% of OPC and 28% of anhydrite)

Results (weight):

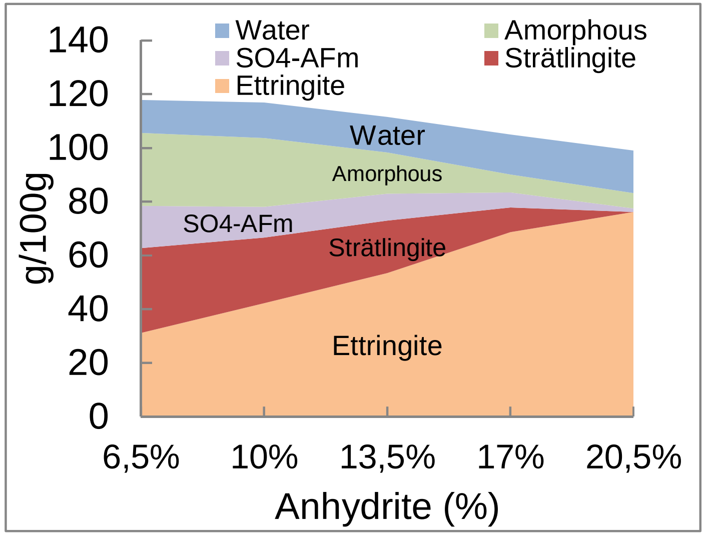


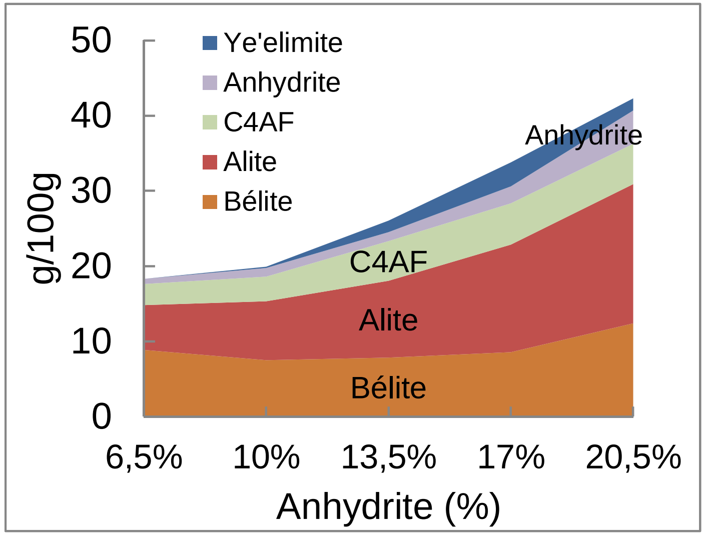


20-30 g of ettringite without gypsum → 13.5 and 16 % of anhydrite.

3. Results and applications

Quantitative analysis after 28 days of hydration (water/cement ratio = 0.5) for 40% of OPC:



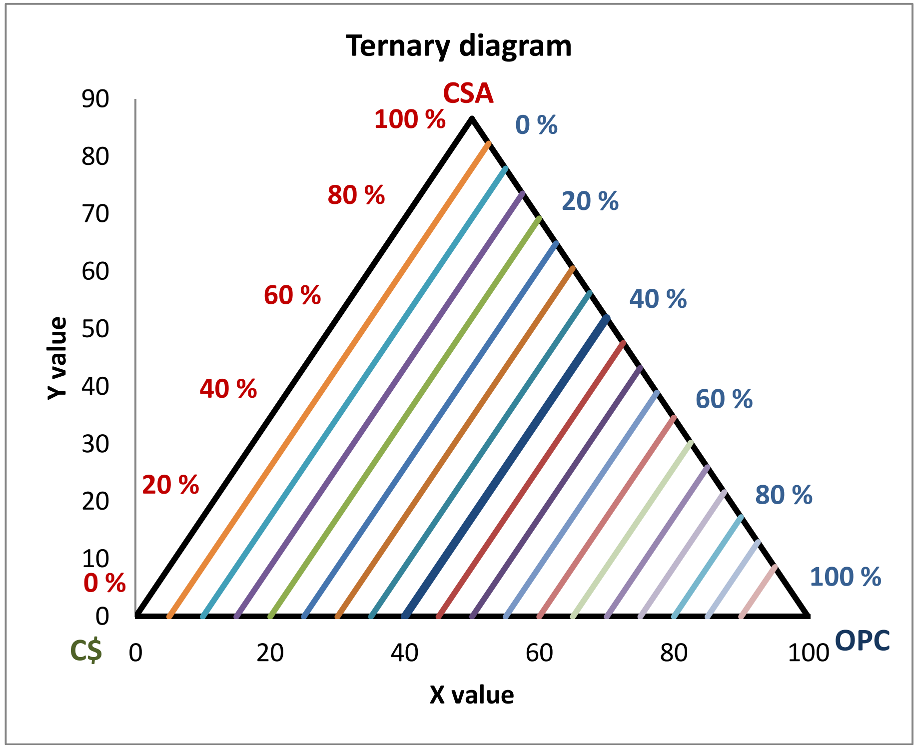


The predicted and observed effects of anhydrite proportion are similar.

However, the ettringite proportion is higher because a part of the OPC has not yet reacted (only 28 days of hydration).

3. Results and applications

Example : other ternary blends containing 20-30 g of ettringite and without gypsum.



Same modeling process with other OPC proportions!

3. Results and applications

Modification of the previous project :

1 - Create a new clone of the process

2 – INPUT : change the OPC, CSA and anhydrite proportion in the process :

- OPC % = 40 → OPC % = modC[8][0],

- CSA % = 0.6 x cNu → CSA % = (1-modC[8][0]/100)*cNu,

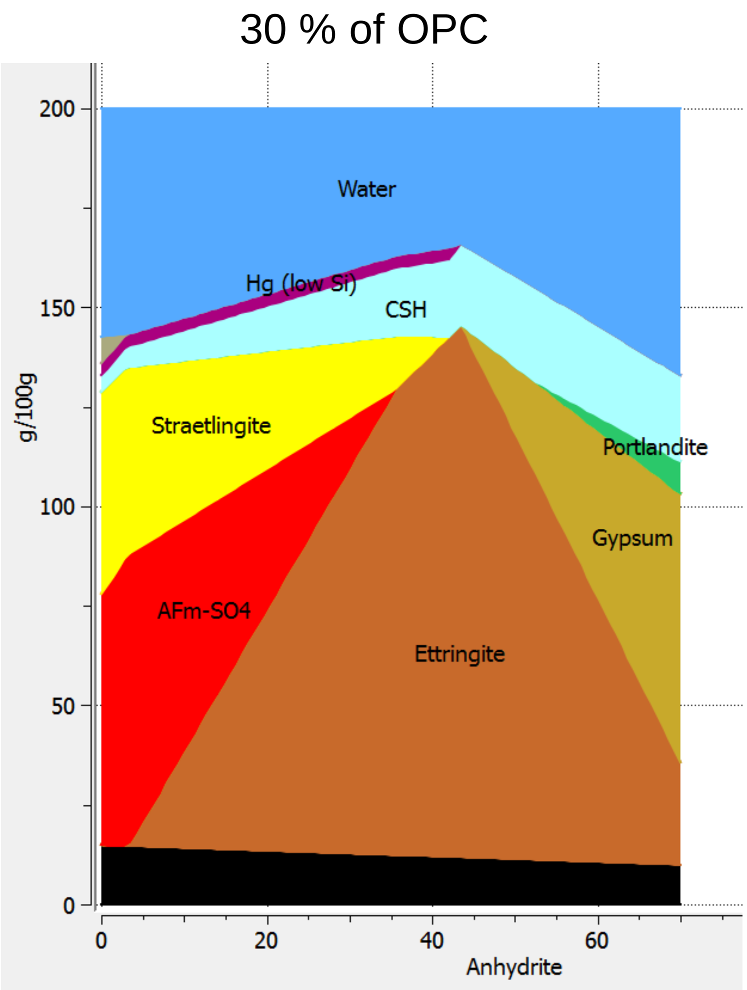
- C$ % = 60 – 0.6 x cNu. → C$ % = ((100 -modC[8][0])-(1-modC[8][0]/100)*cNu),

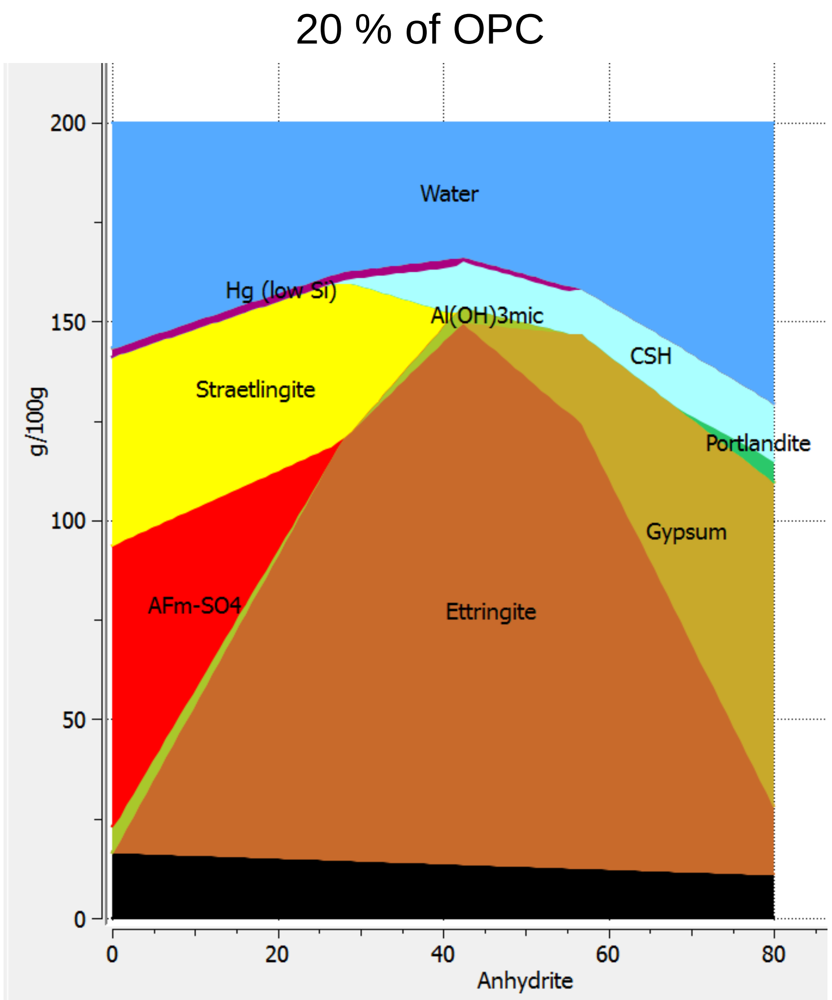
3 – OUTPUT : change the anhydrite percentage ((100 -modC[8][0])-(1-modC[8][0]/100)*cNu) and inert phases proportions

→ The OPC percentage is indicated in the cell [8][0].

3. Results and applications

Lower OPC proportion → increase of ettringite proportion and formation of gibbsite.

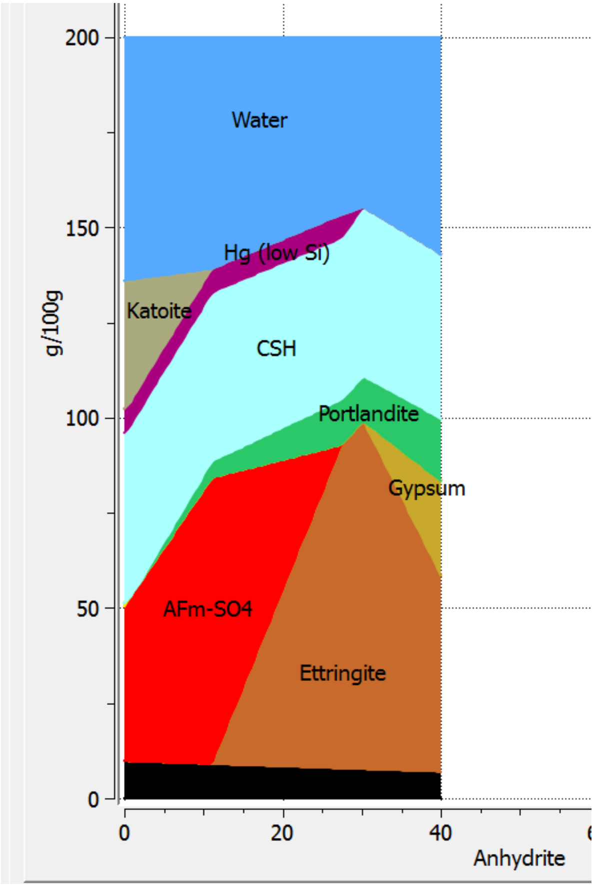




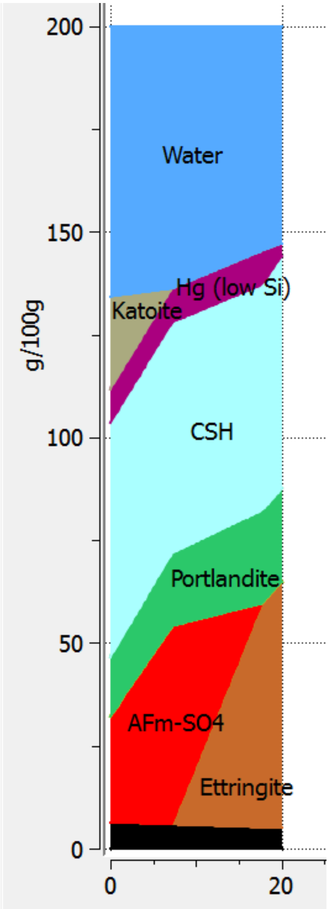
3. Results and applications

Higher OPC proportion → ettringite proportion decreases and katoite (and hydrogarnet) proportion increases (kinetic issue?)

60 % of OPC



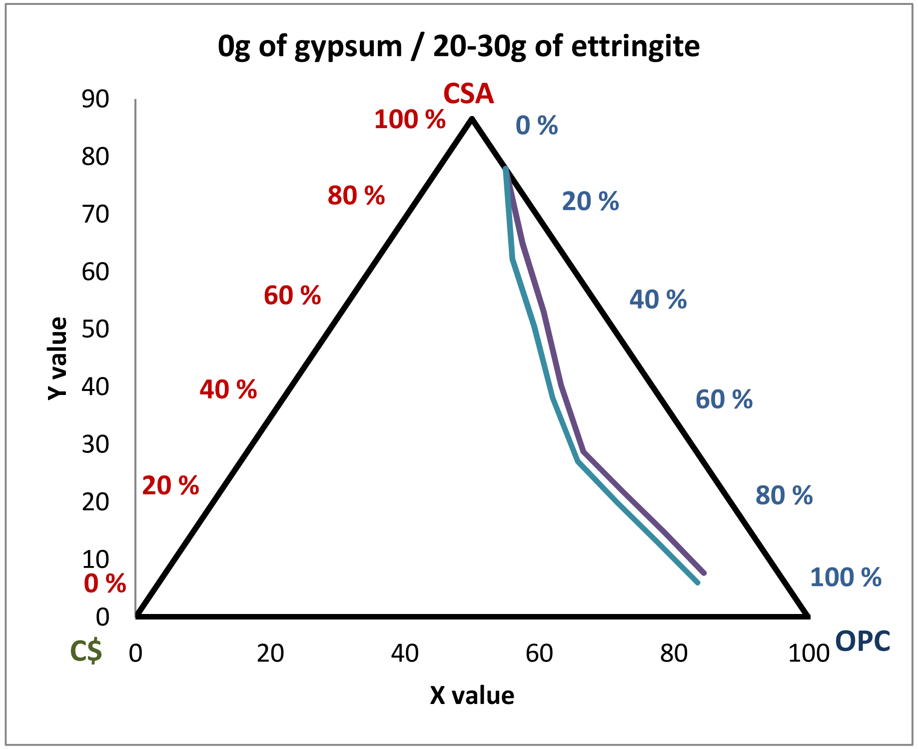
80 % of OPC



You must hinder the formation of other compounds ($Fe(OH)_3$, aluminate phases, etc.)

3. Results and applications

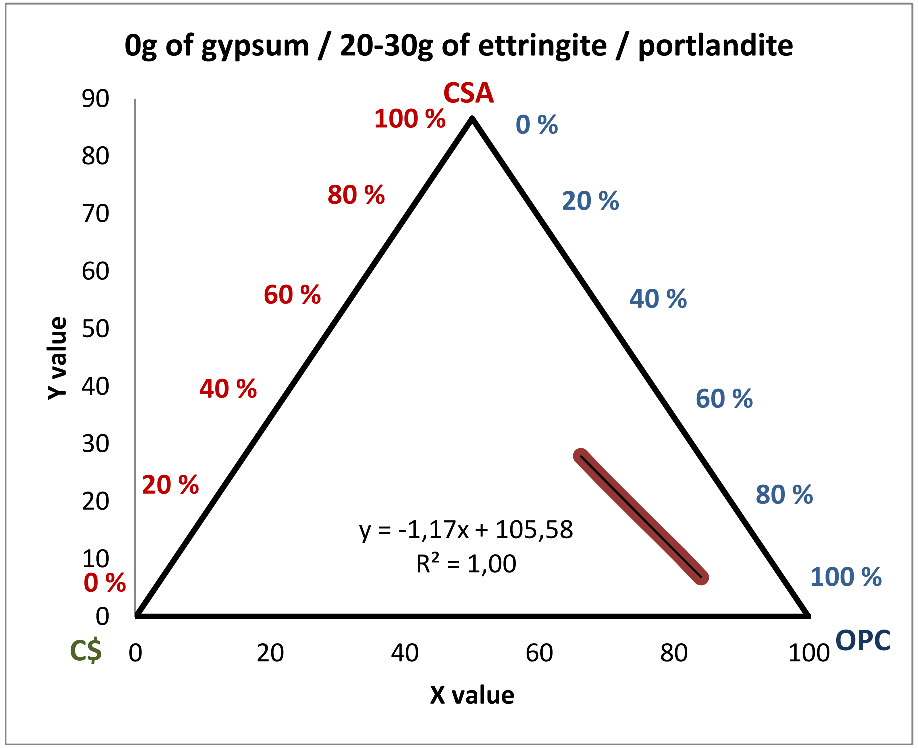
Between the blue and purple lines : blends with 20-30g of ettringite (without gypsum)

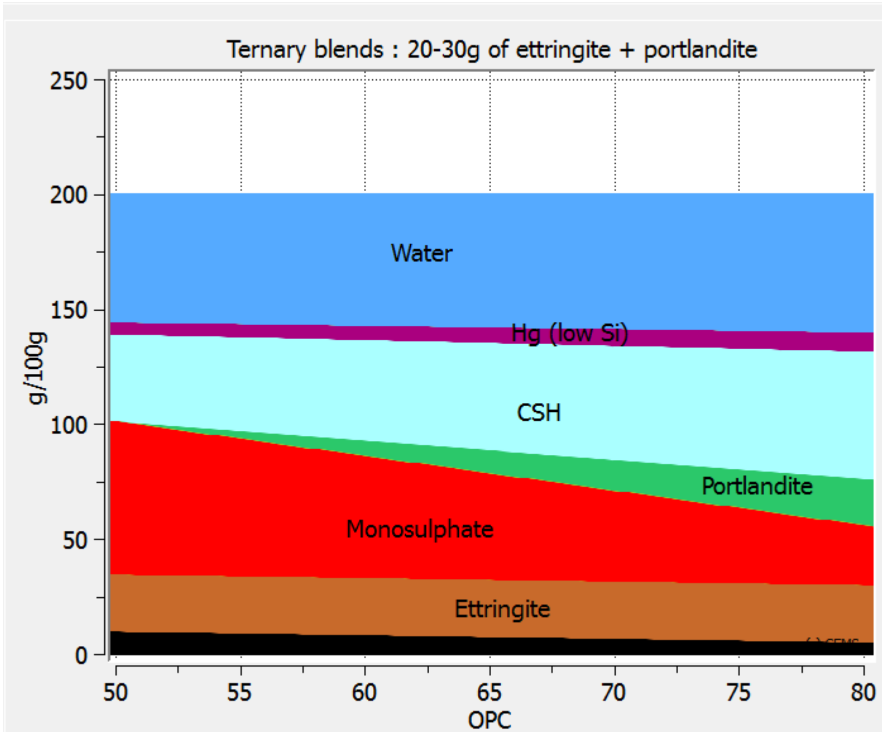


Ettringite proportion is higher than predicted (after 3 months of hydration) due to the slow formation of hydrogarnet and the slow reaction of cement components (C_4AF, C_2S mainly).

3. Results and applications

Blends with porlandite and 25g of ettringite (without gypsum) ?





There should be more than 52% of OPC.

Conclusion

Thermodynamic modeling of CSA – OPC – C$ blends:

→ prediction of the composition and impact of different parameters,

→ helpful for complex blend formulation,

→ must be compared with experiments (hydration kinetic),

→ conditions of hydrogarnet formation in OPC-CSA blends ?

QUESTIONS

Do you have any questions?