Hydration of Belite Calcium Sulfo-Aluminate cement Aether™

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Dr. MORIN Vincent, WALENTA G., GARTNER E., TERMKHAJOMKIT P., BACO I., CASABONNE J.M.
Lafarge Research Center

Aether™

Lafarge & CO_2 - Some Figures

- **About 65% of the CO_2 comes from the limestone and 35% from the fuel**
- **Between 1990-2010, Lafarge decreased its net CO_2 emissions by 20% (from 774 to 630 kg CO_2/t_{cement})**
- **Main conventional levers used to mitigate CO_2:**
  - Increase energy efficiency by optimizing processes
  - Increase cementitious additions into the cement (slag, FA, pozzolans, limestone…)
  - Substitution of fuels (animal meal, tires, etc…)

Lafarge & CO_2 - Some Figures

- **Although the conventional industrial levers still need to be developed, we think they will soon come to a limit and that we will not be able divide our CO_2 emissions by factor 4 (by year 2050)**

⇒ **Other non conventional means need to be developed**:

Since 2003, LAFARGE is engaged in the research and development of a new low-CO2 clinker: Aether™

Lafarge & CO_2 - Some Figures

Two main objectives

- To develop a **new class of clinkers for making cements with similar mechanical performance to conventional OPCs**, and which can be produced in **existing PC plants**, while giving significantly **lower CO2 emissions (25%-30%) in production**
- **Not targeting 'Niche products**' but mainstream products (ready mix, precast products)

Aether™

Aether™ clinker

- **Aether™** is a new, patented* class of low-CO_2 cements based on BCSAF clinkers containing:
  - Belite (C2S) : 40 – 75%
  - Calcium sulfoaluminate (ye'elimite or C4A3$) : 15 - 35 %
  - Ferrite : (C2(A,F)) : 5 – 25%
  - Minor phases: 0,1 – 10 %

**Gartner, E., and Li, G., 2006. World Patent Application WO2006/018569 A2*

Aether™ clinker

'Portland' raw mix

~35%	LOI
~14%	SiO_2
~3%	Al_2O_3
~3%	Fe_2O_3
~43%	CaO
~0.3%	SO_3

'Portland' clinker

C_3S	~ 65%
C_3A	~ 6%
C_2S	~ 15%
$C_2(A,F)$	~ 12%

Aether™ clinker

$C_4A_3\$$	~ 25%
C_2S	~ 55%
$C_2(A,F)$	~ 20%

Aether™ raw mix

LOI	~29%
SiO_2	~12%
Al_2O_3	~11%
Fe_2O_3	~5%
CaO	~37%
SO_3	~3%

- Aether™ main characteristics / Portland:
  - High Alumina and SO_3 content and lower LOI in the raw mix = lower $CaCO_3$
  - No C_3S; C_3A replaced by $C_4A_3\$$; high C_2S content

Aether™ clinker

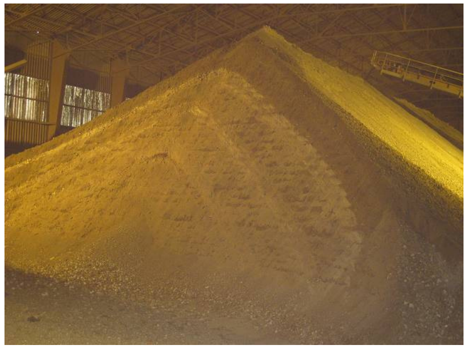
- **Aether™ clinkers can be produced :**
  - in kilns designed for Portland cement clinker production
  - using similar process parameters and fuels
  - with conventional raw materials
  - at lower temperatures (≈1225 -1300℃) than for Portland cement clinker
  - with significantly lower energy that Portland cement clinker
  - Aether cement grinding energy is generally lower than for OPC

The manufacturing of Aether™ generates 20 to 30% less CO_2 per tonne of cement than pure Portland cement (CEM (I) type)

Aether™ industrial trial 2011

- With the support of LIFE+, the European Union's financial instrument for the environment

- Main figures :
  - Semi-dry process
  - Prehomogenization pile ~8000 t.
  - ~ 5500 t. of clinker produced



Aether™ hydration

Cement preparation:

- Aether clinker was ground to a Blaine fineness of 500 m2/g
- Calcium sulfate (anhydrite) ground to 100% passing 100 µm was added to the clinker

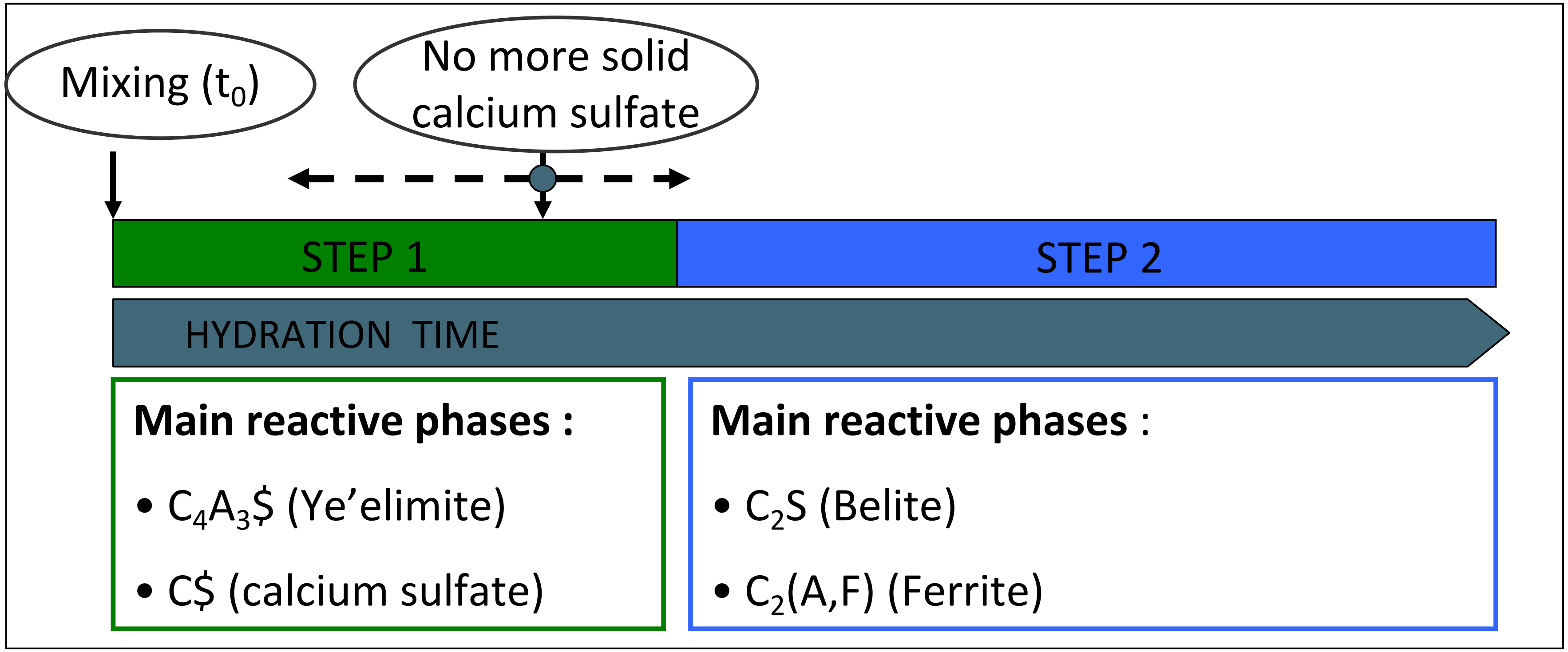
Cement composition:

- 94 % clinker / 6 % Anhydrite

Ye'elimite	Belite	Ferrite	Anhydrite
~28%	~ 48%	~18%	~6%

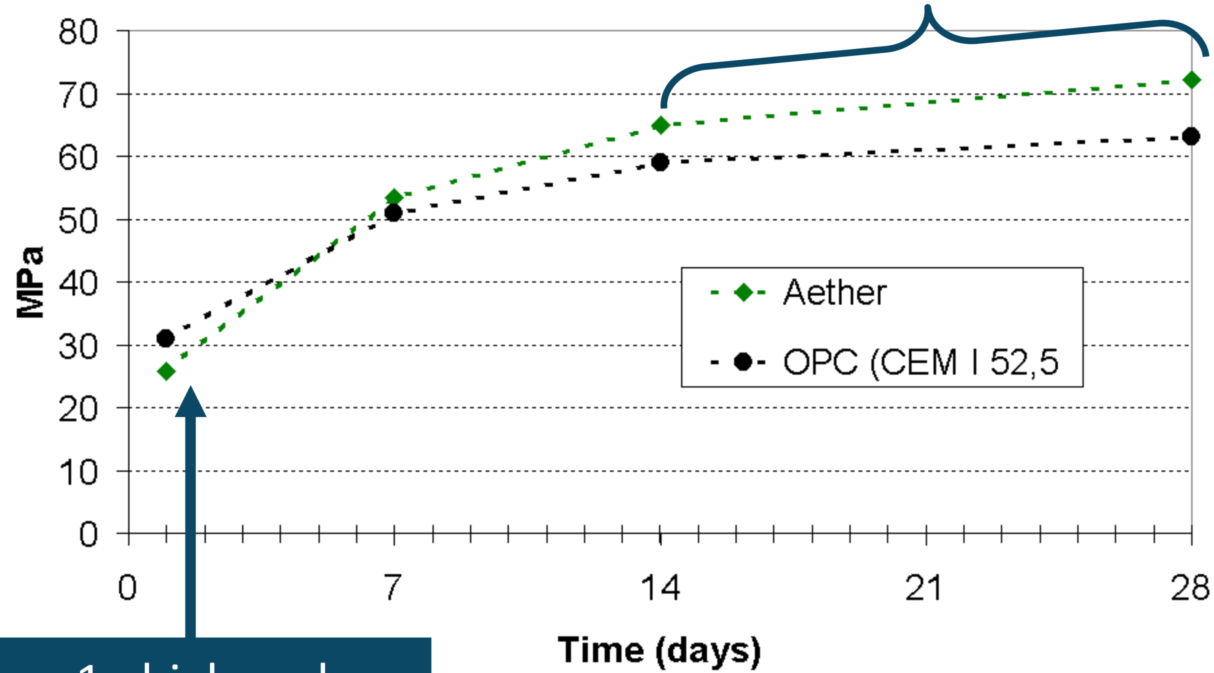
Aether^{TM} hydration

- Global hydration in two main steps:



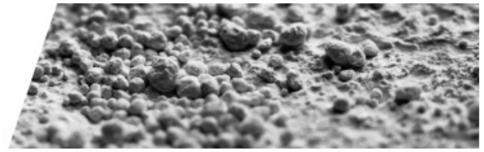
Aether^{TM} hydration

Compressive strength (standard mortar)



Step 2 : middle and long term strength given by Belite and Ferrite hydration

Step 1 : high early strength given by Ye'elimite hydration



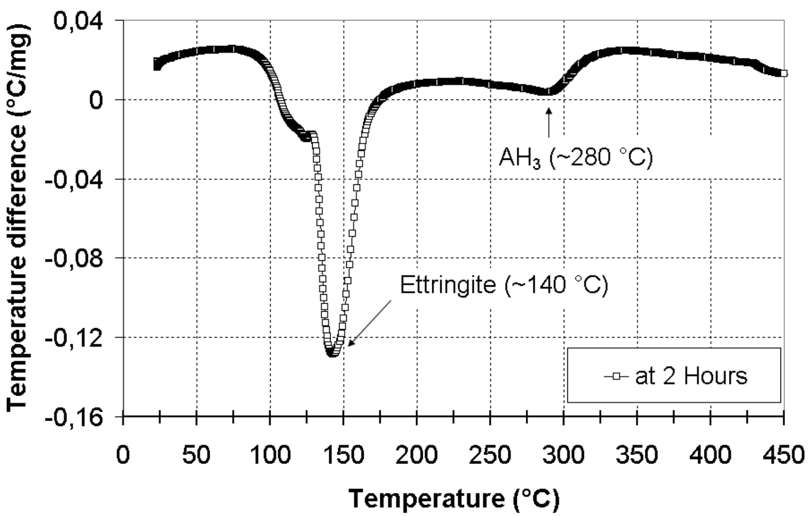
Aether™ hydration: Step 1

- $C_4A_3\$ + 2\ C\$ + 36H \rightarrow C_3A,3C\$,32\ H + 2\ AH_3$

Ettringite (crystalline form) ↑ $C_3A,3C\$,32\ H$

Amorphous or poor crystallised form ↑ AH_3

▼ DTA measurement at 2 hours of hydration



DTA show two main peaks :

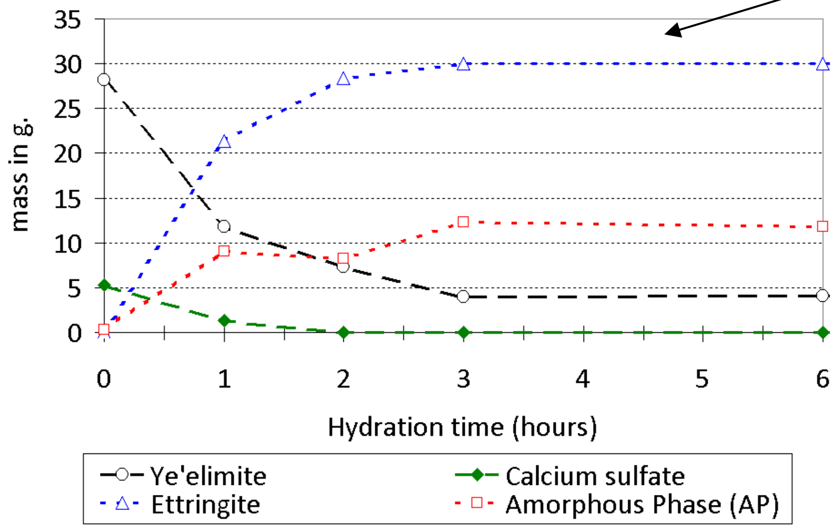
1st peak : ~140°C → Ettringite

2nd peak : ~280°C → AH3

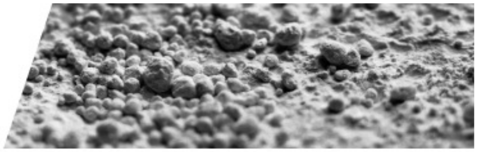
Aether™ hydration: Step 1

Time	TGA measurement (20-220℃)		XRD Rietveld
	Weight loss	Calculated Mass of Ettringite	Mass of Ettringite
1h	**8.5% (9.6 g of water)**	**21 g**	**21 g**
3h	**10.6% (13.6 g of water)**	**27 g**	**30 g**

▼ XRD Rietveld analysis



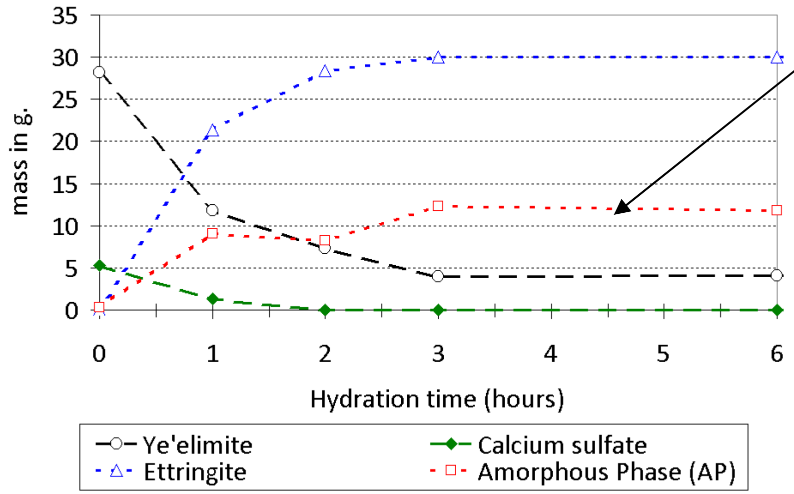
→ Quantification of Ettringite in good agreement between XRD and TGA.



Aether™ hydration: Step 1

Time	TGA measurement (220-450℃)		XRD Rietveld
	Weight loss	Calculated Mass of AH3	Mass of amorphous phase (AP)
1h	**2.6% (2.8 g of water)**	**8.2 g**	**9 g**
3h	**3.7% (4.3 g of water)**	**12.4 g**	**12 g**

▼ XRD Rietveld analysis

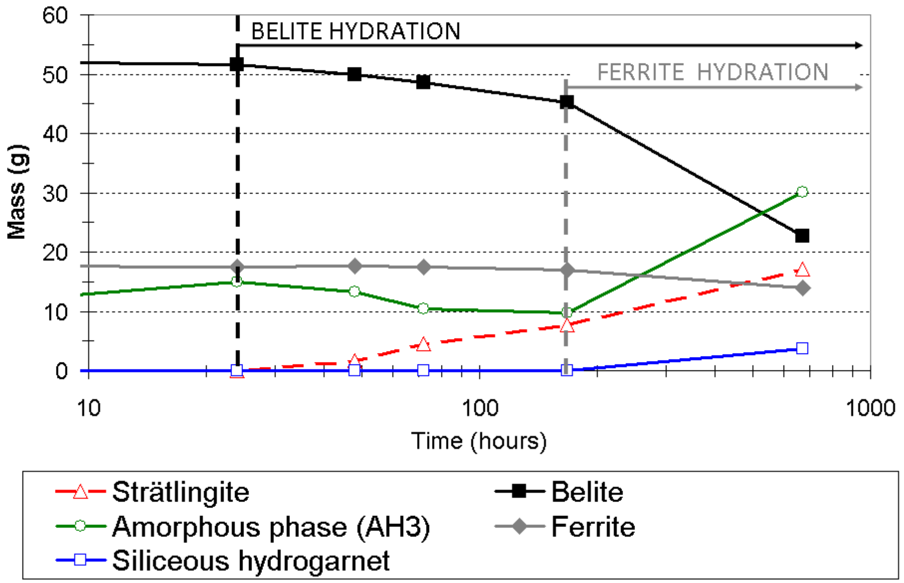


→ The amount of AH3 measured by TGA corresponds well to the amorphous phase calculated by XRD Rietveld refinement.

Aether™ hydration: Step 2

- C_2S + AH3 + 5H → C_2ASH_8 (Stratlingite)
- C_2S + C2(A,F) + 5H → $C_3(A,F)SH_4$ (Hydrogarnet) *+ Ca2+ and OH- in solution*

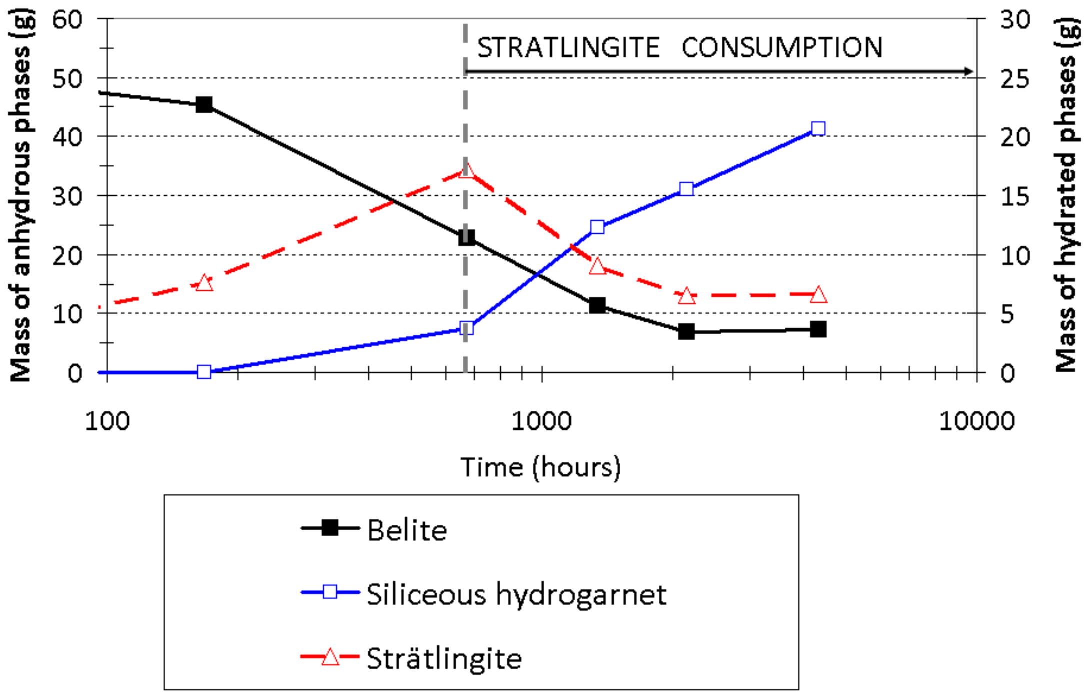
▼ XRD Rietveld analysis

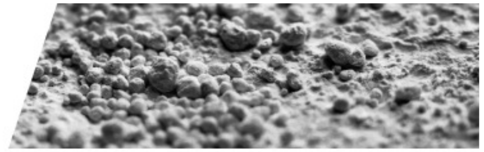


Aether™ hydration: Step 2

- $2C_2S + C_2(A,F)SH_8 + (x-4)H \rightarrow C_3(A,F)SH_4 + C_3S_2H_x$

▼ XRD Rietveld analysis

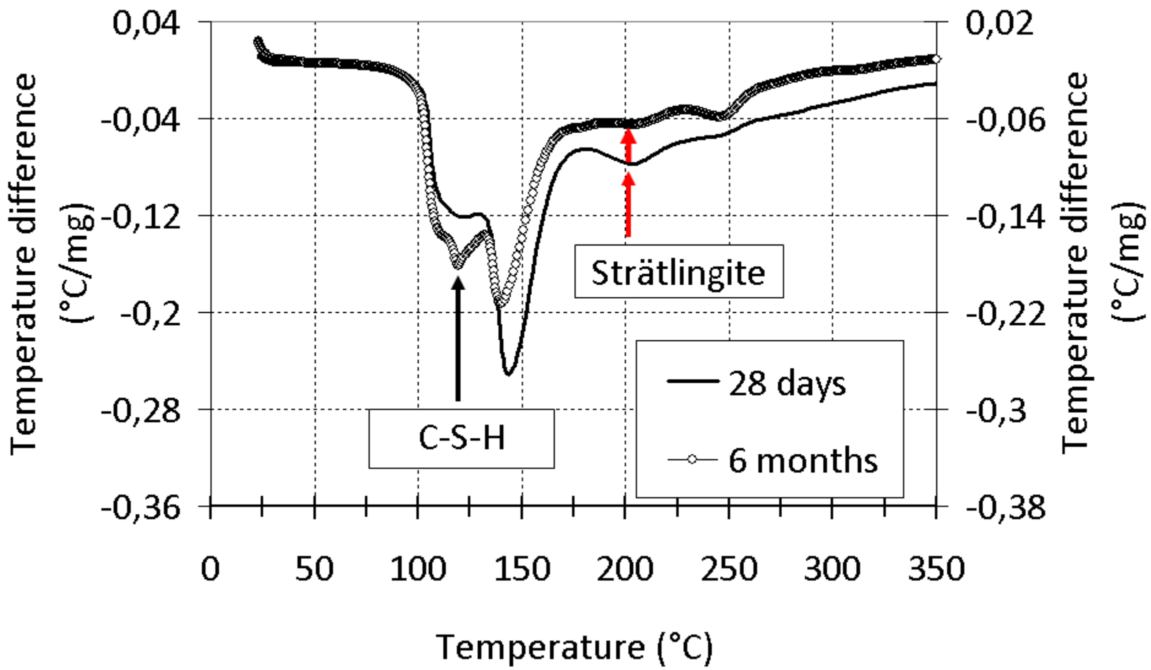




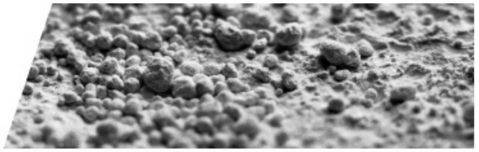
Aether™ hydration: Step 2

- $2C_2S + C_2(A,F)SH_8 + (x-4)H \rightarrow C_3(A,F)SH_4 + C_3S_2H_x$

▼ DTA measurement at 2 hours of hydration

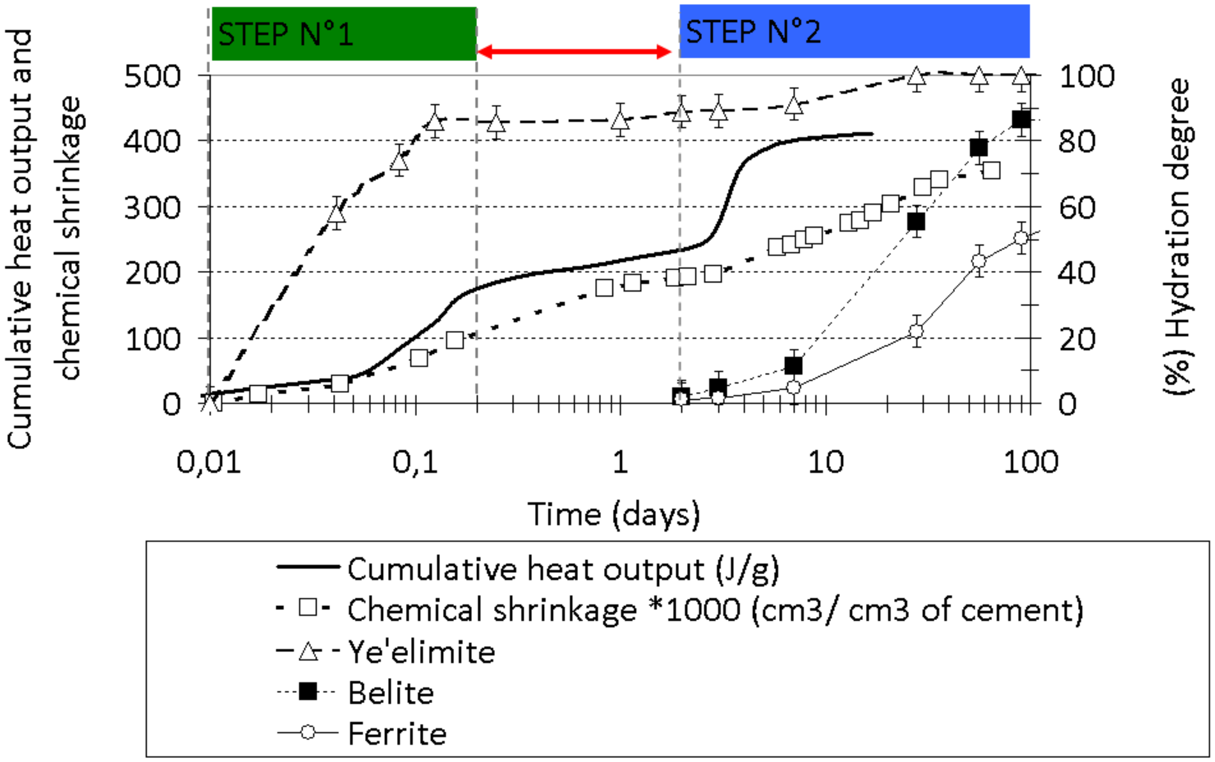


DTA measurement confirms : Stratlingite consumption and C-S-H precipitation



Aether™ hydration: Bilan

There is a 'dormant' period between the end of Ye'elimite hydration and the onset of C_2S hydration (Stratlingite precipitation) : this period can last sometimes a few days



Conclusion

Aether cement based on clinkers containing belite, calcium sulfoaluminate and ferrite phases seem to be a promising alternative to Portland cements :

⇨ Reduction of CO_2 emissions relative to Portland cements.

⇨ Use of similar raw materials and production in industrial installations used to make Portland cements.

⇨ Performance similar to Portland cements in terms of compressive strength.

Aether™

Next steps

More research is needed on :

- **Process and clinkering**
- **Hydration (ex : how to better manage the transition between step N°1 and N°2)**
- **Durability (ex : carbonation , sulfate attack,…)**

=> It will be necessary to develop appropriate standards, before Aether™ cements can be considered a large-scale alternative to Portland cements.