Innovation to improve carbon footprint in the Cement industry

Building Material Analysis meeting – University of Halle, Germany
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With the contribution of the LIFE financial instrument of the European Community

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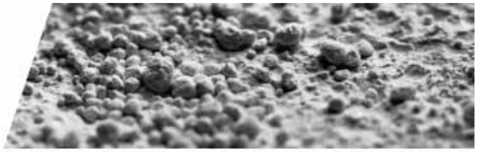


Lafarge & CO2 – Some Figures

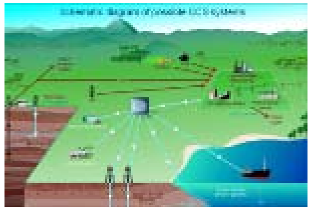
- Year 2010, LAFARGE has produced 130 Mt cement and emitted 95 Mt CO_2
- 65 % of the CO2 emission comes from limestone calcination and 35 % from the combustion process
- Between 1990-2010, net CO_2 Lafarge decreased CO2 emissions by 20% starting from 774 kg CO_2/t_{cement} to 630 kg CO_2/t_{cement} i.e. – 20 Mt CO_2/y
- Main conventional levers used to mitigate CO_2:
  - Reduce specific heat consumption of the cement kiln
  - Increase cementitious additions into the cement (slag, FA, pozzolans, limestone…)
  - Substitution of fuels (animal meal, tires, shredded wastes…)

Some potential non-conventional solutions

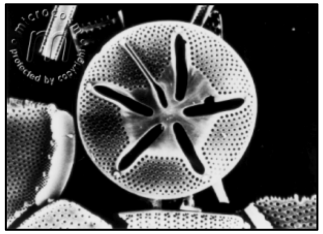
- Although the conventional industrial levers still need to be developed, we think they will soon come to a limit and that we will not be able divide our CO_2 emissions by factor 4 (by year 2050)

  ⇒ Other non conventional means need to be developed:

  - Carbon Capture & Sequestration (CCS)



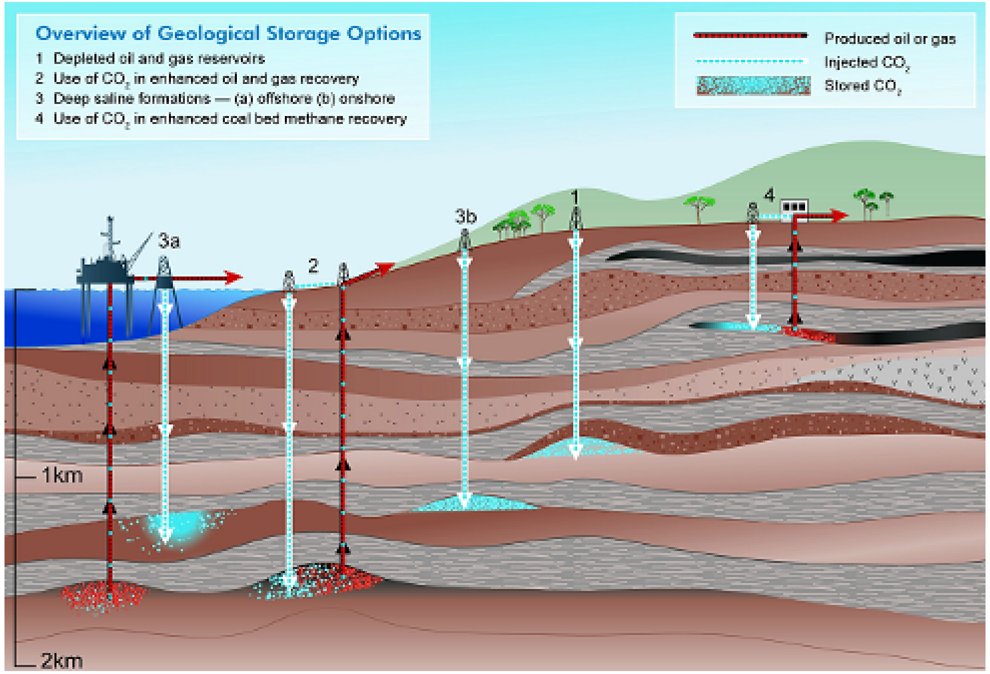
  - Carbon Capture & Transformation (CCT): Micro-Algae



  - Low CO2-intensive product development: AETHER

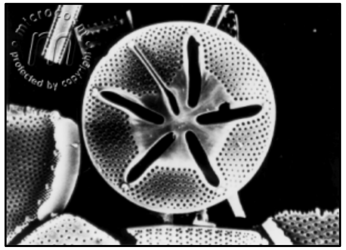
CCS – CO2 Storage in Deep Geological Formation

- CCS is seen as a complementary solution although expensive and not possible everywhere (distance to sequestration site); LAFARGE present in several partnerships going from capture to sequestration (EDF, GDF-Suez, Total, Air Liquide, Veolia Env., Rhodia, ARKEMA, IPF-EN, BRGM…)



Algae ponds – Photo-bio-reactors (PBR)

Algae growing based on Photosynthetic reaction



Micro-algae

+

Sunlight

$+ CO_2 + H_2O \longrightarrow$ **Biomass** $+ O_2$

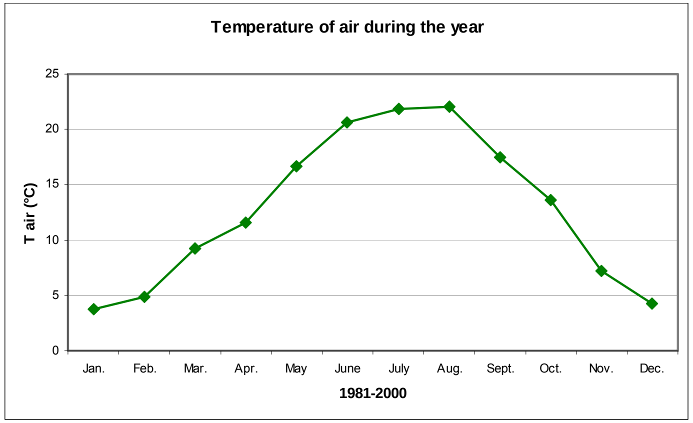
Bio-fuels
biodiesel / bioethanol / methanisation
High value products (omega-3…)

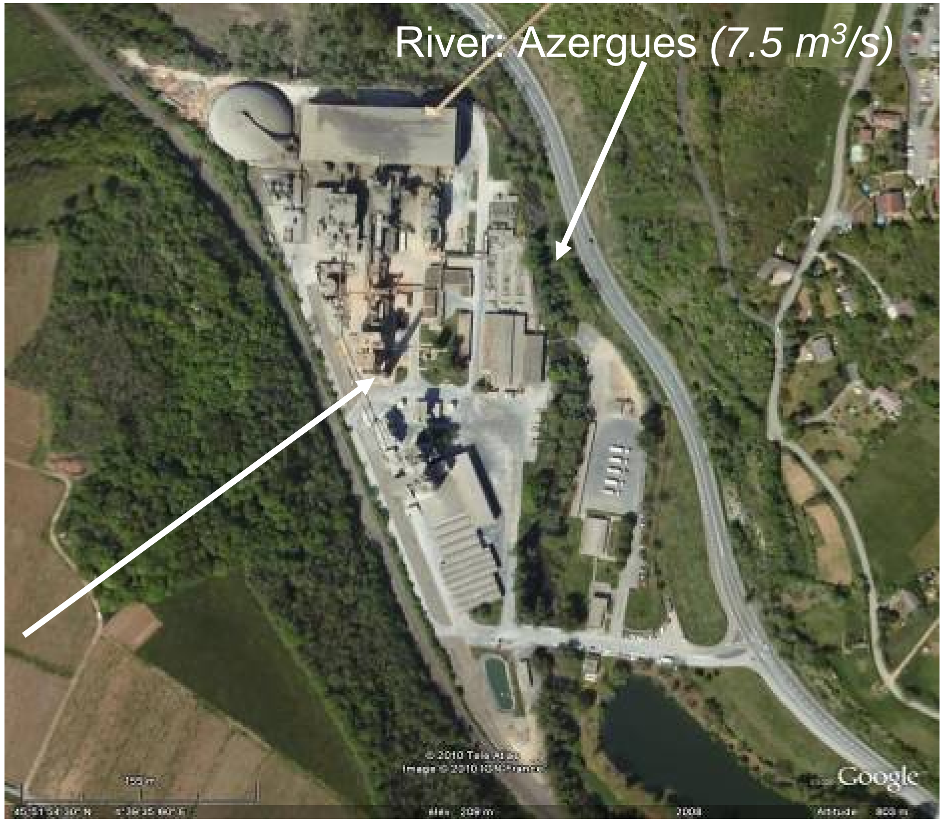
Objective:

- Is it possible to grow Micro-algae using the off gases from Cement Industry ?
- In presence of dust, minor elements, other gases- which gas pre-treatment will be necessary ?
- Develop a first estimation on mass, energy and CO2 balance

Algae Pilot trial - Organisation & Installation

The Lafarge Cement Plant





Localization of the greenhouse and PBR: at the foot of the exhaust stack

(South oriented)

The installed PBR

Exchange tank

Vertical tubular PBR

CO2 balance for 180.500 t/year CO2 treated

1. Existing technology:
   - Total surface needed: 20km²
   - Cost and CO2 balance; 5 000 €/t CO2 processed (without CAPEX)

     → **5.25 t CO_2 produced for 1 t avoided: CO2 balance not acceptable**

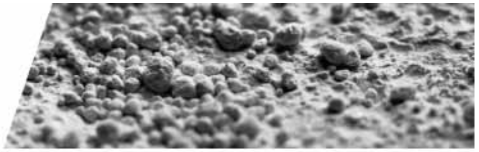
2. Non existing technology (prototypes):
   - Total surface needed: ~4km²
   - Cost and CO_2 balance: **423 €/t CO_2 avoided** (without CAPEX)

     → **0.80 t CO_2 produced for 1 t avoided**

     Total CO_2 captured:- 47 000 t = 26% CO2 reduction

     but Business model not valid

⇒ **Significant technology breakthrough needed for industrial use**



Lafarge’s objectives for Aether: A low CO2 clinker for all types of cement

- Objective:
  - 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 CO_2 emissions (25%-30%) in production**
  - **Not targeting ‘Niche products**’, but mainstream products
- Not looking for specific applications, but looking to replace the ordinary clinker
  - Ready mix, Precast…

Aether = Research & Development

2003 **BCSAF**

9/2009

Life+ Industrialisation & Development
~ 6 Mio€ for 3 years
~50% subvention from European Union

2013

Fundamental & applied research

Project Partner:
Lafarge (Coordinator)
BRE (UK)
MBM (Poland)

Industrial Pilot trials:
Validation of technical feasibility
Active communication

LCR research program

AETHER industrial trial 2011 – Cement plant in France (Burgundy)

- Objective: Produce AETHER clinker at industrial plant
- Conventional Raw Materials used: Limestone – Bauxite –Gypsum –Iron Oxide – Marl
- Process slightly adapted – Production of several thousand t of AETHER clinker – Chemistry and Mineralogy at target ~25% CO_2 reduction confirmed - incl. 15% less energy demand
- Persons implicated from 5 different entities and competences
  - Research
  - Technical centre
  - Plant
  - Communication
  - Marketing
- Properties characterization program ongoing

AETHER industrial trial 2011 – Cement plant in France (Burgundy)

- Most important quality control tool: DX + Rietveld

Many thanks to the excellent & professional support of PANalytical during the pilot trial

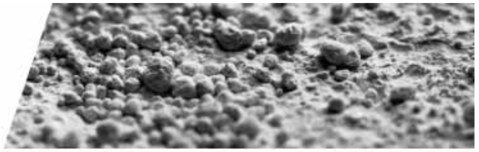
Special thanks to Dr. Füllmann

- Following equipment was used: Cubix + Axios

AETHER Communication tools

Website AETHER:

http://www.aether-cement.eu/



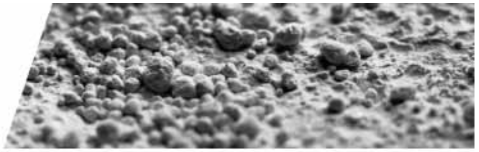
Aether™ cement: global presentation

Aether™ is a new low-CO_2 cement based on:

- Belite: C_2S
- Calcium sulfoaluminate (ye'elimite): $C_4A_3\$$
- Ferrite: $C_2(A,F)$

This new clinker and its mineralogical composition is patented :
(***Gartner, E., and Li, G., 2006. World Patent Application WO2006/018569 A2***)

- Belite: 40 – 75%
- Ye'elimite: 15 - 35 %
- Ferrite: 5 – 25%
- Minor phase: 0,1 – 10%



Aether™ cement: global presentation

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_4AF	~12%

Aether ™ clinker	
$C_4A_3\$$	~25%
C_2S	~55%

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.
- No C_3S and higher C_2S content in clinker.

Aether™ cement: global presentation

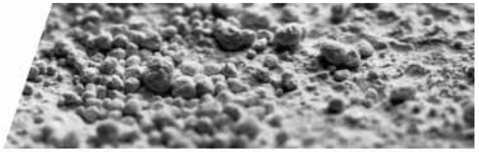
• Boron-containing compounds are introduced into the raw mix in order to stabilize the α'–C_2S phase, which is a more reactive polymorph than β-C_2S.

⇨ We have developed a special Rietveld control file to clearly identify and quantify these two different forms of C_2S and also the other anhydrous phases of Aether ™ .

⇨We also use this control file for Aether ™ clinker production control.

Example: Phase composition of an Aether ™ cement :

Scan file name	Ye'elimite (C4A3$)	Larnite (Beta-C2S)	Alpha´-C2S	Mayenite (C12A7)	Ferrite C2(A,F)	Gehlenite (C2AS)	Anhydrite
Aether cement	35,5	4,1	44,0	0,7	12,4	0,9	2,4

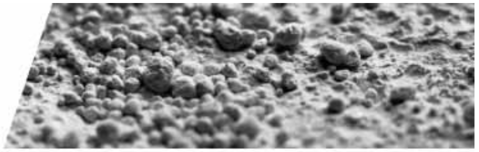


Aether™ : CO2 emissions and manufacturing

⇨ Aether™ is based on raw mix compositions with a lower fossil CO_2 content, resulting in lower CO_2 emissions per unit clinker.

	Cement compound	Raw material used	g. CO2 / g. of pure phase
	C_3S (alite)	Limestone + silica	0.578
	C_2S (belite)	Limestone + silica	0.511
Aether™	$C_2(A,F)$ (ferrite)	Limestone + Alumina + iron oxide	0.362
	$C_4A_3\$$ (ye'elimite)	Limestone + alumina + anhydrite	0.216

E. Gartner – Industrial interesting approaches to low C02 cement, in CCR (34) - 2004



Aether™ : CO2 emissions and manufacturing

Aether™ clinkers can be produced :

✮ in kilns designed for making Portland cement clinker

✮ using similar process parameters and fuels

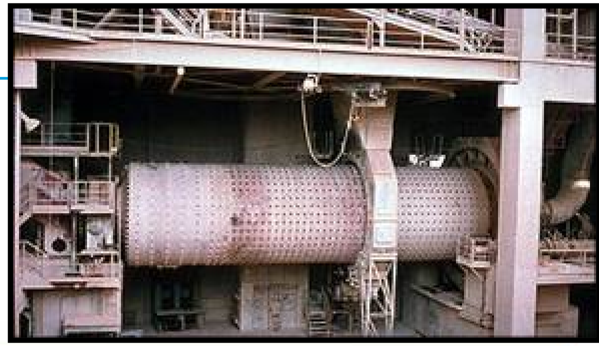
✮ with conventional raw materials.

✮ at lower temperatures (≈1250 -1300°C) than for Portland cement clinker (1400 – 1500°C)

✮ with significantly lower energy that Portland cement clinker

✮ Aether cement grinding energy is also lower than for OPC

⇨ The manufacturing of Aether ™ generates 25 to 30% less CO_2 per tonne of cement than pure Portland cement (CEM (I) type).



Aether™ : CO2 emissions and manufacturing

⇨Aether ™ clinker has already been manufactured in a Lafarge plant using a semi-dry process and industrial raw materials:

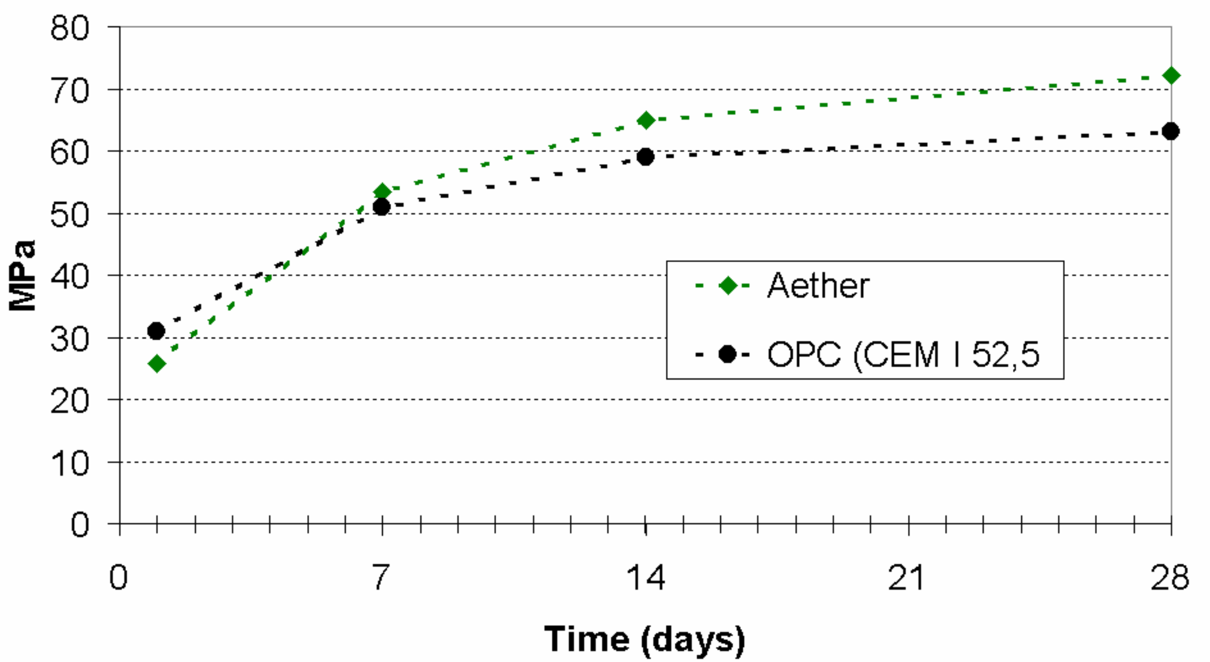
⇨In 2011, 5000 tonnes of two different Aether clinkers (different with phase compositions) were produced.

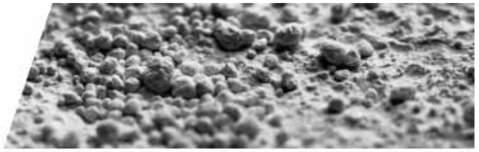
Aether™ : mechanical performance

1- Calcium sulfoaluminate ($C_4A_3\$$) hydration gives the high early strength (6 hours to 2 days)

2- C_2S and $C_2(A,F)$ hydration gives the middle-long term strength.

Compressive strength (standard mortar)





Aether™: hydration mechanism

Experimental

⇨ Aether clinker was ground to a Blaine fineness of about 4000 cm²/g in a lab ball mill.

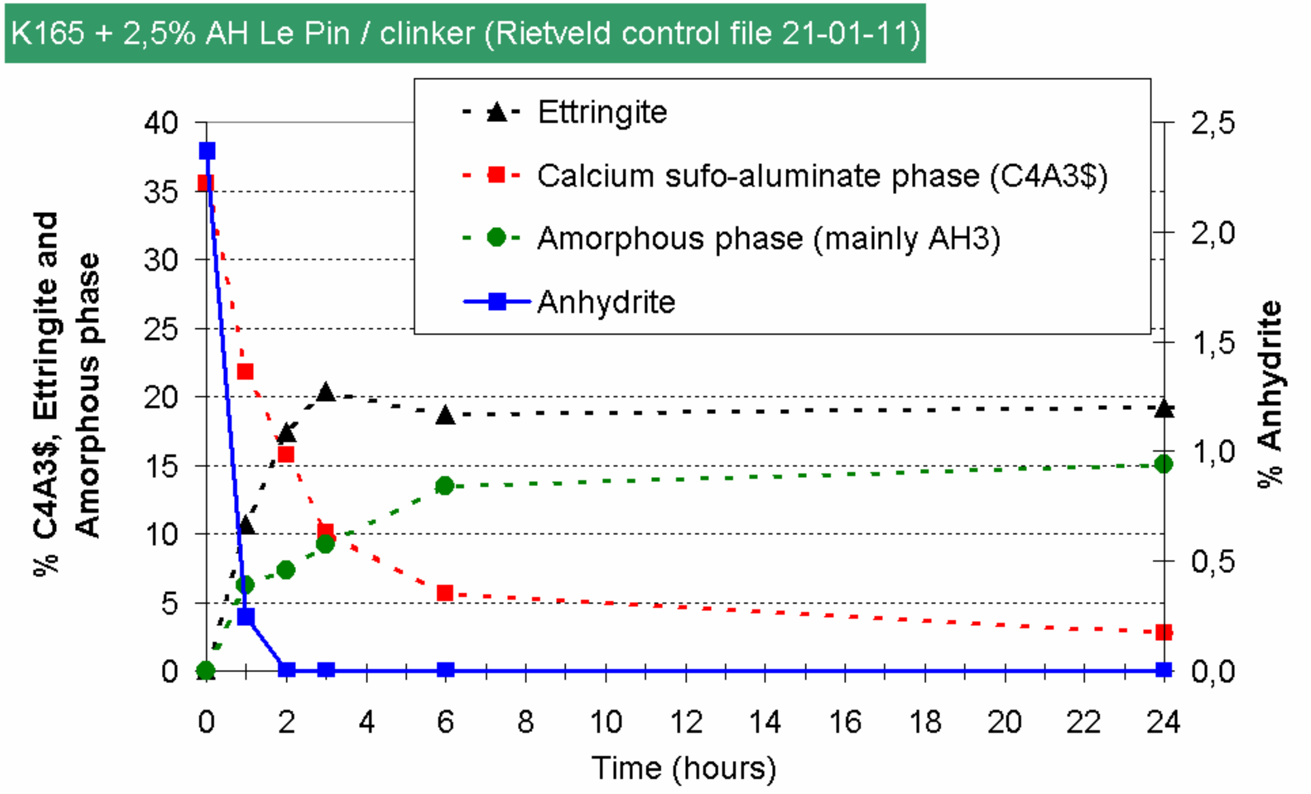
⇨ The ground clinker was then mixed with Anhydrite* (granulometry below 100 µm).

We used several different techniques to follow the hydration:

- DTA, TGA (on stopped samples)
- **XRD Rietveld (hydration stopped) → we have developed a specific control file dedicated to the quantification of hydrates.**
- Isothermal Calorimetry (20°C)
- Electrical Conductivity (20°C)

Aether™: hydration mechanism

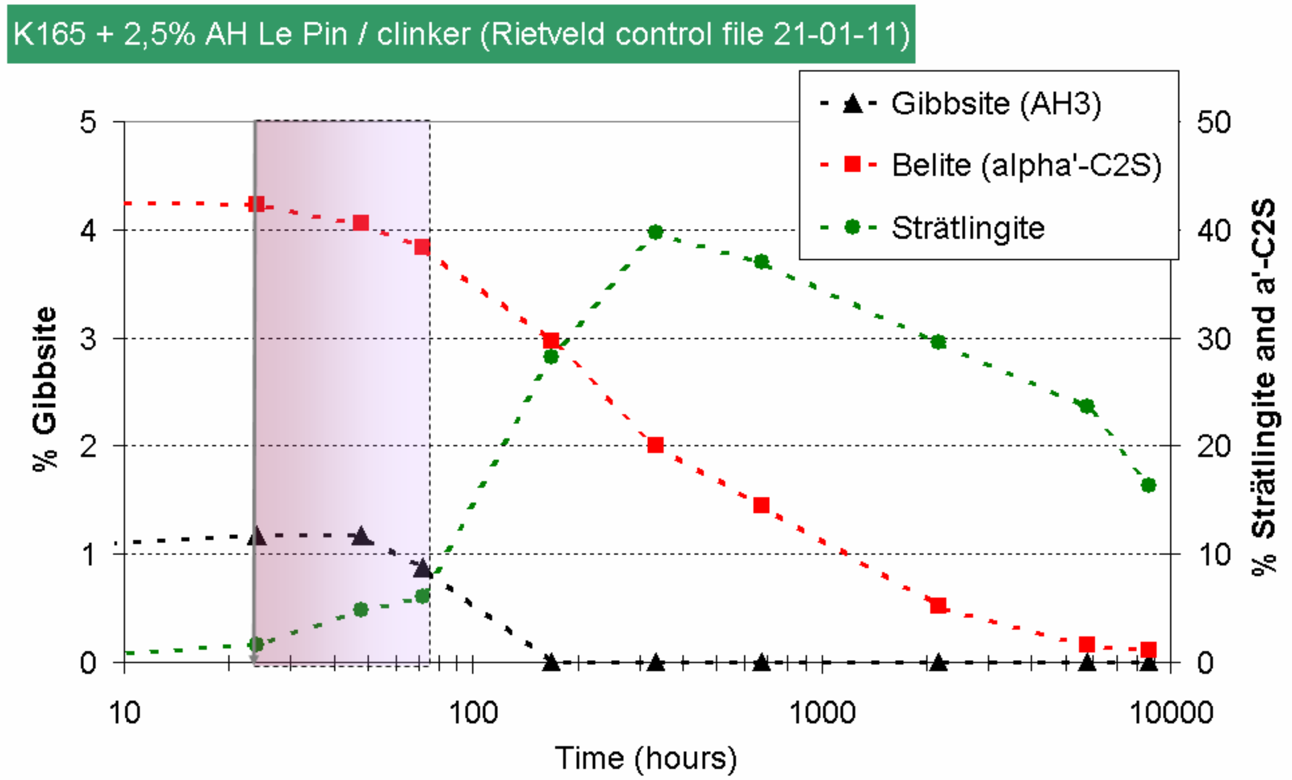
Step 1 : $C_4A_3\$$ hydration



$$C_4A_3\$ + 2C\$ + 38H \rightarrow C_3A \bullet 3C\$ \bullet 32H + AH_3$$

Aether™: hydration mechanism

Step 2: the beginning of C2S hydration

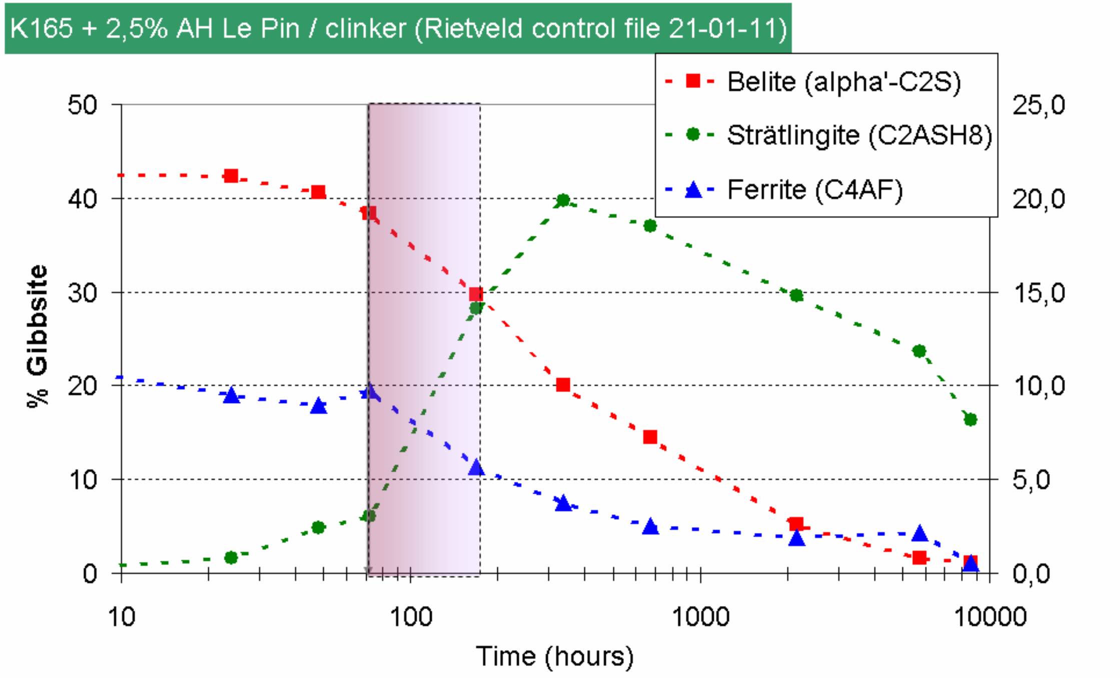


$C_2S + AH_3 + 5H \rightarrow C_2ASH_8$ (Strätlingite)

Aether™ : hydration mechanism

Step 3.1 : C_2S and beginning of $C_2(A,F)$ hydration

⇨ The ferrite phase can provide some alumina and is expected also to participate to the formation of an iron-substituted strätlingite

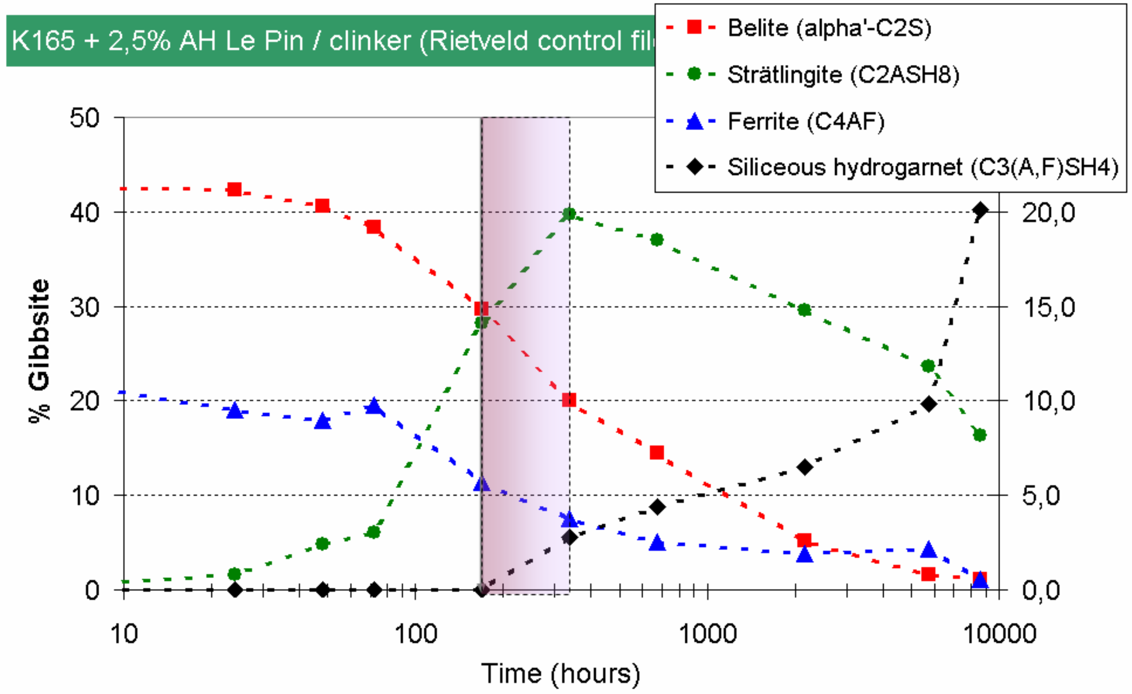


$C_2S + C_2\ (A,F) + 10H \rightarrow C_2(A,F)SH_8$ + Ca $^{2+}$ and OH^- in solution

Aether™ : hydration mechanism

Step 3.2 : C_2S and beginning of $C_2(A,F)$ hydration

⇨ As pH and calcium concentrations increase, siliceous hydrogarnet may be formed directly from C_2S and $C_2(A,F)$ hydration.



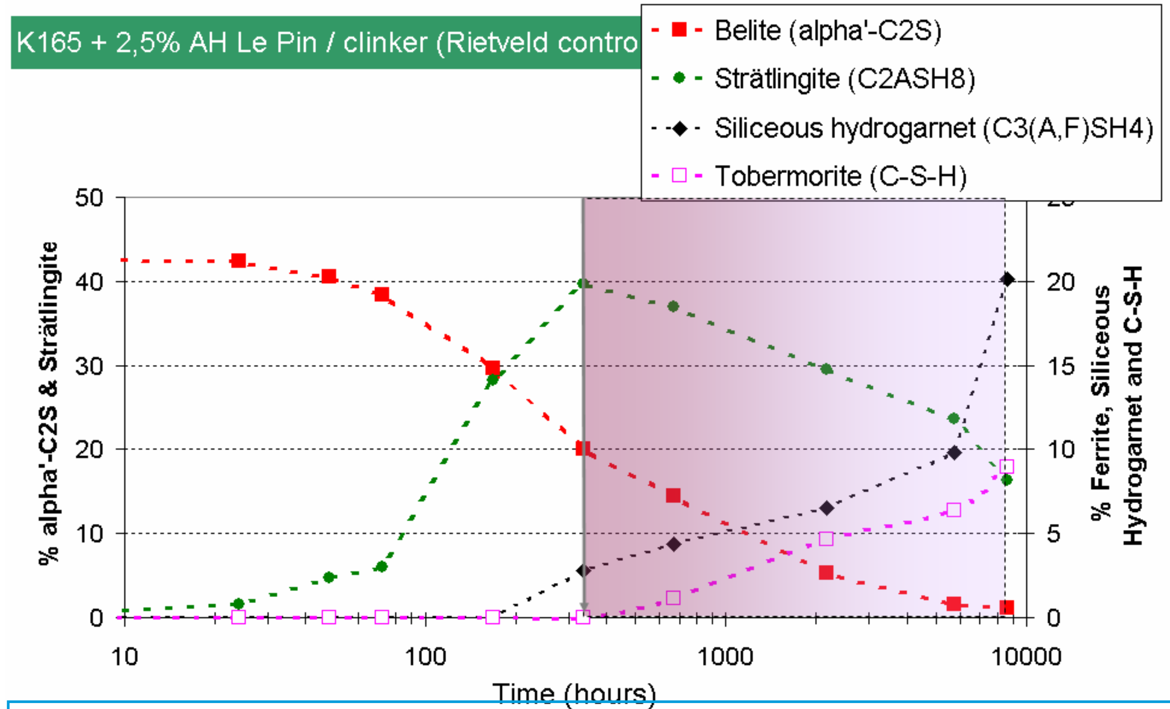
$C_2S + C_2(A,F) + 5H \rightarrow C_3(A,F)SH_4$ + Ca^{2+} and OH^- in solution

Aether™

Aether™ : hydration mechanism

Step 4 : middle and long term hydration

⇨ A middle term (14 days), Strätlingite is no longer stable and reacts with C_2S to form siliceous hydrogarnet and C-S-H (tobermorite peak detected by XRD).



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

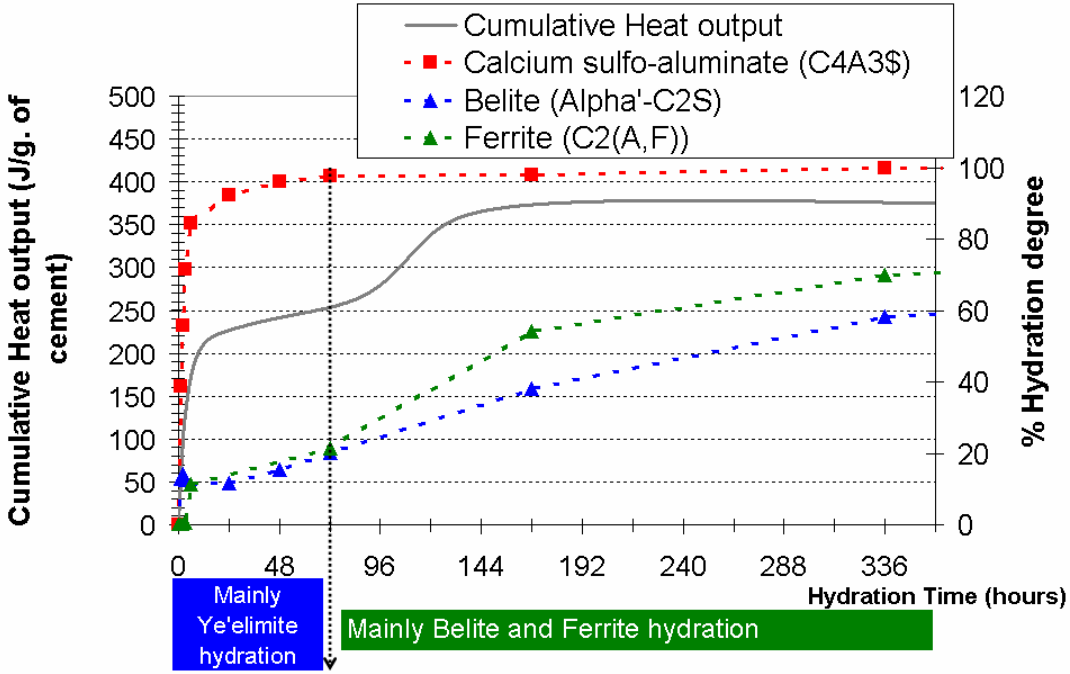
Aether™ : hydration mechanism

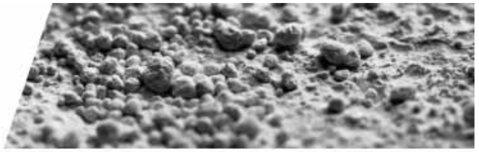
XRD Rietveld vs calorimetry methods

➩ The hydration kinetics of each anhydrous phase (determined by Rietveld quantification) is in good agreement with the evolution of the calorimetric values (cumulative heat flow) :

First period : Calcium Sulfo-Aluminate hydration.

Second period : Belite and Ferrite hydration.





Aether™: Conclusions

➪ Cements based on clinkers containing belite, calcium sulfoaluminate and ferrite phases seem to be a promising alternative to Portland cements. The major points are:

- ➪ Reduction of CO_2 emissions relative to Portland cements
- ➪ Use of similar raw materials and production in industrial installations used to make Portland cements
- ➪ Similar performance to Portland cements

➪ But, more research is needed on process, hydration and durability, in order to develop appropriate standards, before Aether™ cements can be considered a large-scale alternative to Portland cements.

Thank you !

Discussion…