CO2 - New Cements and Innovative Binder Technologies: AETHER (BCSAF) cements

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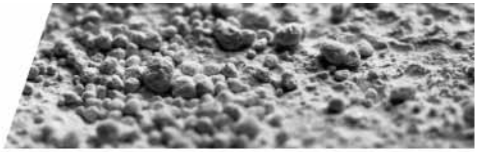
Aether™

LAFARGE & CO_2 - Some Figures

- In 2010, LAFARGE produced 130 Mt cement and emitted 95 Mt CO_2
- About 65% of the CO_2 related to decarbonation of limestone and 35% from fuel combustion
- Between 1990-2010, Lafarge decreased its net CO_2 emissions by 20% (from 774 to 630 kg CO_2/t_{cement}) i.e. a reduction of 20 Mt CO_2/yr
- Main conventional levers used to reduce 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…)



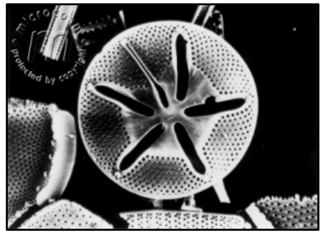
Some potential non-conventional solutions

- 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)

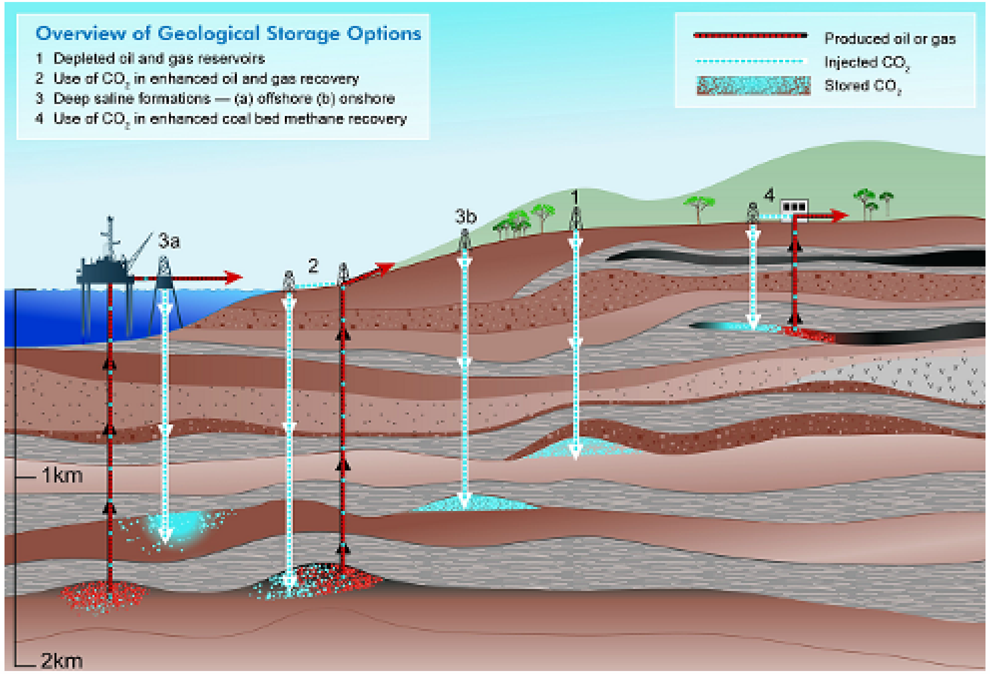
- Carbon Capture & Transformation (CCT): Micro-Algae



- Low CO2-intensive product development: AETHER

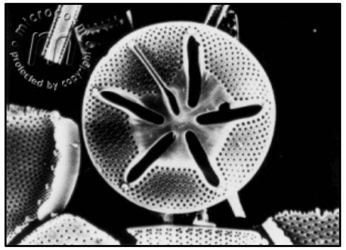
CCS – CO2 Storage in Deep Geological Formation

- 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** $+ O_2$

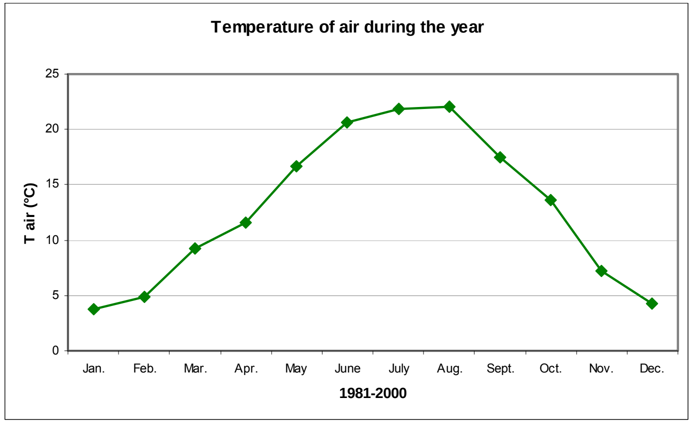
Bio-fuels
biodiesel / bioethanol / methanisation
High value products (omega-3…)

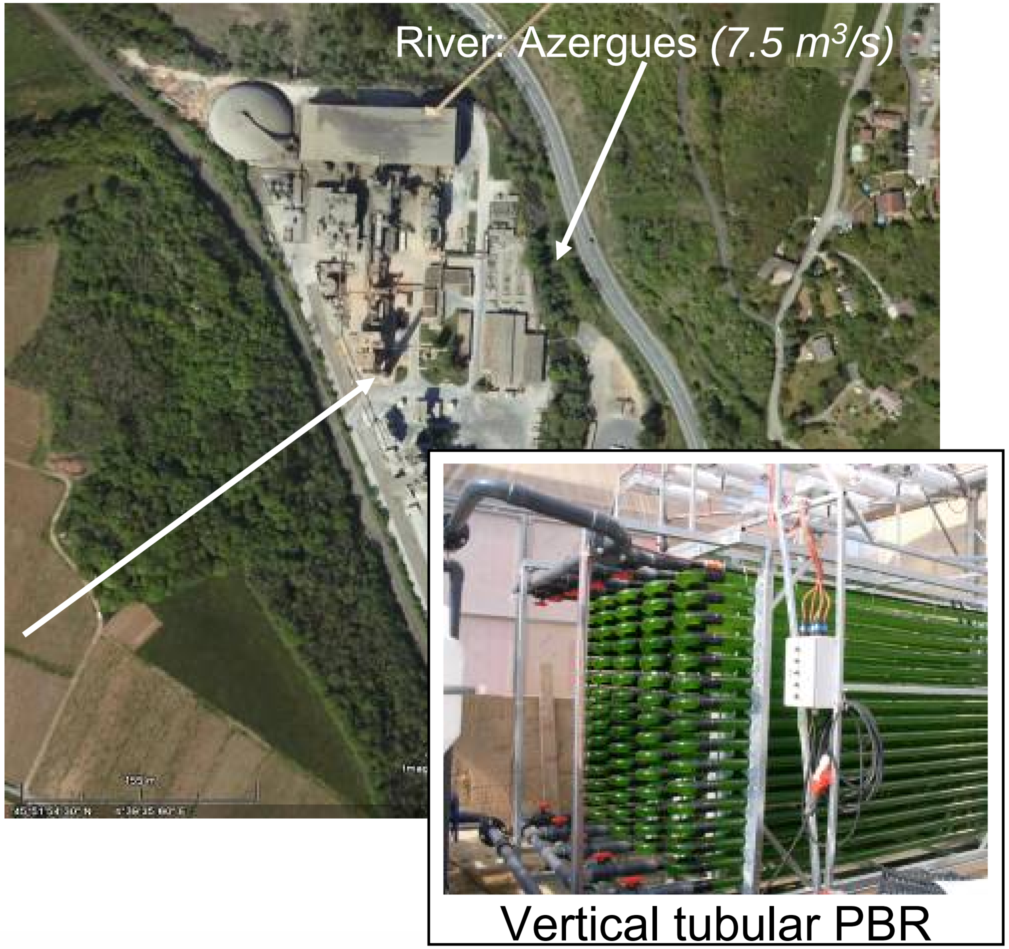
Objective:

- 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

(Facing south)

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

Website AETHER™: http://www.aether-cement.eu/

2003 **BCSAF**

Aether™ 9/2009

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

2013

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

Fundamental & applied research

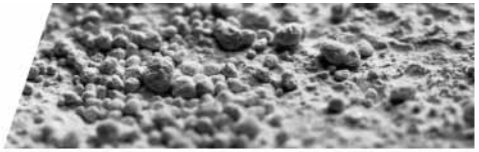
Industrial Pilot trials:
Validation of technical feasibility
Active communication

LCR research program

Aether™ cement: global presentation

- **Aether™** is a new, patented* class of low-CO_2 cements based on BCSAF clinkers containing:
  - Belite: C_2S 40 – 75%
  - Calcium sulfoaluminate (ye'elimite): C4A3$ 15 - 35 %
  - Ferrite : $C_2(A,F)$ 5 – 25%
  - Minor phases: 0,1 – 10%

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



Aether™ : CO2 emissions and manufacturing

⇨ **Aether™** is based on a mineralogical phase composition with lower CO_2 emissions per clinker unit

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
$C_2(A,F)$ (ferrite)	Limestone + Alumina + iron oxide	0.362
$C_4A_3\$$ (ye'elimite)	Limestone + alumina + anhydrite	0.216

Aether™ { C_2S (belite), $C_2(A,F)$ (ferrite), $C_4A_3\$$ (ye'elimite)

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

Aether™ cement: CO2 emissions and manufacturing

'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%
- $C_{2(}A,F)$

Aether™ raw mix

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

- **Aether™** main characteristics vs. Portland:
  - Higher Alumina and SO_3 content and lower LOI of the raw mix = lower $CaCO_3$
  - No C_3S, but $C_4A_3\$$ & higher C_2S content

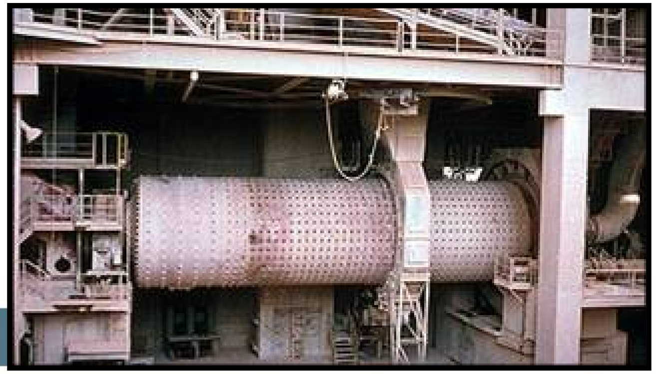
Aether™ Industrial Trial 2011 (Life+) Cement plant in France (Burgundy)

- Objectives
  - Produce AETHER clinker at industrial plant to prove industrial feasibility
  - CO_2 balance validation vs Portland
  - Process experience
  - Produce Aether™ clinker for cement and concrete testing
- Main figures
  - Lepol grate process : semi-dry
  - 7 days of clinker production + 7 days for preparation
  - ~8000t of Raw mix
  - ~5500t of clinker produced

Aether™ cement: CO2 emissions and manufacturing

- **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°C) than for Portland cement clinker (1400 – 1500°C)
  - with significantly lower energy than Portland cement clinker
  - Aether cement grinding energy is 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)



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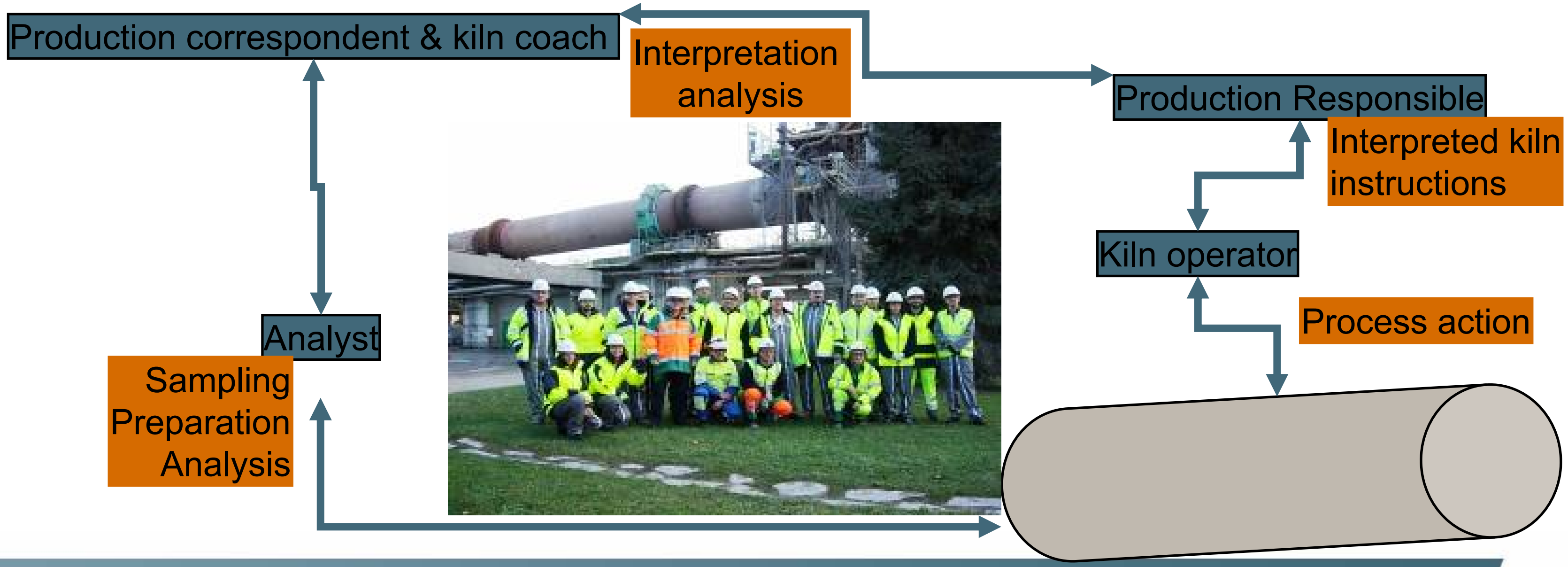
Aether™ Industrial Trial 2011
Cement plant in France (Burgundy)

➢ Specific Organization

- Various competences involved: Plant + Research Center + Technical Center (Eur.+ NA) + Plant experts + Corporate (Communication-Marketing)
- More people involved in shift rotation 24/24, 7/7 as for routine production
- Loop : sampling-analysis-interpretation-process-action



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Aether™ Industrial Trial 2011
Cement plant in France (Burgundy)

- Key points for clinkering control
  - Pelletizing
  - Clinkering
  - Raw mix

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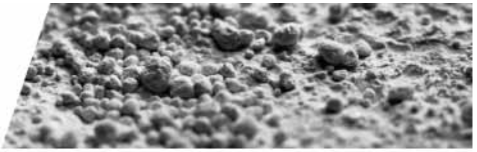
Aether™ Industrial Trial 2011
Cement plant in France (Burgundy)

- Keys points for clinkering control
  - **Raw mix**
    - Quarry + Prehomogenization pile constitution chemistry vs target
      - No technical modification vs Portland production
      - Increased frequency of analytical control
  - **Raw materials**

=> same as for Portland clinker

=> only proportions change vs Portland depending on the final raw mix target

- Limestone
- Marl
- Bauxite
- Iron oxide
- Gypsum

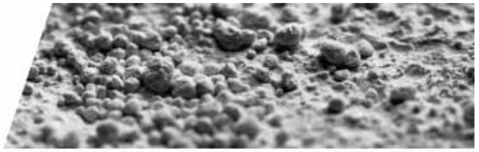


Aether™ Industrial Trial 2011
Cement plant in France (Burgundy)

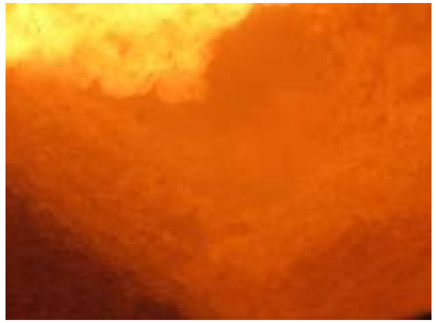
- Keys points for clinkering control
  - **Pelletizing**

    => specific to the Lepol grate process

    - Pellet size (min, max, homogeneity)
      - Control by specific tool developed by the plant based on image analysis
    - Water content
      - Adjusted to obtain target size
      - 10% less than for Portland due to the raw materials proportion : more marl, less limestone

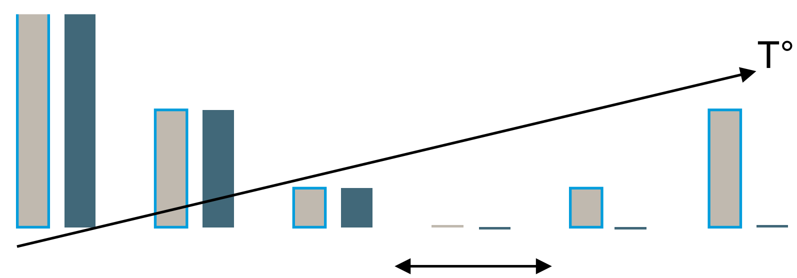


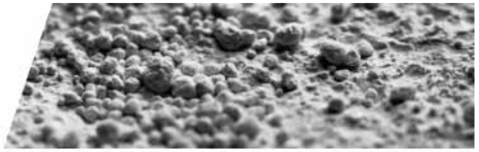
Aether™ Industrial Trial 2011
Cement plant in France (Burgundy)



- Keys points for clinkering control
  - Clinkering - Process parameters
    - **Temperature in clinkering zone**
      - Must be kept within a very narrow range
      - T° low = clinker under burnt, uncompleted combination (free lime, $C_{12}A_7$)
      - T° high = clinker over burnt (loss of "easy" grindability), C4A3$ decomposition, SO_2 emission, ring formation or **melting**

      ⇒ kiln stop





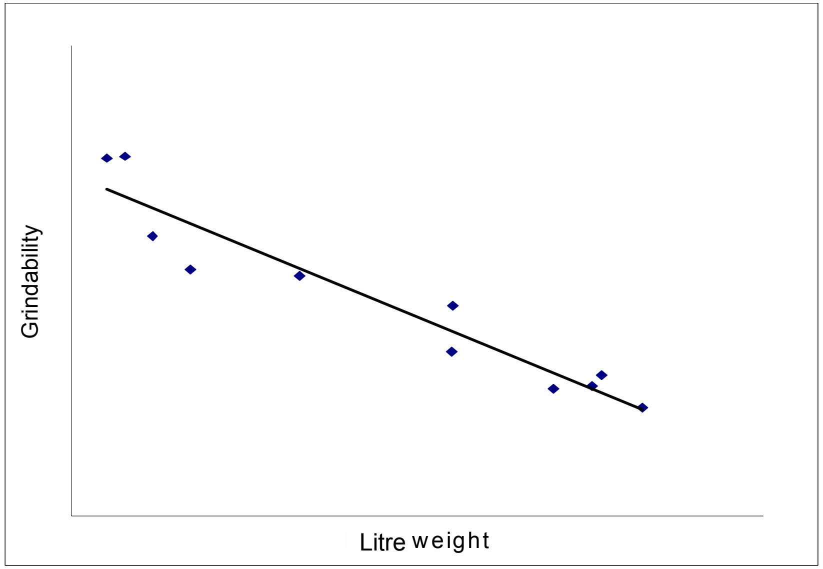
Aether™ Industrial Trial 2011
Cement plant in France (Burgundy)

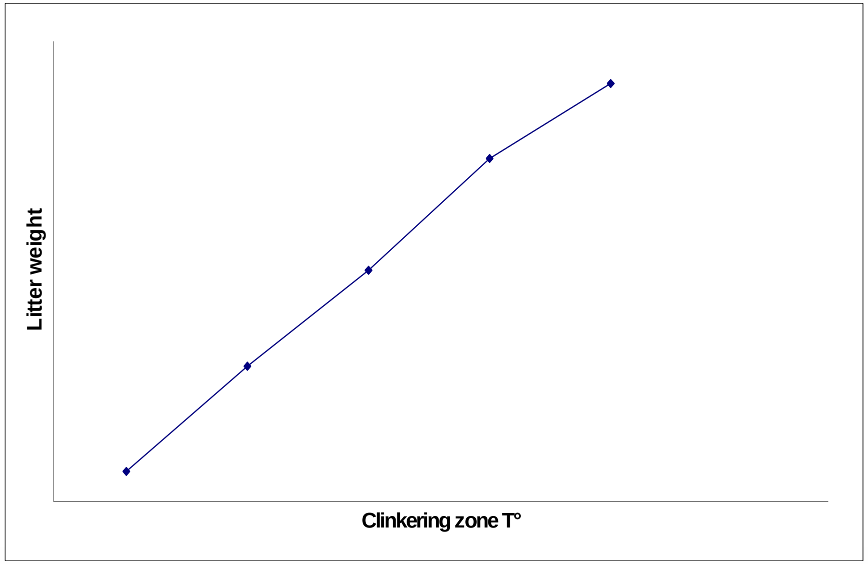
- Keys points for clinkering control
  - Clinkering – Monitoring of Process parameters
    - **Gas emission: NOx, SO_2**
      - Due to lower temperature, **NOx is reduced** vs Portland
      - SO_2 emission is linked to clinkering temperature:
        - If raw mix well designed + clinkering temperature correct, $\Rightarrow$ same SO_2 emissions as for Portland
      - Raw mix and/or T° not strictly monitored = problems SO_2 ⇑

Aether™ production is **similar to Portland** production, but a **higher level of control is needed** for each process step: raw mix design, raw meal preparation, clinkering

AetherTM Industrial Trial 2011
Cement plant in France (Burgundy)

- Keys points for clinkering control
  - Clinkering - Clinker specific parameters
  - **Liter weight**
    - Manual control vs. gamma-densitometer: good correlation
    - Directly linked to temperature in the clinkering zone
    - To be maintained low in order to keep grinding energy low





Aether™ Industrial Trial 2011
Cement plant in France (Burgundy)

- Lafarge developed a special Rietveld control file for Aether™ clinker production control.
  - Identify and quantify the different mineralogical phases including their polymorphs ex: α' and β-C_2S of Aether™

- Most important quality control tool: **X-ray diffraction + Rietveld**

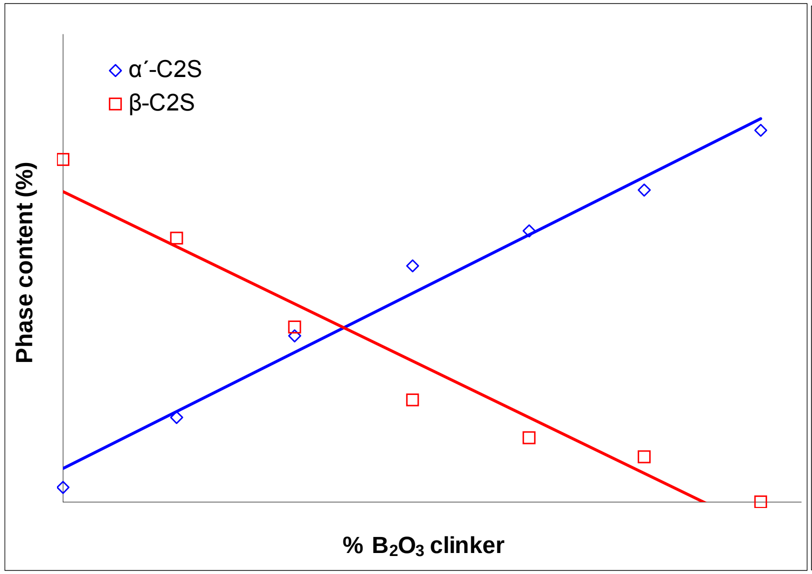
Many thanks to the excellent & professional support of PANalytical during the pilot trial

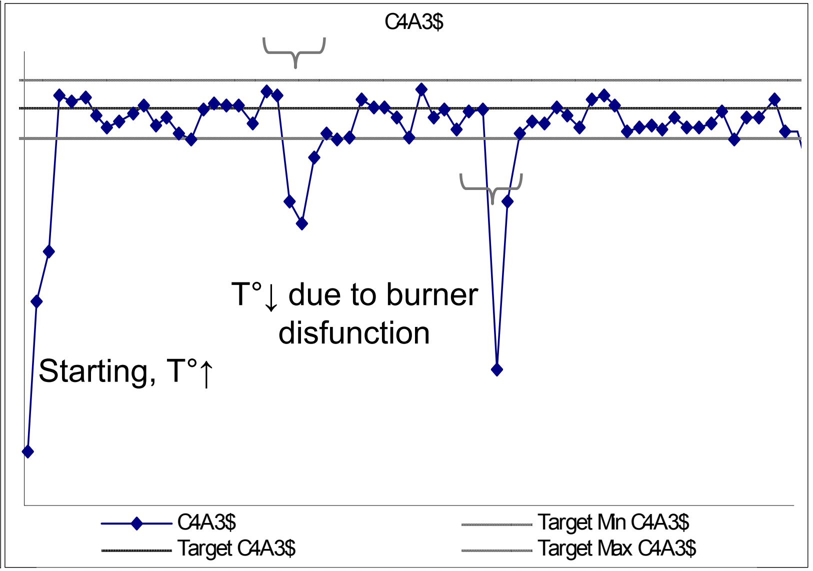
Special thanks to Dr. Füllmann

- Following equipment was used: PANalytical Cubix + Axios

Aether™ Industrial Trial 2011
Cement plant in France (Burgundy)

- Keys points for clinkering control
  - Clinkering - Clinker parameters
    - XRD following the mineralogy

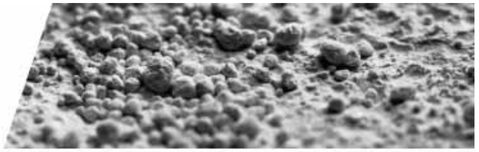




Perfect quantification of α' formation
= control of boron addition

Perfect quantification of phase formation
= control of clinkering process

Aether™



Aether™: Conclusion

AETHER cements based on clinkers containing belite, calcium sulfoaluminate and ferrite seem to be a promising alternative to Portland cements.

⇨ 20%-30% Reduction of CO_2 emissions relative to Portland cements

⇨ Use of similar raw materials and production in existing industrial installations

⇨ Similar concrete 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 cement.

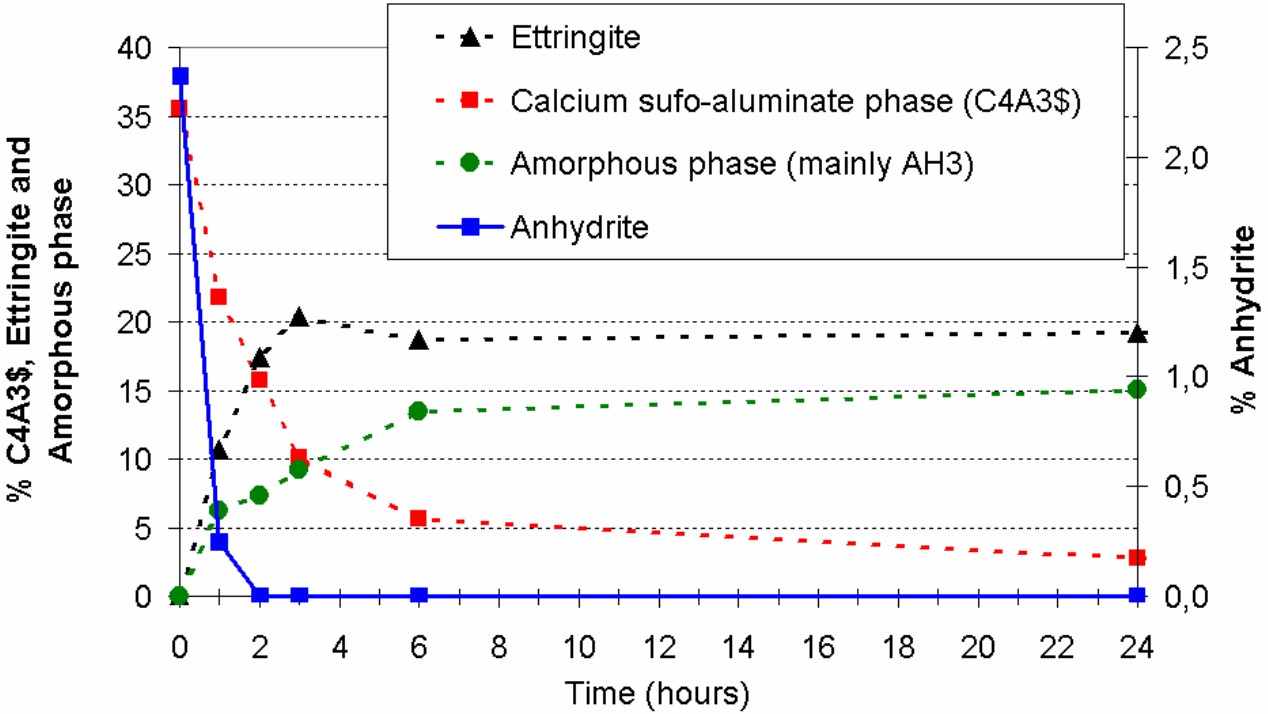
Thank you !

Discussion…

Aether™: hydration mechanism

Step 1 : $C_4A_3\$$ hydration

K165 + 2,5% AH Le Pin / clinker (Rietveld control file 21-01-11)



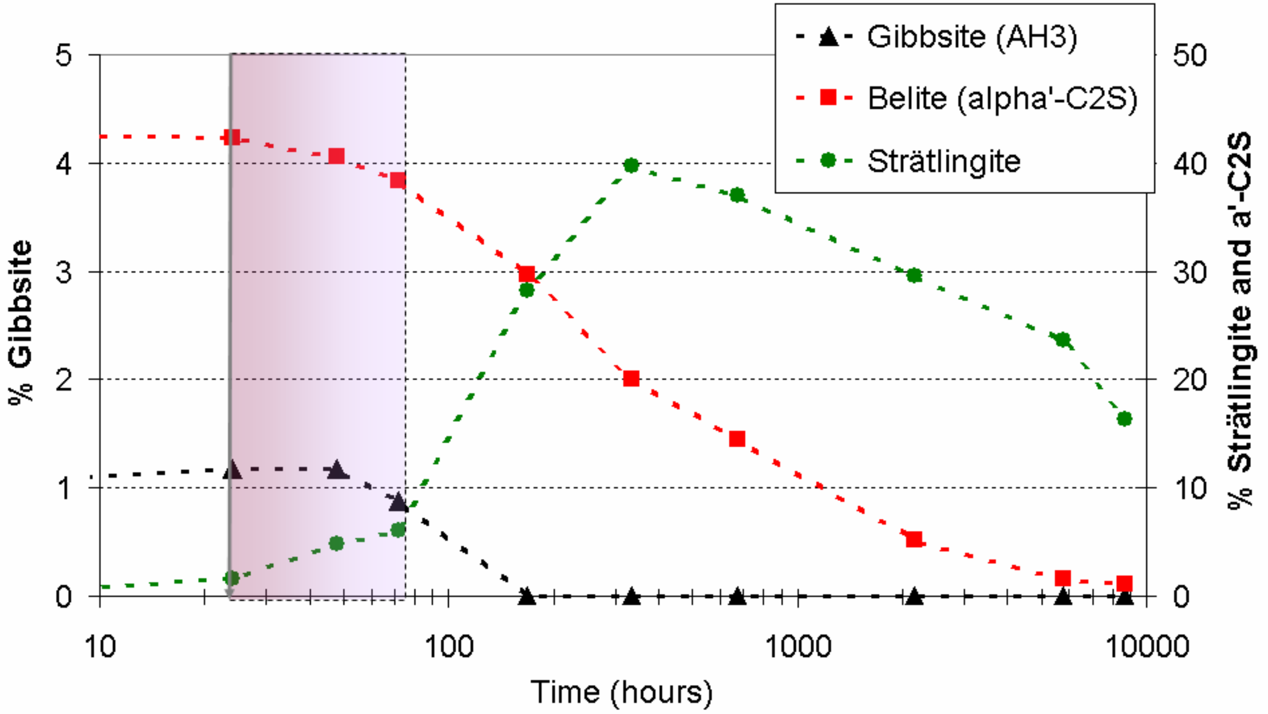
$$C_4A_3\$ + 2C\$ + 38H \rightarrow C_3A \bullet 3C\$ \bullet 32H + AH_3$$

Aether™

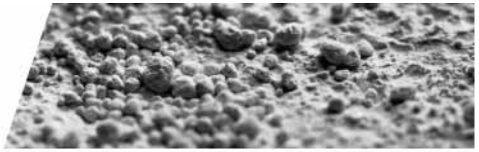
Aether™: hydration mechanism

Step 2: the beginning of C2S hydration

K165 + 2,5% AH Le Pin / clinker (Rietveld control file 21-01-11)



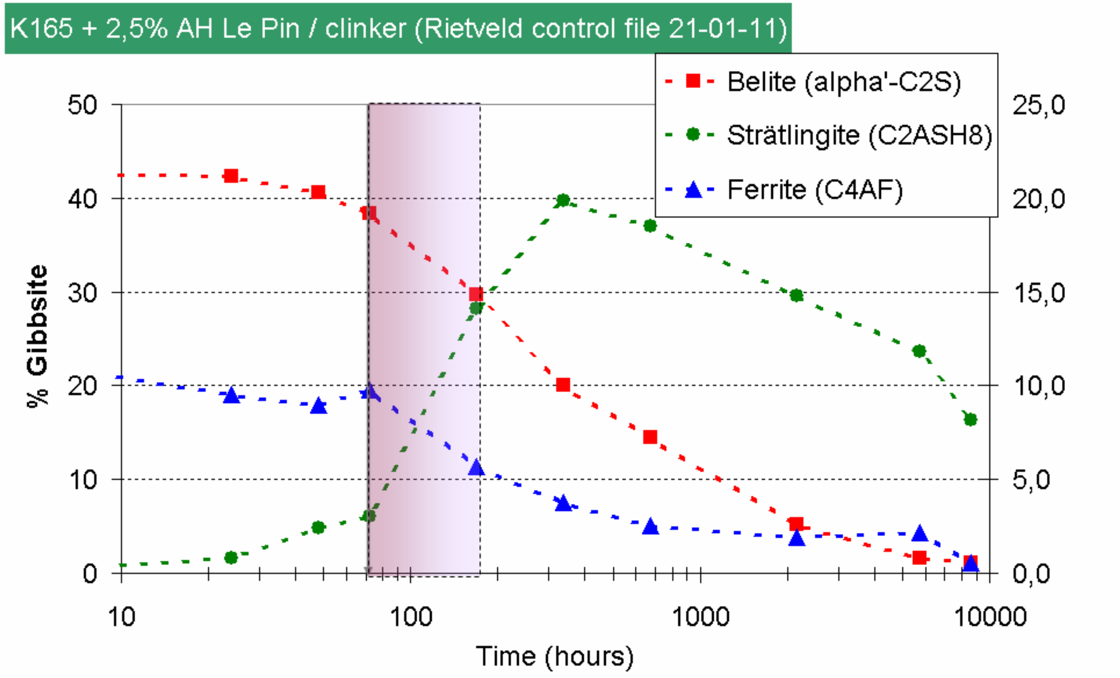
$C_2S + AH_3 + 5H \rightarrow C_2ASH_8$ (Strätlingite)



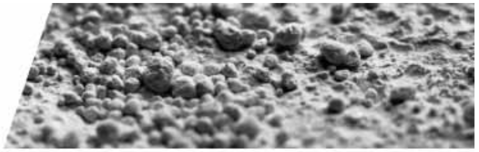
Aether™ : hydration mechanism

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



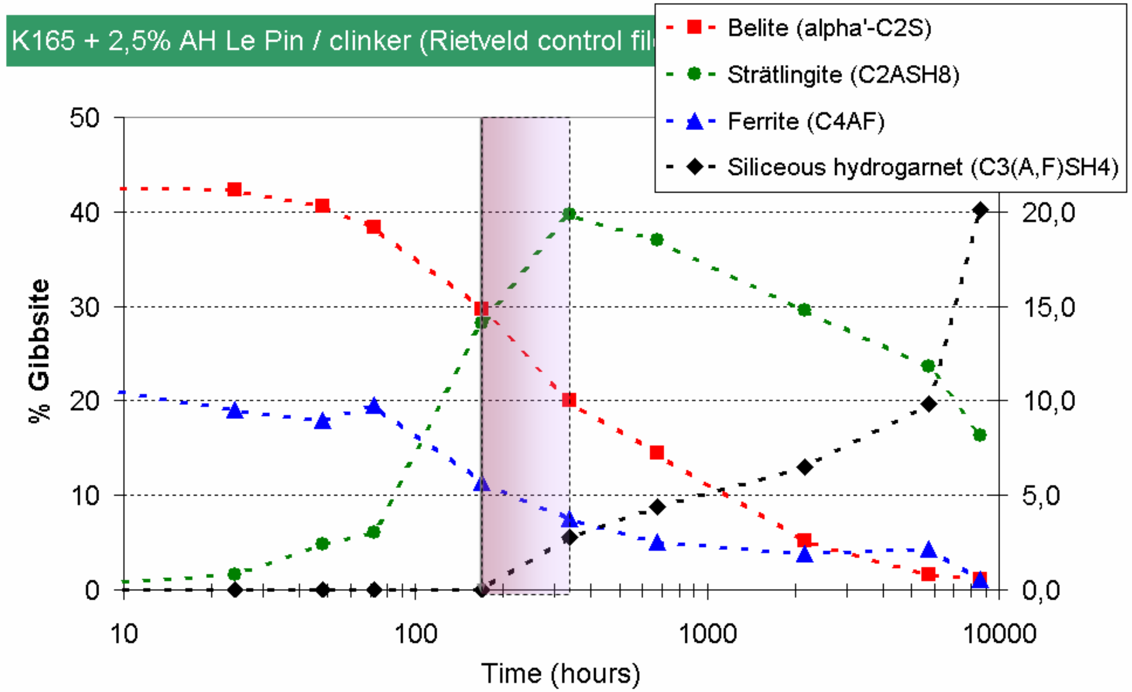
$C_2S + C_2\,(A,F) + 10H \rightarrow C_2(A,F)SH_8$ + Ca $^{2+}$ and OH^- in solution



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.

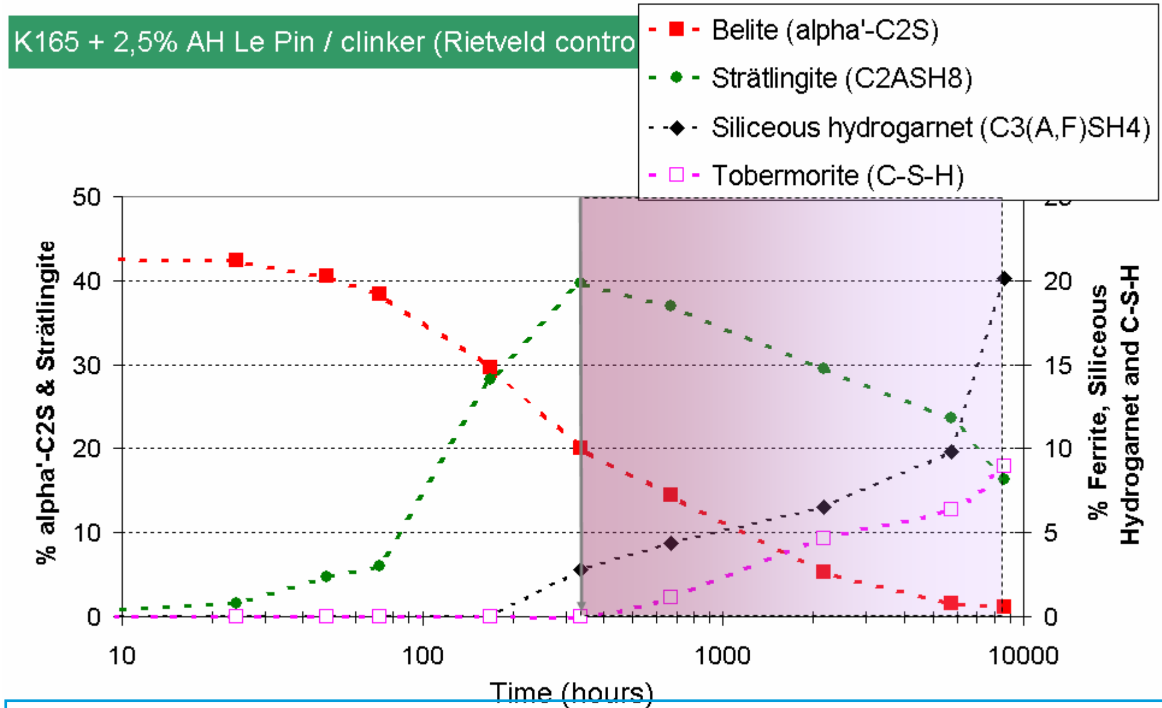


$C_2S + C_2(A,F) + 5H \rightarrow C_3(A,F)SH_4$ + Ca^{2+} and OH^- in solution

Aether™ : 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.