Hydration of Belite Calcium Sulfo-Aluminate cement Aether™

ICCC Madrid – July 4th 2011
Lafarge & CO₂ - Some Figures

- About 65% of the CO₂ comes from the limestone and 35% from the fuel.
- Between 1990-2010, Lafarge decreased its net CO₂ emissions by 20% (from 774 to 630 kg CO₂/t<sub>cement</sub>).
- Main conventional levers used to mitigate CO₂:
  - 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$^{TM}$
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™ 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 %

Aether™ clinker

- **‘Portland’ raw mix**
  - LOI: ~35%
  - SiO₂: ~14%
  - Al₂O₃: ~3%
  - Fe₂O₃: ~3%
  - CaO: ~43%
  - SO₃: ~0.3%

- **‘Portland’ clinker**
  - C₃S: ~65%
  - C₃A: ~6%
  - C₂S: ~15%
  - C₂(A,F): ~12%

- **Aether™ clinker**
  - C₄A₃$: ~25%
  - C₂S: ~55%
  - C₂(A,F): ~20%

- **Aether™ raw mix**
  - LOI: ~29%
  - SiO₂: ~12%
  - Al₂O₃: ~11%
  - Fe₂O₃: ~5%
  - CaO: ~37%
  - SO₃: ~3%

- **Aether™ main characteristics / Portland:**
  - High Alumina and SO₃ content and lower LOI in the raw mix = lower CaCO₃
  - No C₃S; C₃A replaced by C₄A₃$; high C₂S 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 ($\approx 1225 - 1300$°C) than for Portland cement clinker
  - with significantly lower energy than Portland cement clinker
  - Aether cement grinding energy is generally lower than for OPC

The manufacturing of Aether™ generates 20 to 30% less $\text{CO}_2$ 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

<table>
<thead>
<tr>
<th>Ye’elimite</th>
<th>Belite</th>
<th>Ferrite</th>
<th>Anhydrite</th>
</tr>
</thead>
<tbody>
<tr>
<td>~28%</td>
<td>~ 48%</td>
<td>~18%</td>
<td>~6%</td>
</tr>
</tbody>
</table>
Aether™ hydration

- Global hydration in two main steps:

**STEP 1**
- Mixing ($t_0$)
- No more solid calcium sulfate
- Main reactive phases:
  - $C_4A_3$ (Ye’elimite)
  - $C$ (calcium sulfate)

**STEP 2**
- HYDRATION TIME
- Main reactive phases:
  - $C_2S$ (Belite)
  - $C_2(A,F)$ (Ferrite)
Aether™ hydration

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

Step 2: middle and long term strength given by Belite and Ferrite hydration
Aether™ hydration: Step 1

\[ \text{C}_4\text{A}_3\$ + 2 \text{C}\$ + 36\text{H} \rightarrow \text{C}_3\text{A},3\text{C}\$,32 \text{H} + 2 \text{AH}_3 \]

- Ettringite (crystalline form)
- Amorphous or poor crystallised form

▼ 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

<table>
<thead>
<tr>
<th>Time</th>
<th>TGA measurement (20-220°C)</th>
<th>XRD Rietveld</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Weight loss</td>
<td>Calculated Mass of Ettringite</td>
</tr>
<tr>
<td>1h</td>
<td>8.5% (9.6 g of water)</td>
<td>21 g</td>
</tr>
<tr>
<td>3h</td>
<td>10.6% (13.6 g of water)</td>
<td>27 g</td>
</tr>
</tbody>
</table>

▲ XRD Rietveld analysis

→ Quantification of Ettringite in good agreement between XRD and TGA.
Aether™ hydration: Step 1

<table>
<thead>
<tr>
<th>Time</th>
<th>TGA measurement (220-450°C)</th>
<th>XRD Rietveld</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Weight loss</td>
<td>Calculated Mass of AH3</td>
</tr>
<tr>
<td>1h</td>
<td>2.6% (2.8 g of water)</td>
<td>8.2 g</td>
</tr>
<tr>
<td>3h</td>
<td>3.7% (4.3 g of water)</td>
<td>12.4 g</td>
</tr>
</tbody>
</table>

The amount of AH3 measured by TGA corresponds well to the amorphous phase calculated by XRD Rietveld refinement.
Aether™ hydration: Step 2

- $C_2S + AH_3 + 5H \rightarrow C_2ASH_8$ (Stratlingite)

- $C_2S + C2(A,F) + 5H \rightarrow C_3(A,F)SH_4$ (Hydrogarnet) + Ca$^{2+}$ 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
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.
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.