**Introduction**

Concrete is made of cement, water, rock, and sand.

**Worldwide most used cement is Portland cement.**

- **Decomposition of limestone** (60% of the total CO₂ generated in the process)
- **Combustion of fuel** to reach 1450°C (40% of the total CO₂ generated in the process)

Production step is the most emissive step.

**Solutions to reduce the CO₂ footprint of cement**

- **Replacing a proportion of the fossil fuel by alternative fuels**
  - Biomass
  - Waste tires
  - Waste oil, Plastics

- **Partial substitution of raw materials**
  - Partial replacement of cement raw materials: municipal waste incinerator ash
  - Mineralizers: fluorine and SO₃

- **Developing green binders**
  - Low CO₂ binders

- **Partial substitution of cement by supplementary cementitious materials (SCMs)**

- **Use of alternative cements**
  - Inorganic materials

**Alternative cement: concept and requirements**

- An alternative cement is an inorganic cement that can be used as a complete replacement of Portland cement or blended hydraulic cements.

To be considered as a good opportunity, it needs to respect a set of requirements:

- Raw materials must be globally abundant, locally available in order to have a small transportation distances + obtainable at low cost
- Stable quality of raw materials and composition for a stable production
- Technical feasibility at industrial scale
- Lower CaO demand in the final products
- Possibility of recycling of its own waste and by-products
Motivation to develop alternative cements

- Lower environmental impact
- The need for specific properties (unattainable with Portland cement)
- Rapid strength development
- Specific durability requirements: improve ASR performance, better resistance to sulfate and chloride
- Reduced cost (both initial and life cycle cost)

A wide range of alternative cements

- Calcium Aluminate Cement (CAC)
- Calcium Sulfoaluminate Cement (CSA)
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- etc...

Calcium aluminate cement (CAC)

Hydraulic cement also known as "high-alumina cement, HAC" and "ciment fondu"

Was first developed as a replacement to the poor resistance of Portland cement to sulfate environments

This cement is a fast setting cement but it is not stable

Was widely used to repair runways during World War II

Ref: Lea’s Chemistry of Cement and Concrete - 5th edition, 2019

Calcium aluminate reactive phases

Amorphous: one amorphous phase

Limestone + Bauxite θ 1450-1600°C

Sintered or fused

CAC

the only suitable mineral on a scale for cement production
### Manufacturing process of CACs

- The alumina content is the main factor that determines the manufacturing method.
- **Reverberatory furnace (Fusion)**: Most common method.
- **Rotary kiln**: Production of standard grades (>40% Al₂O₃).

### Composition range for CAC

<table>
<thead>
<tr>
<th>Grade</th>
<th>Colour</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>SiO₂</th>
<th>Fe₂O₃ + FeO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard/low alumina</td>
<td>Grey or buff to black</td>
<td>36 - 42</td>
<td>36 - 42</td>
<td>3 - 8</td>
<td>12 - 20</td>
</tr>
<tr>
<td>Low alumina, low iron</td>
<td>Light buff or grey to white</td>
<td>48 - 60</td>
<td>36 - 42</td>
<td>3 - 8</td>
<td>1 - 3</td>
</tr>
<tr>
<td>Medium alumina</td>
<td>White</td>
<td>65 - 75</td>
<td>25 - 35</td>
<td>&lt; 0.5</td>
<td>&lt; 0.5</td>
</tr>
<tr>
<td>High alumina</td>
<td>White</td>
<td>≥ 80</td>
<td>&lt; 20</td>
<td>&lt; 0.2</td>
<td>&lt; 0.2</td>
</tr>
</tbody>
</table>

### Mineralogy of CAC

- **5 intermediate calcium aluminate phases:**
  - Tricalcium aluminate (Ca₃Al₂O₆, C₃A): produces flash set if C₂S is not added.
  - Dodecalcium hepta-aluminate (Ca₁₂Al₁₄O₃₃ or C₁₂A₇): always present in CAC.
  - Monocalcium aluminate (CaAl₂O₄ or CA₂): Main component >40%.
  - Monocalcium dialuminate (CaAl₄O₇ or CA₂): found in higher-alumina grade.
  - Monocalcium hexa-aluminate (CaAl₁₂O₁₉ or CA₆): rarely present.

### Microstructure of CAC

- **Crystalline CAC**: Polyphase: several phases.
- **Amorphous CAC**: One phase chemically homogeneous that includes all the components of CAC.

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*Ref: Lea’s Chemistry of Cement and Concrete, fifth edition, 2019.*
Hydration of CAC with water alone

- The hydration of CAC depends on temperature and age

\[ \text{CA} + 10\text{H} \rightarrow \text{CAH}_{10} \]
\[ 3\text{CA} + 11\text{H} \rightarrow \text{C}_{2}\text{AH}_8 + \text{AH}_3 + 3\text{H}_2 \]

Metastable hydrates (hexagonal aluminate hydrate)

Stable hydrates (cubic hydrates)

- Conversion process impacts properties (strength and durability): led to some damage in the past

How can this conversion process be avoided/reduced? → change the phase assemblage

SCMs addition to reduce conversion of CAC

- Silica fume and GGBS favour the formation of strätlingite (C$_2$ASH$_8$) instead of C$_3$AH$_6$

CAC with GGBS:

- Conversion process impacts properties (strength and durability): led to some damage in the past

CaSO$_4$ (C$_3$S) to reduce conversion of CAC

- C$_3$S addition: new hydrates appear and metastable hydrates formation is reduced

\[ 3\text{CA} + 3\text{C}_3\text{S}_4 + (38-3x)\text{H} \rightarrow \text{C}_3\text{A} \cdot 3\text{C}_3\text{S} \cdot \text{H}_{32} + 2\text{AH}_3 \]

- After C$_3$ depletion monosulfoaluminate is formed

\[ 6\text{CA} + \text{C}_3\text{A} \cdot 3\text{C}_3\text{S} \cdot \text{H}_{32} + 16\text{H} \rightarrow 3\text{C}_3\text{A} \cdot \text{C}_3\text{S} \cdot \text{H}_{13} + 4\text{AH}_3 \]

CaSO$_4$ to reduce conversion of CAC

- CaSO$_4$ filled the voids

- Total porosity

- Strengths were improved
**Blends of CAC with PC and C$**

- Hydration is different from pure CAC systems.
- CAC, C$, and PC proportions can be varied depending on the desired properties.

Zone 1: binary system of CAC and PC: quick or flash setting → small repair works

Zone 2: addition of C$ to avoid flash setting

Zone 2→3: reduction of PC: Ettringite is a major hydrate

Rapid strength development
Rapid drying
Shrinkage compensation

Zone 1, 2 and 3 are the most important composition zones from an application standpoint.


**Main hydration product**

Ettringite

$3CaO.Al_2O_3.3CaSO_4.32H_2O$

**Low density 1.8g/cm³**

High water content

Good space filling

Crystallographic hexagonal cell

Other hydrates also forms...

<table>
<thead>
<tr>
<th>Binder phase</th>
<th>Ions</th>
<th>Hydrates</th>
</tr>
</thead>
<tbody>
<tr>
<td>CA/Al(OH)$_4$</td>
<td>Ca$^{2+}$</td>
<td>C$_3$A$_3$H (AFt)</td>
</tr>
<tr>
<td>CA/Al(OH)$_4$</td>
<td>Ca$^{2+}$</td>
<td>C$_3$A.C$.H$ (AFm)</td>
</tr>
<tr>
<td>CA/Al(OH)$_4$</td>
<td>SO$_4^{2-}$</td>
<td>C-S-H</td>
</tr>
</tbody>
</table>

**Morphology of ettringite**

Low density 1.8g/cm³

High water content

Good space filling

Ref: Lea's cement chemistry book, 2019

**Schematic evolution of hydrates**

**Compressive strength**

- Limestone
  - Early age: Limestone acts as fillers → has a physical effect and strongly affect the kinetics
  - Late age: Limestone reaction depends on the amount of calcium sulfate in the system
  - IF C$ reacts completely → the remaining CA will react with calcite → Hc and Mc formation
  - IF C$ remaining → Limestone acts as fillers

- Slag
  - Early age: Slag acts as fillers during the first 4 days
  - Late age: Sulfate depletion → pH increases → the slag release silica → C$_2$ASH$_8$ (Strätlingite) formation
  - With an excess of C$ → pH stays below 11.5 and thus the slag dissolution is slowed down

Ref: J. Bizzozero, EPFL thesis (2014)
Examples of applications of CAC

- Repair of precast element
- Fixing mortar on road surface
- Self-leveling underlay
- Repairs of airport runways and ramps

A wide range of alternative cements

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Calcium sulfoaluminate cement (CSA)

- Main anhydrous phase of CSA is Ye’elimite: \( \text{Ca}_4\text{Al}_6\text{O}_{12}(\text{SO}_4) \rightarrow 30-70\% \
- Is a Ye’elimite rich-cement
- Was patented in 1960 by Klein, the aim was to achieve shrinkage compensation
- Same raw materials as PC: Limestone, clay, bauxite and calcium sulfate
- CSA has lower CaO and SiO\(_2\) but far higher Al\(_2\)O\(_3\) and SO\(_3\) compared to PC

Ye’elimite rich-cements type

- Ye’elimite rich-cements can be classified in two groups:
  - High belite cement, known as BYF: with/without Boron
    - Main mineralogical phases are: belite \( \text{C}_2\text{S} \), \( \text{C}_4\text{A}_\text{S} \) and ferrite \( \text{C}_4\text{AF} \)
  - Low belite cement, known as CSA
This cement can be also easier ground in the manufacturing process of CSA. Alternative cements, such as Ye’elimite-rich cements, have great advantages in terms of capital investment costs. Raw materials include Al-rich (Kaolin, Bauxite) with less limestone requirement. Lower clinkering temperature (~1250°C ± 50°C) results in a significant reduction in CO₂ emissions from calcination.

**Manufacturing process of CSA**

1. Raw materials:
   - Al-Rich (Kaolin, Bauxite)
   - Less limestone requirement
2. Clinker + gypsum or anhydrite
   - This cement can be also easier ground
3. Lower clinkering temperature = 1250°C ± 50°C

**Raw Materials**

- Limestone
- Al-rich (Kaolin, Bauxite)
- Gypsum/Anhydrite

<table>
<thead>
<tr>
<th>Main Components</th>
<th>OPC</th>
<th>CSA</th>
<th>BYF</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₃S</td>
<td>50-70%</td>
<td>0-5%</td>
<td>0-5%</td>
</tr>
<tr>
<td>C₂S</td>
<td>10-20%</td>
<td>0-55%</td>
<td>45-75%</td>
</tr>
<tr>
<td>C₆A₆</td>
<td>45-75%</td>
<td>0-5%</td>
<td>20-45%</td>
</tr>
<tr>
<td>Aluminates</td>
<td>0-5%</td>
<td>0-5%</td>
<td>2-40%</td>
</tr>
<tr>
<td>Raw Materials</td>
<td>Limestone</td>
<td>High Alumina Clay</td>
<td>Limestone</td>
</tr>
<tr>
<td>Limestone</td>
<td>Limestone</td>
<td>Anhydrite or Gypsum</td>
<td>Anhydrite</td>
</tr>
<tr>
<td>Burning Temperature (°C)</td>
<td>1450</td>
<td>~1250</td>
<td>~1250</td>
</tr>
<tr>
<td>CO₂ from Calcination (kg CO₂/ton clinker)</td>
<td>335</td>
<td>345</td>
<td></td>
</tr>
</tbody>
</table>

**Main anhydrous phases in CSA**

Ye’elimite:
- Pure aluminosilicate that contains calcium instead of sodium
- Two stable modifications: cubic symmetry at temperature above 800°C and undergoes phase transition to an orthorhombic symmetry at room temperature

Calcium aluminates (several intermediate phases):
- Tricalcium aluminate (C₃A)
- Krotite (CA)
- Grossite (CA₂)
- Mayenite (C₁₂A₇)

Calcium sulfate or Anhydrite: present as a minor phase in CSA

**Hydration of Ye’elimite (C₄A₃$)$**

- Ye’elimite with water
  \[ C₄A₃$ + 18H \rightarrow C₆A₆H₁₂ + 2AH₃ \]
  - Molar ratio ≥ 1:2
- Ye’elimite with CSH₂
  \[ 2C₄A₃$ + 2CSH₂ + 52H \rightarrow C₆A₆H₁₂ + 2CAH₃ + 4AH₃ \]
  - Molar ratio < 1:2
Hydration of Ye’elimite (Ca$_4$Al$_3$)$\delta$

Stage I: Initial dissolution and formation of amorphous AH$_3$ and Ettringite

Stage II: ± nucleation + growth of mainly ettringite

Stage III: Onset Ms + AH$_3$ formation

Stage IV: Anhydrous depletion continuous growth of hydrates

Stage V: Transformation Recrystallization and continuous growth

Effect of calcium sulfate addition

Gypsum

Shorter dormant period (with gypsum)

It accelerates the hydration of Ye’elimite

Ye’elimite: Gypsum > 1:2 : ett / AH$_3$ form

Ye’elimite: Gypsum < 1:2 : Ms after Gypsum depletion

Different peak shape to gypsum

Shortened dormant period

Anhydrite

Shorter dormant period (with anhydrite)

Belite > 60% → Ettringite is no longer stable

Belite > 75% → Portlandite formation occurs

Belite > 80% → Strätlingite is no longer stable

Phase assemblage from thermodynamic modelling

Ye’elimite (the main reacting phase) and gypsum dissolve rapidly

Ettringite, Ms and AH$_3$ are stable hydrate phases

Silicate containing phase belite and fluorellestadite dissolve much slower, leading to the formation of strätlingite (at later age)

Hydration reaction of BYF: Ca$_4$Al$_3$S-C$_2$S-CS-H$_2$O

Belite

- Strätlingite formation
- Consumed AH$_3$
- Stabilized C-S-H and monosulfate

Belite > 60%

- Ettringite is no longer stable
- Portlandite formation occurs

Belite > 80%

- Strätlingite is no longer stable

Ref: M. B. Haha, et al., Advances in understanding ye’elimite-rich cements, (2019)
Properties of CSA cements

- Control the properties by adjusting the composition

<table>
<thead>
<tr>
<th>Compressive strength development (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 d</td>
</tr>
<tr>
<td>3 d</td>
</tr>
<tr>
<td>7 d</td>
</tr>
<tr>
<td>28 d</td>
</tr>
<tr>
<td>90 d</td>
</tr>
<tr>
<td>120 d</td>
</tr>
</tbody>
</table>


Applications

- CSA
  - Shrinkage compensation
  - Road reparation
  - Special work: sulfate resistance

BYF
- Rapid setting
- Concrete construction

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- etc...

Reactive Belite rich Portland Cement (RBPC)

- Also known as high belite cement (HBC), is an hydraulic cement that belongs to the same family as PC
- Main anhydrous phases: $C_2S$, $C_3S$, $C_4AF$, $C_3A$ ($C_2S$ is the most abundant one)
- The difference to PC is the belite / alite ratio ($C_2S > 40\%$ and $C_3S < 35\%$)
- Can be manufactured in conventional cement plants with lower burning temperature (~ 1350 °C)
- To make belite sufficiently reactive: $SO_3$ or rapid clinker cooling might be needed
**EPFL**

**Reactive Belite rich Portland Cement (RBPC)**

**RBPC Vs PC**

- Lower water demand
- Similar setting time to PC
- Lower early age strength but higher later age strength
- Lower drying shrinkage
- Better resistance to sulfates and chloride (less CH )

**Applications**

The maximum concrete temperatures reached with RBPC can be much lower than with PC to avoid thermal cracking especially in large concrete pours (in mass concrete applications, such as dams).

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**EPFL**

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**EPFL**

**Carbonatable calcium silicate cements (CCSC)**

- Low lime calcium silicates, such as Wallastonite (CaSiO$_3$, Cs) can harden by carbonation

\[
\text{CaSiO}_3(s) + \text{CO}_2(g) \rightarrow \text{CaCO}_3(s) + \text{SiO}_2(s)
\]

**Major advantages** of CCSC technology:

- Low CO$_2$ due to low calcium content → 30% less CO$_2$ emission than in PC production
- Absorption of additional CO$_2$ during curing (consuming 300kg of CO$_2$ per ton during curing)
- Ability to reach final high strength in 24h (28 days strength of PC)

**Limitations:**

- Mainly suited to the fabrication of precast articles but not too large cross section to allow thorough curing
- Because of its low pH <9, the steel is not protected by concrete against corrosion

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**EPFL**

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Magnesium Oxides derived from Magnesium silicates (MOMS)

- New type of MgO-based hydraulic cement, called magnesium hydroxy-carbonate cement
- Mixture of MgO + hydrated magnesium (hydroxy-)carbonates

Properties:
- Good water resistance
- Relatively high level of CO₂ capture in the hydration product

Applications:
- Not yet been seriously explored

Raw materials:
- Magnesium silicate rocks
  - Olivines
  - Peridotite
  - Serpentine

Manufacturing process: different from PC
- MgO can be hardened by direct carbonation at modest CO₂ pressures
- Demonstrated on a small scale

Thank you for your attention
Questions?