Development of pore solution chemistry and hydrate assemblages during hydration of calcium sulfoaluminate cements

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Outline

- Introduction
- Used cements
- Hydration of calcium sulfoaluminate cements
  - Isothermal heat flow calorimetry
  - X-ray diffraction analysis
  - Thermogravimetric analysis
  - Pore solution chemistry
  - Microstructure (SEM)
  - Thermodynamic modelling
- Conclusions
## Comparison OPC - CSA

<table>
<thead>
<tr>
<th></th>
<th>OPC</th>
<th>CSA</th>
</tr>
</thead>
<tbody>
<tr>
<td>main phases *</td>
<td>$\text{C}_3\text{S}, \text{C}_2\text{S}, \text{C}_3\text{A}, \text{C}_4\text{AF}$</td>
<td>$\text{C}_4\text{A}_3\text{s}$ (= ye‘elimite)</td>
</tr>
<tr>
<td>raw materials</td>
<td>limestone &amp; clay</td>
<td>limestone, bauxite &amp; anhydrite</td>
</tr>
<tr>
<td>burning temperature</td>
<td>$\approx 1450$ °C</td>
<td>$\approx 1250$ °C</td>
</tr>
<tr>
<td>$\text{CO}_2$-release from raw materials **</td>
<td>$\text{C}_3\text{S}$: $1.80$ g / ml $\text{C}_3\text{S}$</td>
<td>$\text{C}_4\text{A}_3\text{s}$: $0.56$ g/ml $\text{C}_4\text{A}_3\text{s}$</td>
</tr>
<tr>
<td>grindability</td>
<td>medium</td>
<td>easy</td>
</tr>
<tr>
<td>gypsum addition</td>
<td>$\approx 4$-8 wt.-%</td>
<td>$\approx 20$-25 wt.-%</td>
</tr>
<tr>
<td>w/c total hydration</td>
<td>$\approx 0.4$</td>
<td>$\approx 0.8$</td>
</tr>
<tr>
<td>hydration products</td>
<td>C-S-H phases, CH, AFt, ...</td>
<td>AFt, AFm, Al(OH)$_3$ gel</td>
</tr>
</tbody>
</table>

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* Cement notation: $C = \text{CaO}$, $S = \text{SiO}_2$, $A = \text{Al}_2\text{O}_3$, $F = \text{Fe}_2\text{O}_3$, $H = \text{H}_2\text{O}$, $s = \text{SO}_3$

CSA-Cements …

… have attracted new interest during the climate debate as they:

- need lower burning temperatures,
- release less CO₂ from the raw meal (less limestone),
- yield a higher volume of hydrate phases (higher water/cement ratio)

compared to ordinary Portland cement.

Besides that, they are of interest concerning waste encapsulation.

But they have some drawbacks:

- environment (SO₂ release)
- risk of expansion (ettringite is main hydration product)
CSA-cements: risk of expansion

United States Patent 4409030, 1983:
Material for destroying concrete structures

... comprises a mixture of ... coarse-grained quicklime ... and ... cement. The cement may contain calcium sulfoaluminate ... The material is blended with water and then injected into holes formed in the body to be destroyed, the material expanding as it hydrates to crack and fracture the body.

Basic research is needed to understand the hydration mechanisms of calcium sulfoaluminate based systems!
Hydration of pure ye‘elimite

(1) $\text{C}_4\text{A}_3\text{s} + 18 \text{H} \rightarrow \text{C}_3\text{A} \cdot \text{CsH}_{12} + 2 \text{AH}_3$ \hspace{1cm} (monosulfate)

(2) $\text{C}_4\text{A}_3\text{s} + 2 \text{CsH}_2 + 24 \text{H} \rightarrow \text{C}_3\text{A} \cdot 3\text{CsH}_{32} + 2 \text{AH}_3$ \hspace{1cm} (ettringite)

(3) $\text{C}_4\text{A}_3\text{s} + 6 \text{CH} + 8 \text{CsH}_2 + 74 \text{H} \rightarrow 3 \text{C}_3\text{A} \cdot 3\text{CsH}_{32}$

heat flow calorimetry

w/c = 2
Hydration kinetics of CSA cements: influence of calcium sulfate

**gypsum**

- CSA clinker
- CSA / gypsum 86/14
- CSA / gypsum 76/24
- CSA / gypsum 68/32
- CSA / gypsum 61/39
- OPC, w/c = 0.50

**dead-burnt anhydrite**

- CSA clinker
- CSA / anhydrite 86/14
- CSA / anhydrite 76/24
- CSA / anhydrite 68/32
- CSA / anhydrite 61/39
- OPC, w/c = 0.50

**reactive calcium sulfate:**
Enables to control early hydration

**calcium sulfate with poor reactivity:**
„chaotic“ early hydration

* amounts of gypsum given as anhydrous calcium sulfate
Strength development of CSA cements

- very high strength despite high water/cement-ratio
- gypsum increases early strength

EN 196-1 - mortars

compressive strength / MPa

<table>
<thead>
<tr>
<th>Material</th>
<th>Compressive Strength / MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>CSA clinker</td>
<td></td>
</tr>
<tr>
<td>CSA / gypsum 86/14</td>
<td></td>
</tr>
<tr>
<td>CSA / gypsum 68/32</td>
<td></td>
</tr>
<tr>
<td>OPC, w/c = 0.50</td>
<td></td>
</tr>
<tr>
<td>w/c = 0.70</td>
<td></td>
</tr>
</tbody>
</table>

empa
### Used CSA-cements - composition

#### Chemical analysis

<table>
<thead>
<tr>
<th></th>
<th>CSA-1</th>
<th>CSA-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>35.4</td>
<td>41.2</td>
</tr>
<tr>
<td>SiO₂</td>
<td>3.2</td>
<td>6.9</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>35.5</td>
<td>26.8</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.88</td>
<td>0.88</td>
</tr>
<tr>
<td>MgO</td>
<td>0.76</td>
<td>0.75</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.05</td>
<td>0.13</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.21</td>
<td>0.40</td>
</tr>
<tr>
<td>TiO₂</td>
<td>1.8</td>
<td>1.2</td>
</tr>
<tr>
<td>SO₃</td>
<td>16.8</td>
<td>19.5</td>
</tr>
<tr>
<td>L.O.I.</td>
<td>5.1</td>
<td>1.84</td>
</tr>
</tbody>
</table>

#### Potential phase content

<table>
<thead>
<tr>
<th></th>
<th>CSA-1</th>
<th>CSA-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₄A₃s</td>
<td>50</td>
<td>54</td>
</tr>
<tr>
<td>CA</td>
<td>8</td>
<td>-</td>
</tr>
<tr>
<td>C₂AS</td>
<td>15</td>
<td>-</td>
</tr>
<tr>
<td>C₂S</td>
<td>-</td>
<td>17</td>
</tr>
<tr>
<td>Cs</td>
<td>-</td>
<td>22</td>
</tr>
<tr>
<td>CsH₂</td>
<td>22</td>
<td>-</td>
</tr>
<tr>
<td>others *</td>
<td>5</td>
<td>7</td>
</tr>
</tbody>
</table>

* mainly titanium containing phases

#### Water/cement ratio

- CSA-1: 0.72
- CSA-2: 0.80
Isothermal heat flow calorimetry
Hydration (XRD) of CSA-1

Y - ye'elimite
C - calcium aluminate
Ge - gehlenite
G - gypsum
E - ettringite
M - monosulfate

intensity / -

2θ / °
Hydration (TGA) of CSA-1

The graph shows the hydration process of CSA-1 over time, with temperatures ranging from 20°C to 1000°C. The x-axis represents the temperature in °C, and the y-axis represents the relative weight in % and the differential relative weight in %. The graph includes lines for unhydrated conditions and hydrated conditions at various time intervals (1h, 2h, 5h, 8h, 16h, 2d, 7d). Key hydrated phases are indicated: ettringite, Al(OH)₃-gel, gypsum, and monosulfate.
Pore solution composition of CSA-1

- **Concentration / mmol/l**
  - Fe
  - Si
  - Al
  - OH
  - Ca
  - K
  - S
  - Na

- **pH**
  - Consumption of gypsum

- **Time / h**
  - 1
  - 10
  - 100
  - 1000

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EMPA
Hydration (XRD) of CSA-2

Y - ye’elimite
B - belite
A - anhydrite
M - monosulfate
E - ettringite
S - strätlingite
(C₂ASH₈)

(intensity / -)

2θ / °

unhydrated

2 h

4 h

6 h

8 h

10 h

12 h

14 h

16 h

18 h

20 h

22 h

24 h

26 h

28 h

30 h

32 h

34 h

36 h

38 h

40 h

42 h

44 h
Hydration (TGA) of CSA-2

The graph shows the hydration process of CSA-2 over time, with temperature on the x-axis and relative weight on the y-axis. The graph includes different hydration states at various time intervals:

- Unhydrated (0 h)
- 1 h
- 2 h
- 4 h
- 6 h
- 8 h
- 10 h
- 12 h
- 16 h
- 1 d
- 2 d
- 3 d
- 4 d
- 5 d
- 7 d
- 14 d
- 21 d
- 28 d

The hydration process is depicted through the change in relative weight over temperature, with specific hydration products indicated:

- Ettringite (Al(OH)_3 - gel)
- Monosulfate
- Strätlingite

The graph illustrates the decrease in relative weight with increasing temperature, indicating the hydration process and the formation of the aforementioned hydration products.
Pore solution composition of CSA-2

[Graph showing concentration vs. time for various elements and pH]

- Elements: Fe, Si, OH, Na, S, Ca, K, Al
- Concentration scale: mmol/l
- Time scale: h
- pH scale: 10.9 to 12.9

Consumption of anhydrite
Microstructure of **CSA-1** and **CSA-2**

**CSA-1**
- E = ettringite
- C = clinker
- G = gypsum
- Gel = gel-like phases

**CSA-2**
- S = strätlingite
Thermodynamic modelling

Composition of cement

I Slowly soluble solids
\[ \text{C}_4\text{A}_3\text{s}, \text{CA}, \text{C}_2\text{S} \quad K_2\text{O} \]
\[ \Rightarrow \text{Dissolution kinetics} \quad \text{Na}_2\text{O} \]
\[ \text{(XRD)} \quad \text{MgO} \]

II Rapid soluble solids
\[ \text{K}_2\text{SO}_4 \quad \text{gypsum} \]
\[ \text{Na}_2\text{SO}_4 \quad \text{anhydrite} \]
\[ \text{CaO} \]

III Water
\[ \text{H}_2\text{O} \]

thermodynamic modelling

GEMS-PSI

- Ca\(^{2+}\)
- CaOH\(^{+}\)
- speciation
- CaSO\(_4\)^0

ettringite
monosulfate
Al(OH)\(_3\) gel
C-S-H
strätlingite, …
Modelling: solid phases of CSA-1

- Pore solution
- $C_4A_3s$
- Inert phases ($C_2AS$, CT)
- Gypsum
- $CA$
- Monosulfate
- $Al(OH)_3$ gel
- Ettringite

Data points: XRD ($C_4A_3s$, CA)
TGA (pore solution)

Lines: modelling
Modelling: liquid phases of CSA-1

lines: modelling
data points: experimental

[Graph showing concentration changes over time for various elements: Na, Al, Ca, S, OH, with lines representing modelling and data points representing experimental results.]
Modelling: solid and liquid phase of CSA-2

Up to now, the hydration has been modelled only with insufficient accuracy (poor correlation with experimental data, especially with pore solution composition), mainly due to:

- some uncertain thermodynamic data (e. g. \( \text{CAH}_{10} \))
- kinetic restraints (slow dissolution of anhydrite)

=> work in progress
Conclusion – hydration of CSA cements (I)

Solid phases:
- ettringite formation until CaSO₄ is (almost) used, then monosulfate occurs
- Al(OH)₃ gel forming by-product of hydration
- with C₂S als minor phase (CSA-2) strätlingite forms after 28 d
- dissolution of calcium sulfates hindered

Pore solution:
- first hours: dominated by alkalis, calcium and sulfate
  pH 10.5 - 10.8
- when CaSO₄ (almost) used: mainly alkalis, OH and Aluminum
  pH 12.5 - 12.8 after 28 d
Conclusion – hydration of CSA cements (II)

**Microstructure:**
- CSA-1: quite dense already after 18 hours, very dense after 28 days despite high w/c of 0.72
- CSA-2: dense, but inhomogeneous large strätlingite crystals after 28 days

**Application:**
- binder for various applications (e.g. "plaster" boards)
- acceleration of OPC or slag hydration in ternary blends also incorporating gypsum or anhydrite
- shrinkage reducing / expansive agent
- waste encapsulation