In-Situ Clinkering Study of Belite Sulfoaluminate Clinkers by Synchrotron X-Ray Powder Diffraction

Dra. Ángeles G. De la Torre
Universidad de Málaga
Outline

1. Introduction to the environmental problem
2. Introduction to belite calcium sulfoaluminate (BCSA) cements
3. BCSA clinkering from synchrotron data
4. Conclusions
1. Introduction to the environmental problem

Cement industry contribution to greenhouse gases emissions

\[ \text{CaCO}_3 \xrightarrow{\Delta} \text{CaO} + \text{CO}_2 \]

Other emissions: ~ 0.34 T from fuel burning
~ 0.10 T from electricity

0.54 Tons / ton of clinker

✓ Cement industry contributes to the global warming of the planet in \( \approx 4\% \)

CO\(_2\) emissions relationship between

**OPCs** (based on alite, belite and others) &

**BCSAs** (based on belite, C\(_4\)A\(_3\)S, and others)

Iron-rich BCSA

Quantification of the CO\(_2\) savings

~ 10% from substituting alite by belite (smaller LSF)
~ 15% from partial substitution of CaCO\(_3\) by CaSO\(_4\)
~ 5% from burning the clinker at 1300 °C (fuel saving)
2. Introduction to belite calcium sulfoaluminate (BCSA) cements

<table>
<thead>
<tr>
<th>Estimated phase composition</th>
<th>belite</th>
<th>ye’elimite</th>
<th>ferrite</th>
<th>others</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₂S</td>
<td>51</td>
<td>29</td>
<td>19</td>
<td>&lt;1</td>
</tr>
<tr>
<td>C₄A₃S</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₄AF</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

C₂S Polymorphism

Compressive strength (standard mortar)

Activation is highly desirable
3. BCSA clinkering from synchrotron data

**Samples studied**

<table>
<thead>
<tr>
<th></th>
<th>CaO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>SO₃</th>
<th>Na₂O</th>
<th>B₂O₃</th>
<th>C₄A₃S</th>
<th>C₂S</th>
<th>C₄AF</th>
<th>CA</th>
<th>C₁₇A₇</th>
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</thead>
<tbody>
<tr>
<td>Pure-C₄A₃S</td>
<td>36.8</td>
<td>-</td>
<td>50.1</td>
<td>-</td>
<td>13.1</td>
<td>-</td>
<td>-</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fe_BSA_B0</td>
<td>52.7</td>
<td>17.5</td>
<td>19.2</td>
<td>6.6</td>
<td>4.0</td>
<td>0.0</td>
<td>0.0</td>
<td>30</td>
<td>50</td>
<td>20</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fe_BSA_B1</td>
<td>52.0</td>
<td>17.2</td>
<td>18.9</td>
<td>6.5</td>
<td>3.9</td>
<td>0.5</td>
<td>1.0</td>
<td>30</td>
<td>50</td>
<td>20</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fe_BSA_B2</td>
<td>51.3</td>
<td>17.0</td>
<td>18.6</td>
<td>6.4</td>
<td>3.8</td>
<td>0.9</td>
<td>2.0</td>
<td>30</td>
<td>50</td>
<td>20</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Al_BSA</td>
<td>52.0</td>
<td>17.4</td>
<td>26.6</td>
<td>-</td>
<td>3.9</td>
<td>-</td>
<td>-</td>
<td>30</td>
<td>50</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
</tbody>
</table>

**Powder diffraction data collection**

- **Metallic sample holder**
- **MgO refractory capillary**
- **Pt capillary** Ø=0.6 mm
- **Decarbonated raw mixture**
- **Refractory ceramic adhesive**

**Data collection**

- ESRF (Grenoble)
- ID31 diffractometer
- \( \lambda = 0.29980 \, \text{Å} \)
- Debye Scherrer configuration
- Capillaries were spun
- Angular range 2.5-30° (in 2q)
- 15 minutes per run
- 3 runs for a single pattern

Real temperature was determined by Pt peak positions
Checked by CaO thermal expansion
3. BCSA clinkering from synchrotron data
3. BCSA clinkering from synchrotron data

Pure $\text{C}_4\text{A}_3\text{S}$

Decomposition/melting

Crystalline components

SO$_3$

Al$_2$O$_3$

(100%)

SO$_3$

CaO

CaSO$_4$

CA

$\text{Cr}_2\text{A}_7$

C$_3$A

$\text{C}_4\text{A}_3\text{S}$

(100%)
Iron-rich BCSA clinkering from synchrotron data

(a) B0 @ 1070 °C

(b) B1 @ 1215 °C

(c) B2 @ 1295 °C
3. BCSA clinkering from synchrotron data

**BCSA**

Liquid phase (melting) $\rightarrow$ indirectly inferred $\rightarrow$ maximum values for crystalline $\text{C}_4\text{A}_3\text{S}$ & $\text{C}_4\text{AF}$ on heating.

$\alpha'_H\text{C}_2\text{S}$ $\rightarrow$ $\alpha\text{C}_2\text{S}$

$\text{C}_4\text{AF}$ melting $\rightarrow$ $\text{C}_4\text{A}_3\text{S}$ melting/decomposition
3. BCSA clinkering from synchrotron data

BCSAF obtained in-situ

BCSA

$C_4AF$ and $C_4A_3S$ are completely melted at the temperature from which these clinkers are quenched

$C_4A_3S$ does not re-crystallize from the melting
Conclusions

✓ Pure $\text{C}_4\text{A}_3\text{S}$ mechanism formation. CA, $\text{C}_{12}\text{A}_7$ & $\text{C}_3\text{A}$ are transitory phases. Melting/decomposition starts: 1365-1400 ºC.

✓ $\text{C}_2\text{S}$ polymorph transformations have been followed.
  $\alpha'_\text{H}-\text{C}_2\text{S} \rightarrow \alpha-\text{C}_2\text{S}$ polymorphic transformation temperature decreases as $\text{B}_2\text{O}_3$ content increases.

✓ $\text{C}_4\text{A}_3\text{S}$ decomposition is promoted by the apparition of liquid phase.

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In situ powder diffraction study of belite sulfoaluminate clinkering

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Ángeles G. De la Torre, Antonio J. M. Cuberos, Gema Álvarez-Pinazo,
Ana Cuesta and Miguel A. G. Aranda*

Contact or further information
mgd@uma.es http://webpersonal.uma.es/~mgd/