Early Age Reactions of Sulphate Phases that Contribute to Early Stiffening of Hydraulic Cements

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Introduction

- Investigate if there are **mineralogical** reasons that can lead to early stiffening of hydrated portland cements.
  - Understand the reactions (mineralogical changes) that occur with the various forms of sulphate in portland cements
  - Composition by XRF does not give information about mineralogy
    - XRD used to identify mineral phases present before and after hydration that may contribute to early stiffening → better correlation with performance

- Number of different sulphate minerals in portland cement:
  - Alkali sulphates (arcanite and aphthitalite), calcium sulphates (gypsum, hemihydrate, beta-anhydrite, gamma-anhydrite), and calcium langbeinite
  - Sulphate minerals have different **solubilities**
Introduction

- Early stiffening:
  - Flash set – development of stiffness with evolution of considerable heat, where plasticity cannot be regained upon mixing without additional water (more severe)
  - **False set** – development of stiffness without much heat evolution, where plasticity may be regained by further mixing without additional water (less severe)
    - In practice the main issue is **placing** and **finishing** of the concrete

- A number of cements were investigated
  - Had poor ‘**finishability**’ or early stiffening reported in the field
  - Gave unacceptable results when tested according to **ASTM C 359** (Standard Test Method for Early Stiffening of Hydraulic Cement - Mortar Method)
Experimental methods

- XRD with Rietveld whole pattern fitting – to identify/quantify mineral components of interest, in the anhydrous cement and after hydration (e.g., 3-15 min, 4-6 hr, 24 hr).
  - XRD sample preparation (on hydrated pastes):
    - Mixed a cement paste at w/cm of 0.3 for 90 sec
    - Allowed to hydrate for 3 min (or 5 min, etc.)
    - Place about 5 g of cement paste in 50 mL vial, add 45 mL of acetone, and shake for 2 min (to stop hydration)
    - Centrifuge to separate acetone
    - Grind with mortar and pestle (<38 µm)
    - XRD performed using Cu-Kα radiation (λ of 1.541874 Å)
    - Rietveld analysis done with PANalytical X’Pert Highscore Plus 2.1, using initial crystal structures from the ICSD
Experimental methods

- ASTM C 359 Standard Test Method for Early Stiffening of Hydraulic Cement → mortar penetration test

- Isothermal calorimetry using TAMAir conduction calorimeter – to determine how the various forms of sulphate affect the heat evolution
  - Cement pastes mixed at w/c of 0.4 for 90 sec
  - 23°C for 7 days (168 h)
Example 1 – Too much hemihydrate

- Cement where it was reported there was increased water demand for mixing, false setting or early stiffening tendency, issues with handling and placing
- Cement had ~3.6% SO$_3$, low alkali sulphates (0.52% Na$_2$O$_e$), 1% gypsum, and **4.1% hemihydrate**
- Too much hemihydrate (dehydration of gypsum)
Example 1 – Too much hemihydrate

- Upon hydration all hemihydrate disappeared, but gypsum was precipitated in the cement paste.
- Solubility of hemihydrate (or rate of) is greater than gypsum:
  - Pore solution becomes super-saturated wrt gypsum
  - $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O} + \frac{3}{2}\text{H}_2\text{O} \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
  - Gypsum crystals are tabular – causes thickening of cement paste.

### Graph

**Counts**

- **Cement**
- **Cement paste - hydrated 5 min (w/cm = 0.3)**

**Position [°2Theta]**

- Ettringite
- Hemihydrate
- Gypsum

**Counts**

- Ettringite
- Hemihydrate
- Gypsum

**Graph Details**

- Peaks for Ettringite, Hemihydrate, and Gypsum are clearly visible.
- The hydrated cement paste shows a significant increase in the intensity of the Gypsum peak compared to the control.
- The Ettringite peak is also evident but less pronounced in the hydrated sample.

The graph illustrates the changes in the mineral composition post-hydration, highlighting the precipitation of gypsum and the continued presence of hemihydrate, contributing to the thickening of the cement paste.
Example 1 – Too much hemihydrate

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**Cement paste - hydrated 5 min (w/cm = 0.3)**

- C3S - Alite (M3) 66.3 %
- C2S - ß-Belite 6.1 %
- C3A - Aluminate cubic 3.5 %
- C3A - Na-Aluminate ortho 1.8 %
- C4AF - Brownmillerite 9.0 %
- Periclase 1.0 %
- Calcium oxide - Lime 0.4 %
- Potassium sulfate - Arcanite 0.2
- Calcite 0.2 %
- Quartz 0.0 %
- Gypsum 3.0 %
- Calcium sulfate hemihydrate 0.1 %
- Anhydrite 0.5 %
- Portlandite 0.0 %
- Aphtithalite 0.0 %
- Ettringite 2.7 %

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Example 2 – Formation of syngenite

- Cement when tested in accordance with ASTM C 359 (mortar penetration test) indicated there could be issues with early stiffening.
- Cement had 3.4% SO$_3$, relatively high alkali sulphates (1.14% Na$_2$O$_e$), 2.6% gypsum, 0.9% hemihydrate, 0.8% anhydrite.

ASTM C 359 (mortar method)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixing Water</td>
<td>191 mL (180 mL)</td>
</tr>
<tr>
<td>Initial penetration</td>
<td>46 mm</td>
</tr>
<tr>
<td>5-min penetration</td>
<td>33 mm</td>
</tr>
<tr>
<td>8-min penetration</td>
<td>19 mm</td>
</tr>
<tr>
<td>11-min penetration</td>
<td>11 mm</td>
</tr>
<tr>
<td>Remix penetration</td>
<td>24 mm</td>
</tr>
<tr>
<td>Early Stiffening Amount</td>
<td>35 mm</td>
</tr>
<tr>
<td>Average Early Stiffening Rate</td>
<td>4.6 mm/min (lower is better)</td>
</tr>
<tr>
<td>Early Stiffening Recovery</td>
<td>52 % (higher is better)</td>
</tr>
</tbody>
</table>
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Example 2 – Formation of syngenite

- Hemihydrate consumed; no precipitation of gypsum
- Formation of syngenite (~3%) upon hydration (from dissolution of calcium sulphates and potassium sulphates)
  - $\text{Ca}^{2+} + 2\text{SO}_4^{2-} + 2\text{K}^+ + \text{H}_2\text{O} \rightarrow \text{K}_2\text{SO}_4\cdot\text{CaSO}_4\cdot\text{H}_2\text{O}$
  - Less soluble than anhydrite (removal of sulphate from solution)
  - Syngenite crystals are prismatic to acicular (spherulitic)

![Graph showing X-ray diffraction patterns of hemihydrate, syngenite, ettringite, and gypsum.](image-url)
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Example 3 – Calcium langbeinite

- Clinkers high in K₂O and SO₃ may contain calcium langbeinite (K₂SO₄·2CaSO₄)
- Cement reported to have problems with finishing
- Cement had **2% Ca-langbeinite**, high alkali sulphates
Example 3 – Calcium langbeinite

- Upon hydration Ca-langbeinite is completely consumed
- All of the hemihydrate and half of gypsum is consumed
- **3.8% syngenite** formed

\[ K_2SO_4 \cdot 2CaSO_4 + 3H_2O \rightarrow K_2SO_4 \cdot CaSO_4 \cdot H_2O + CaSO_4 \cdot 2H_2O \]
Calcium langbeinite & calcium sulphates

- Calcium langbeinite is considered an effective set-controlling agent (very water soluble)
- Clinker with 2.6% SO₃ (2.4% Ca-langbeinite) was interground with gypsum, hemihydrate, or beta-anhydrite
  - The more soluble the calcium sulphate source, the greater the tendency for early stiffening → more syngenite formed early

<table>
<thead>
<tr>
<th>ASTM C 359 (mortar method)</th>
<th>Clinker (2.6% SO₃)</th>
<th>+ 2.6% Gypsum</th>
<th>+ 2.4% Hemihydrate</th>
<th>+ 2.0% Anhydrite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial penetration</td>
<td>49</td>
<td>49</td>
<td>49</td>
<td>49</td>
</tr>
<tr>
<td>5-min penetration</td>
<td>49</td>
<td>45</td>
<td>21</td>
<td>48</td>
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<td>8-min penetration</td>
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</tr>
<tr>
<td>11-min penetration</td>
<td>49</td>
<td>9</td>
<td>4</td>
<td>30</td>
</tr>
<tr>
<td>Remix penetration</td>
<td>49</td>
<td>49</td>
<td>49</td>
<td>49</td>
</tr>
<tr>
<td>Early Stiffening Amount</td>
<td>0</td>
<td>40</td>
<td>45</td>
<td>19</td>
</tr>
<tr>
<td>Average Early Stiffening Rate</td>
<td>0.0</td>
<td>4.7</td>
<td>6.6</td>
<td>2.2</td>
</tr>
<tr>
<td>Early Stiffening Recovery</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Syngenite (3 minutes)</td>
<td>1.4</td>
<td>3</td>
<td>3.4</td>
<td>2.2</td>
</tr>
</tbody>
</table>
Isothermal calorimetry (high SO$_3$ clinker)

- 2.6% SO$_3$ clinker with addition of gypsum, hemihydrate, or beta-anhydrite (~3.7% total SO$_3$)
  - Initial peak only slightly higher with hemihydrate or gypsum
  - Addition of calcium sulphate slightly delays main silicate peak
Isothermal calorimetry (low SO$_3$ clinker)

- 0.95% SO$_3$ clinker with addition of gypsum, hemihydrate, or beta-anhydrite (~3.4% total SO$_3$)
  - Addition of calcium sulphate significantly lowers initial peak
  - Addition of calcium sulphate significantly accelerates main silicate peak

![Graph showing heat flow vs. hydration time for different clinker compositions.](image)
Summary

- Too much hemihydrate (from dehydration of gypsum) can cause early stiffening due to precipitation of gypsum upon hydration, and can increase the early heat of hydration.

- High levels of potassium sulphates can contribute to formation of syngenite upon hydration causing early stiffening.

- Calcium langbeinite in the cement can lead to formation of syngenite upon hydration; with the addition of a rapidly soluble calcium sulphate, syngenite formation, and hence, early stiffening increases.

- Calcium sulphates have differing affects on early hydration when added to clinkers with low SO$_3$ versus high SO$_3$. 