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

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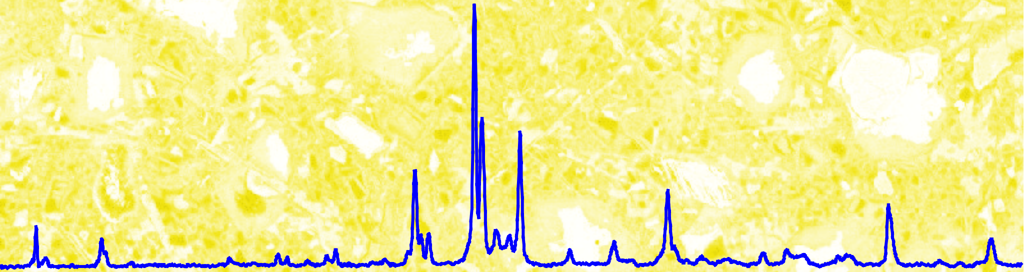


Introduction

- 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 indentify/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

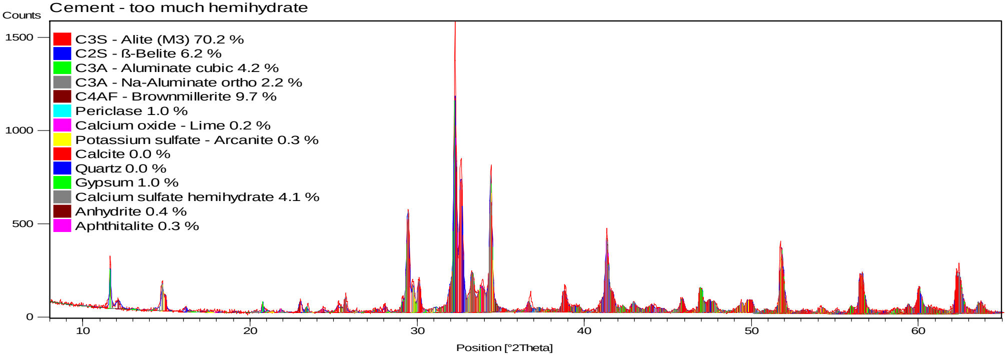
Experimental methods

- 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)

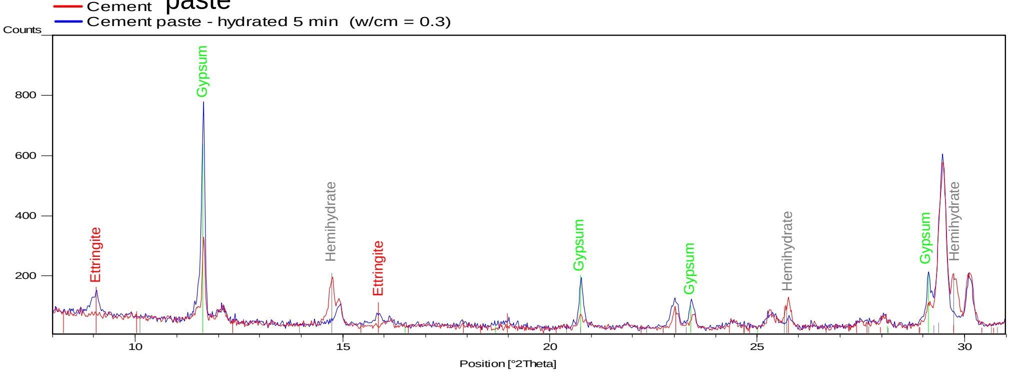
Example 1 – Too much hemihydrate

- 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_2O_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
    - $CaSO_4{\cdot}\frac{1}{2}H_2O + \frac{3}{2}H_2O \rightarrow CaSO_4{\cdot}2H_2O$
    - Gypsum crystals are tabular – causes thickening of cement paste



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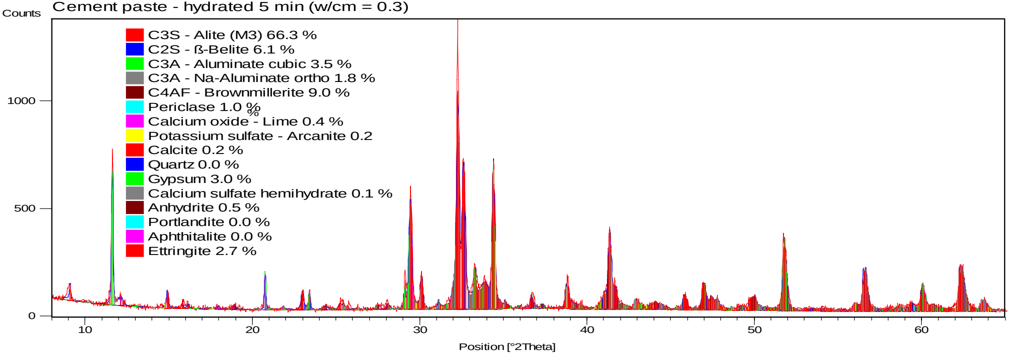

Example 2 – Formation of syngenite

- 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_2O_e), 2.6% gypsum, 0.9% hemihydrate, 0.8% anhydrite

ASTM C 359 (mortar method)

Mixing Water	191	mL	(180 mL)
Initial penetration	46	mm	
5-min penetration	33	mm	
8-min penetration	19	mm	
11-min penetration	11	mm	
Remix penetration	24	mm	
Early Stiffening Amount	35	mm	
Average Early Stiffening Rate	4.6	mm/min	(lower is better)
Early Stiffening Recovery	52	%	(higher is better)

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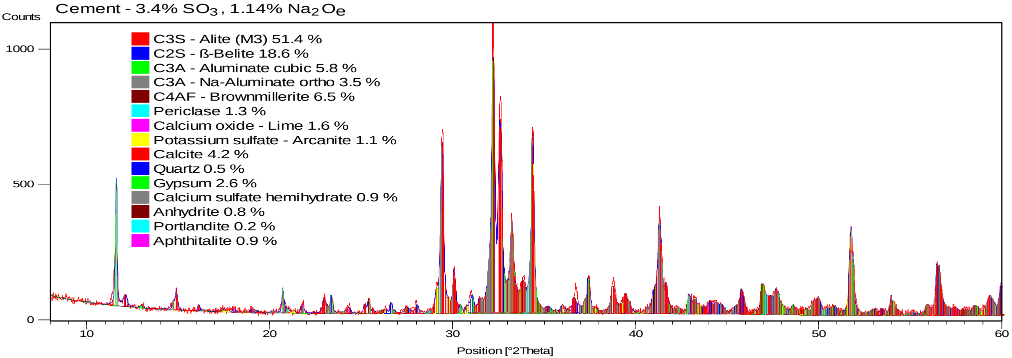
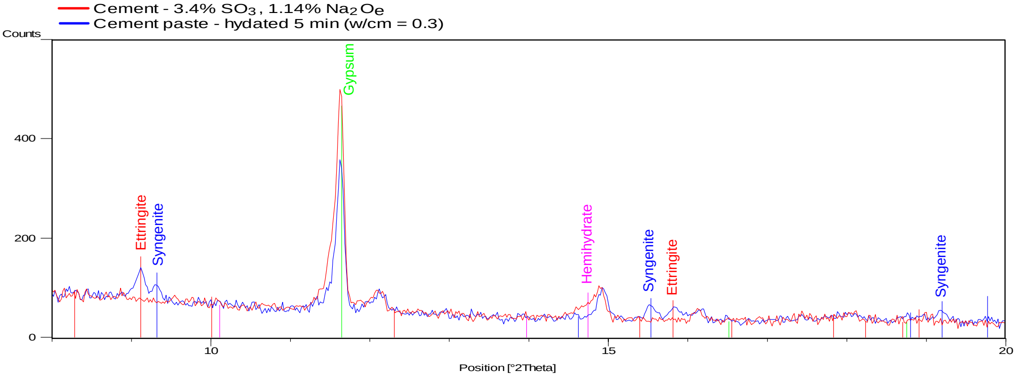


Example 2 – Formation of syngenite

- Hemihydrate consumed; no precipitation of gypsum
- Formation of **syngenite** (~3%) upon hydration (from dissolution of calcium sulphates and potassium sulphates)
  - $Ca^{2+} + 2SO_4^{2-} + 2K^+ + H_2O \rightarrow K_2SO_4 \cdot CaSO_4 \cdot H_2O$
  - Less soluble than anhydrite (removal of sulphate from solution)
  - Syngenite crystals are prismatic to acicular (spherulitic)



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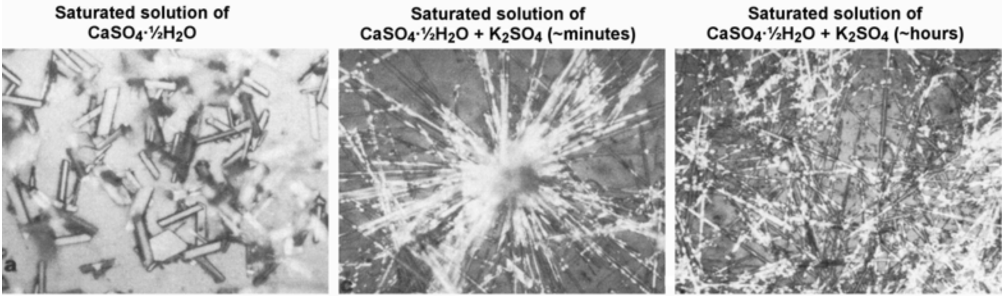
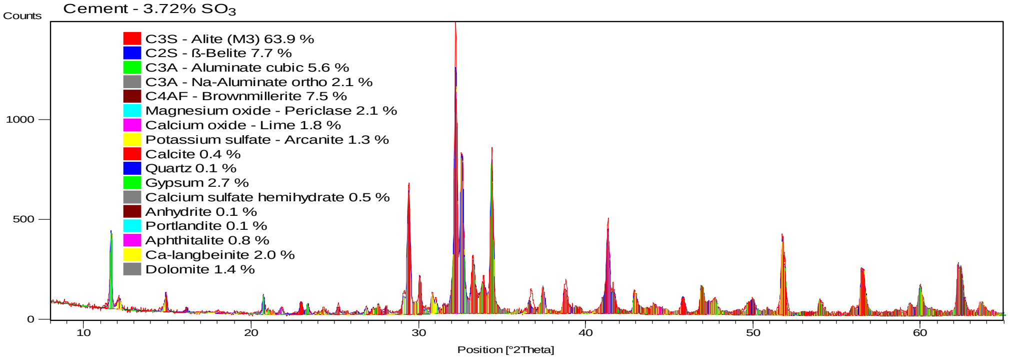


Shen et al., J Dent Res (1981)

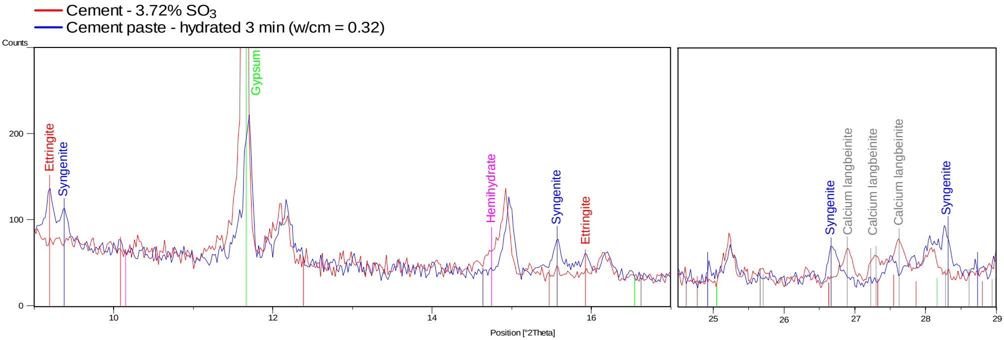
Example 3 – Calcium langbeinite

- Clinkers high in K_2O and SO_3 may contain calcium langbeinite ($K_2SO_4 \cdot 2CaSO_4$)
- 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

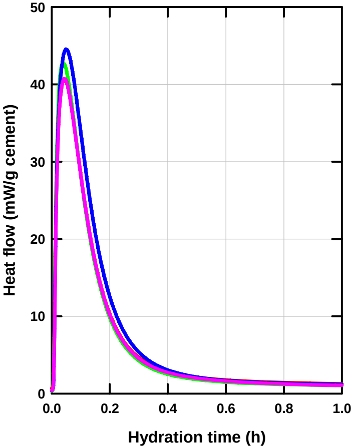
- Calcium langbeinite is considered an effective set-controlling agent (very water soluble)
- Clinker with 2.6% SO_3 (2.4% Ca-langbeinite) was interground with gypsum, hemihydrate, or beta-anhydrite
  - The **more soluble** the calcium sulphate source, the greater the tendency for early stiffening → **more syngenite** formed early

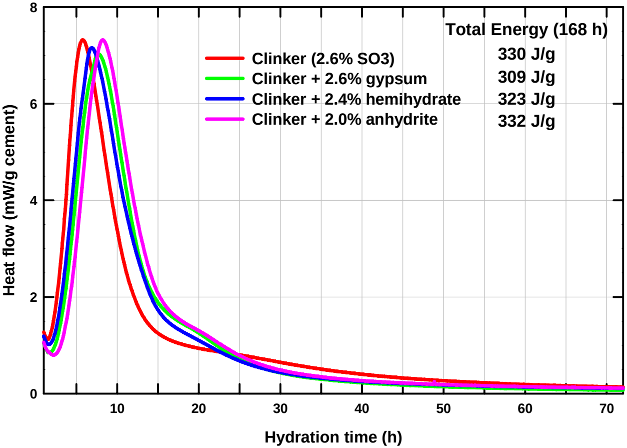
ASTM C 359 (mortar method)

	Clinker (2.6% SO_3)	+ 2.6% Gypsum	+ 2.4% Hemihydrate	+ 2.0% Anhydrite	
Initial penetration	49	49	49	49	mm
5-min penetration	49	45	21	48	mm
8-min penetration	49	14	9	48	mm
11-min penetration	49	9	4	30	mm
Remix penetration	49	49	49	49	mm
Early Stiffening Amount	**0**	**40**	**45**	**19**	**mm**
Average Early Stiffening Rate	**0.0**	**4.7**	**6.6**	**2.2**	**mm/min**
Early Stiffening Recovery	100	100	100	100	%
Syngenite (3 minutes)	**1.4**	**3**	**3.4**	**2.2**	**%**

Isothermal calorimetry (high SO_3 clinker)

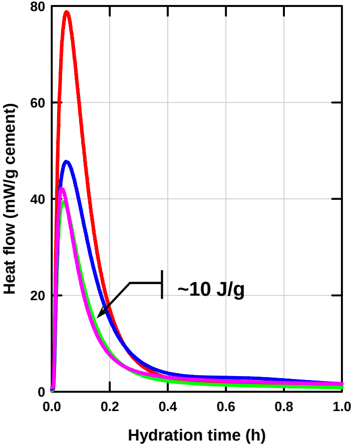
- 2.6% SO_3 clinker with addition of gypsum, hemihydrate, or beta-anhydrite (~3.7% total SO_3)
  - Initial peak only slightly higher with hemihydrate or gypsum
  - Addition of calcium sulphate slightly delays main silicate peak

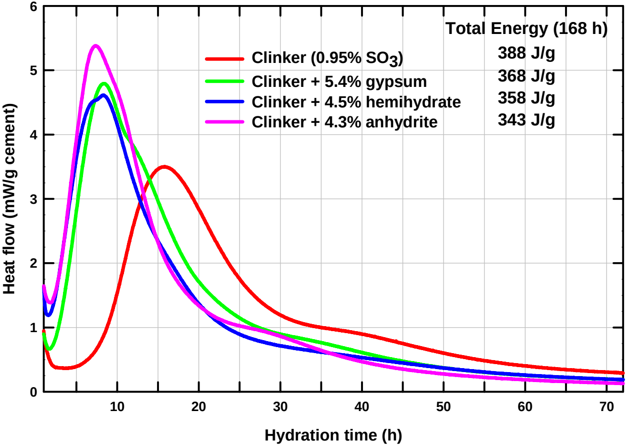




Isothermal calorimetry (low SO_3 clinker)

- 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





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