The Beneficial Effect of Slag on Low Temperature Sulfate Resistance of Concrete Produced with Portland-limestone Cements and Supplementary Cementitious Materials

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Background

• Portland-limestone cement with up to 15% inter-ground limestone was included in CSA A3000 in 2008 and adopted in CSA A23.1 in 2009.

• **Advantages:**
  • Sustainability (reducing greenhouse gas emissions),
  • Energy saving (reducing fuel needed for clinker production).

• **Limitation:**
  • One of the major concerns about PLC is its resistance against sulfate attack, especially at low temperature due to the thaumasite sulfate attack.

• Both CSA A3000-08 and CSA A23.1-09 did not allow the use of PLC in concretes subjected to moderate or severe sulfate exposures, even when blended with SCMs, until sufficient research was conducted.
Changes to CSA Standards since 2009

• Based on results of preliminary research by Ramezanianpour, a new 5 °C mortar bar sulfate resistance test method was adopted in 2010 along with an 18-month expansion limit: CSA A3004-C8 Procedure B before the use of PLC in concretes subjected to moderate or severe sulfate exposures was allowed when used with sufficient proportions of SCMs.

• Then, CSA A23.1-14 allowed the use of PLC in concretes subjected to sulfate exposures, if concrete had a maximum W/CM ratio of 0.40 for all sulfate exposure classes, the minimum replacement levels of SCMs were used, and both the 23 °C and 5 °C maximum expansion requirements (CSA A3004-C8 Procedures A and B) were met.

• However, based on this research, CSA A3004-C8 Procedure B was withdrawn from CSA A3000 in 2017 and all three requirements for using PLC in sulfate exposures were removed from CSA A23.1 in 2018.
Types of sulfate attack

1. Conventional sulfate attack:
   • Reaction between sulfate ions and $C_3A$ in the cement,
   • Resulting in the formation of gypsum and ettringite,
   • Causing expansion and cracking.

2. Physical sulfate attack:
   • Wick action concentrates $Na_2SO_4+Na_2SO_4\cdot10H_2O$ in pores (thenardite-mirabilite phase changes),
   • When water evaporates (in arid zones) and leaves salts behind, progressive cracking and spalling of concrete surfaces occur.
3. Thaumasite sulfate attack:
- Reaction between sulfate ions, C-S-H, and carbonate ions at low temperature (~5-10 °C) and very wet environments,
- Resulting in the formation of thaumasite,
- Resulting in the consumption and disintegration of calcium-silicate cement paste matrix with loss of concrete cohesiveness and strength.

\[
\text{SO}_4 + \text{H}_2\text{O} + \text{CO}_3 \quad \text{at} \quad \text{Low temp.} \\
\downarrow \\
\text{CaSiO}_3\cdot\text{CaCO}_3\cdot\text{CaSO}_4\cdot15\text{H}_2\text{O} \\
\text{Thaumasite} \\
\text{A soft, white, pulpy mass}
\]
Problem statement

• No standard test methods exist in North American standards for evaluating the sulfate resistance of concrete regardless of the damage mechanism except USBR 4908-92.

• There is little data on the use of portland-limestone cement in combination with supplementary cementitious materials in concrete.

• Previous research (Ramezanianpour and Hooton, 2013a and 2013b) focused on mortar bar expansion tests leading to development/evaluation of CSA A3004-C8 Procedure B.

• But do these results adequately predict concrete performance?
Research objectives

• To evaluate the sulfate resistance of concrete mixtures produced with portland and portland-limestone cements and supplementary cementitious materials in both laboratory and field exposures at low temperatures.

• To investigate the causes, mechanisms, and depth of deterioration in damaged concrete mixtures exposed to sulfates:
  • **Causes**: the formation of ettringite and/or thaumasite,
  • **Mechanisms**: filling air voids only or by degradation due to disruption of the paste matrix,
  • **Depth of deterioration**: surface damage only or progressive damage toward the interior.
Experimental program

• 53 concrete mixtures were cast:
  • $W/CM = 0.40, 0.50, \text{ and } 0.70$,
  • **Cements**: GU, PLC (with 9%, 10.5%, and 15% limestone), 3 HS, 2 HSL, 2 MS, and HSb,
  • **SCMs**: slag, silica fume, metakaolin, and fly ash.

• Sulfate resistance tests:
  • Measurement of length and mass changes,
  • Making visual inspections,
  • Measurement of resonant frequency,
  • **Mineralogical** analysis (X-Ray diffraction),
  • **Microstructural** analyses (micro X-ray fluorescence spectrometry and scanning electron microscopy).
Laboratory exposure

- Constant temperature of $5 \pm 1 \, ^\circ\text{C}$
- $50 \times 50 \times 285 \, \text{mm prisms}$
- From each concrete mixture:
  - 3 prisms in $\text{Ca(OH)}_2$
  - 3 prisms in $\text{Na}_2\text{SO}_4$
  - 3 prisms in $\text{MgSO}_4$
- Concentration of sulfate solutions:
  
<table>
<thead>
<tr>
<th>W/CM = 0.40 and 0.50</th>
<th>33,800 ppm (same as ASTM C1012) until 19 months, and 15,000 afterwards.</th>
</tr>
</thead>
<tbody>
<tr>
<td>W/CM = 0.70</td>
<td>1,500 ppm</td>
</tr>
</tbody>
</table>
Field exposure

- Variable temperature of \(~1.5 \text{ – } 20.5 \, ^\circ\text{C}\)
- \(75 \times 75 \times 285 \, \text{mm prisms}\)
- From each concrete mixture:
  - 3 prisms in \(\text{Ca(OH)}_2\)
  - 3 prisms in \(\text{Na}_2\text{SO}_4\)
  - 3 prisms in \(\text{MgSO}_4\)
- Concentration of sulfate solutions:
  
<table>
<thead>
<tr>
<th>W/CM</th>
<th>Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.40</td>
<td>15,000 ppm</td>
</tr>
<tr>
<td>0.50 and 0.70</td>
<td>1,500 ppm</td>
</tr>
</tbody>
</table>
- Highest known concentration in Canada is 14,600 ppm in Alberta.
<table>
<thead>
<tr>
<th>Visual condition</th>
<th>Abbreviation [Rating]</th>
<th>Sample photos</th>
</tr>
</thead>
<tbody>
<tr>
<td>Excellent Condition – No visible damage</td>
<td>UND [0]</td>
<td></td>
</tr>
<tr>
<td><strong>Minor damage</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Slight</strong> mass loss and/or cracking at some corners and/or some longitudinal edges</td>
<td>MIN [1]</td>
<td></td>
</tr>
<tr>
<td><strong>Minor to Moderate damage</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Slight to moderate</strong> mass loss and/or cracking at some corners and/or some longitudinal edges Localized scaling at some edges or corners</td>
<td>MIN-MOD [2]</td>
<td></td>
</tr>
<tr>
<td><strong>Moderate damage</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Moderate</strong> mass loss and/or cracking at some corners and/or some faces Localized scaling at some faces</td>
<td>MOD [3]</td>
<td></td>
</tr>
<tr>
<td><strong>Moderate to Severe damage</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Moderate to severe</strong> mass loss and/or cracking at most of the faces and corners Widespread scaling at most of the faces</td>
<td>MOD-SEV [4]</td>
<td></td>
</tr>
<tr>
<td><strong>Severe damage</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Severe</strong> mass loss from all faces and both ends Complete peeling of surface paste from all faces and both ends</td>
<td>SEV [5]</td>
<td></td>
</tr>
</tbody>
</table>
**Visual condition of (PC-slag / PLC-slag) vs HS - W/CM=0.40**

**Laboratory exposure to 5 °C Na$_2$SO$_4$ (33,800 / 15,000 ppm SO$_4^{2-}$)**

<table>
<thead>
<tr>
<th>GU</th>
<th>GU-40S</th>
<th>HS#1</th>
<th>PLC10.5</th>
<th>PLC10.5-40S</th>
<th>PLC10.5-50S</th>
<th>HS#2</th>
<th>PLC15</th>
<th>PLC15-40S</th>
<th>PLC15-50S</th>
<th>HS#3</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2y 9m)</td>
<td>(5y 9m)</td>
<td>(5y 7m)</td>
<td>(3y 10m)</td>
<td>(3y 10m)</td>
<td>(3y 10m)</td>
<td>(3y 10m)</td>
<td>(5y 9m)</td>
<td>(5y 9m)</td>
<td>(5y 8m)</td>
<td>(3y 10m)</td>
</tr>
<tr>
<td>(All prisms failed)</td>
<td>(One broken / one cut)</td>
<td>(The other 2 prisms were cut for SEM)</td>
<td>(All prisms failed)</td>
<td>(All prisms failed)</td>
<td>(The other 2 prisms were cut for SEM)</td>
<td>(MIN [1])</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Notes:**
- MOD [3]
- MOD-SEV [4]
- MIN [1]
- SEV [5]
Visual condition of (PC-slag / PLC-slag) vs HS - W/CM=0.40
Field exposure to 3-16 °C Na₂SO₄ (15,000 ppm SO₄²⁻)

<table>
<thead>
<tr>
<th>GU</th>
<th>GU-40S</th>
<th>HS#1</th>
<th>HS#2</th>
</tr>
</thead>
<tbody>
<tr>
<td>5y 6m</td>
<td>5y 6m</td>
<td>5y 6m</td>
<td>3y 9m</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>PLC10.5</th>
<th>PLC10.5-40S</th>
<th>PLC10.5-50S</th>
<th>HS#2</th>
</tr>
</thead>
<tbody>
<tr>
<td>3y 9m</td>
<td>3y 9m</td>
<td>3y 9m</td>
<td>3y 9m</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>PLC15</th>
<th>PLC15-40S</th>
<th>PLC15-50S</th>
<th>HS#3</th>
</tr>
</thead>
<tbody>
<tr>
<td>5y 6m</td>
<td>5y 6m</td>
<td>5y 6m</td>
<td>3y 9m</td>
</tr>
</tbody>
</table>
Lab specimens were more damaged than field specimens due to excessively high concentration of sulfates in the first year of exposure.
Length and mass changes of (PC-slag / PLC-slag) vs HS -W/CM=0.40 Field exposure to 3-16 °C Na$_2$SO$_4$ (15,000 ppm SO$_4^{2-}$)

Negligible mass change (<1%) for all PC-slag and PLC-slag mixtures.
Backscattered electron images using scanning electron microscope W/CM=0.40 - Laboratory exposure to 5 °C Na$_2$SO$_4$ (33,800 / 15,000 ppm SO$_4^{2-}$)
Sulfur elemental mapping using scanning electron microscope W/CM=0.40 - Laboratory exposure to 5 °C Na$_2$SO$_4$ (33,800 / 15,000 ppm SO$_4^{2-}$)
Backscattered electron images and **sulfur** and **magnesium** elemental mapping using scanning electron microscope - W/CM=0.40

Laboratory exposure to 5 °C MgSO$_4$ (33,800 / 15,000 ppm SO$_4^{2-}$)

PLC15-50S is no worse than HS cement in MgSO$_4$ exposure.
Backscattered electron images of PLC15 concrete mixture using scanning electron microscope - W/CM=0.40
Laboratory exposure to 5 °C Na$_2$SO$_4$ (33,800 / 15,000 ppm SO$_4^{2-}$) – 5y 2m

Near surface

In depth

<table>
<thead>
<tr>
<th>Paste</th>
<th>Near surface</th>
<th>C-S-H / E / T</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>In depth</td>
<td>C-S-H</td>
</tr>
<tr>
<td>Voids</td>
<td>Near surface</td>
<td>E+T / G / T</td>
</tr>
<tr>
<td></td>
<td>In depth</td>
<td>G / CH</td>
</tr>
</tbody>
</table>
Backscattered electron images of PLC15-40S concrete mixture using scanning electron microscope - W/CM=0.40

Laboratory exposure to 5 °C Na$_2$SO$_4$ (33,800 / 15,000 ppm SO$_4^{2-}$) – 5y 2m

Near surface

In depth

<table>
<thead>
<tr>
<th>Paste</th>
<th></th>
<th>Voids</th>
</tr>
</thead>
<tbody>
<tr>
<td>Near surface</td>
<td>C-S-H / E / T</td>
<td>Near surface</td>
</tr>
<tr>
<td>In depth</td>
<td>C-S-H</td>
<td>In depth</td>
</tr>
</tbody>
</table>
Backscattered electron images of HS#1 concrete mixture using scanning electron microscope - W/CM=0.40
Laboratory exposure to 5 °C Na$_2$SO$_4$ (33,800 / 15,000 ppm SO$_4^{2-}$) – 5y 3m

Near surface

In depth

Sulfate products in PLC15-40S are essentially the same as in HS cement.

<table>
<thead>
<tr>
<th></th>
<th>Paste</th>
<th>Voids</th>
</tr>
</thead>
<tbody>
<tr>
<td>Near surface</td>
<td>C-S-H / E / T</td>
<td>T / E+T+G</td>
</tr>
<tr>
<td>In depth</td>
<td>C-S-H</td>
<td>CH</td>
</tr>
</tbody>
</table>
Conclusions

1. As with room temperature exposure, at low temperatures, concrete mixtures made with 100% high C₃A cements with or without limestone are not sulfate-resistant.

2. In the field exposure, for an equal level of SCMs, the presence of limestone had no impact on sulfate resistance of concrete.

3. In the laboratory and based on visual condition, PLC15 required 50% slag for equal performance to GU cement with 40% slag. However, also based on similar visual condition, in the field exposure, 40% slag was sufficient when used with both PLC15 and GU.

4. The sulfate resistance of PC+SCM and PLC+SCM concrete mixtures at W/CM ratios of 0.40 and 0.50 is equal to or better than that of traditional highly and moderately sulfate-resistant portland and blended cements (CSA A3001 HS, HSB, MS, and MSb).
Conclusions --- Cont’d

5. For all concrete mixtures, the sulfate resistance in field exposure at annual temperatures ranging from 1.5 to 20.5 °C was better than in the laboratory at 5 °C. This is due to more realistic very severe field concentrations of sulfate solutions as found in western Canada, variable temperature exposures, and the larger prism sizes used in the field exposure.

6. In damaged concrete prisms made with or without portland-limestone cements, the initial signs of deterioration from ettringite were in the form of cracking, spalling, and loss of materials at the corners and edges of the concrete prisms. Thaumasite was only detected near the surface at later ages after initial damage caused by formation of ettringite and gypsum. Therefore, it was concluded that thaumasite was not the primary cause of deterioration.
7. From microstructural analysis using SEM/EDX and micro XRF, the following conclusions are made based on the progression of damage:

a) Regardless of damage, the sulfate penetration at any given time was limited to 1-2 mm. However, the depth of deterioration in magnesium sulfate exposure was more extensive, up to 5 mm below the surface, compared to sodium sulfate exposure. As expected, exposure to magnesium sulfate solution is more aggressive than sodium sulfate solution for all concrete mixtures.

b) In concrete showing damage, after damage to the paste mainly by ettringite formation, 1-2 mm layers progressively spalled off. However, voids were filled partially or completely with ettringite, thaumasite, gypsum, or a mixture of them.

c) Thaumasite formation in voids occurred in all mixtures examined including HS cement. Therefore, there is no relationship to the presence of limestone in the cement used.

d) There was no damage to surface layers of concrete mixtures with sufficient levels of slag even after 5.5 years of exposure and the ingress of sulfate ions only resulted in partial or complete filling of the air voids in the outer 1-2 mm.

e) Below the surface layer, regardless of damage, voids were only partially filled with gypsum or calcium hydroxide.
Conclusions --- Cont’d

8. Although in mortar bar tests, such as ASTM C1012, expansion is the criteria for failure, with concrete prisms having bigger cross sections, the deterioration mainly occurs at the surface and does not affect the interior of the prisms until extensive damage has occurred, thus preventing expansion. Therefore, monitoring mass change of concrete prisms in combination with visual inspection are better tools to evaluate sulfate resistance than measuring the length change.

9. The results of this experimental research in both laboratory and field exposures can be used to develop a standard test method for evaluating the sulfate resistance of concrete, since no standard test methods currently exist in North American standards except USBR 4908-92.

10. As the result of this research, the Canadian A3000 and A23.1 standards have been changed to allow the use of portland-limestone cement together with SCMs in sulfate exposures without any low-temperature testing or other restrictions.
Thank You!