Decreasing the Clinker Component in Cementing Materials: Performance of Portland-Limestone Cements in Concrete in combination with Supplementary Cementing Materials

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DEPARTMENT OF CIVIL ENGINEERING

NRMCA Sustainability Forum
PLC in CSA Standards

- In 2008, a new class of Portland-Limestone cements was added to CSA A3001, with up to 15% blended or interground limestone replacing cement clinker.
- The CO$_2$ emissions from PLC are ~10% less relative to Type GU Portland cement.
- In addition, fewer raw materials and less energy are used to produce PLC.
- When properly optimized, the limestone is not inert and contributes to the properties of the cement.
- PLC have to meet the same set time and strength development performance as portland cement of the same type (eg. GU ---same as ASTM Type I)
Portland-Limestone Cements in CSA Standards

- PLC allowed in the A3000 Cementitious Materials standard in 2008 and to the A23.1 concrete standard in 2009
- Building codes are being updated in 2010 to include these changes
PLC in blended cements

- In April 2010, CSA A3000 balloted to also allow 15% limestone in CSA blended cements.
Use of limestone cements

• 1965 Heidelberger produces 20% limestone cement in Germany for specialty applications
• 1979 French Cement Standards allows limestone additions.
• 1983 CSA A5 allows 5% in Type 10 (now GU) cement
• 1990, 15+/-5% limestone blended cements being used in Germany
• 1992, in UK, BS 7583 allows up to 20% in Limestone Cement
• 2000 EN 197-1 allows 5% MAC (Typ. Limestone) in all 27 common cements, as was commonly practiced in various European cement standards prior to that
• 2000 EN 197-1 creates CEM II/A-L (6-20%) and CEM II/B-L (21-35%)
• 2003 CSA A3001 allows 5% in other Types than GU
• 2004 ASTM C 150 allows 5% in Types I-V
• 2007 AASHTO M85 allows 5% in Types I-V
• 2008 CSA A3001 includes PLC with up to 15% limestone
Cement types sold in Europe 1999 - 2004 (according to Cembureau data)

PLC had the largest use in 2004

Most portland-composite cements contain limestone too
ASTM and PLC

- At least 2 producers in the USA are making 10% limestone cements under ASTM C1157.
- ASTM C595 may be amended to allow for PLC blended cements.
- Thomas & Hooton are preparing a PCA report summarizing the Canadian data.
Why Portland-Limestone Cements (PLC)?

- Portland Cement manufacturing produces CO₂
  - Limestone decomposition
  - Fuel consumption
- Governments are preparing cap and trade limits on point source CO₂ emissions
- PLC (CEM IIA-L) has been in use in Europe for > 20 years and is now the most widely used cement type
More Sustainable Cementing Materials

SCMs (and blended cements)

<table>
<thead>
<tr>
<th>Portland cement type</th>
<th>Blended hydraulic cement type</th>
<th>Portland-limestone cement type</th>
</tr>
</thead>
<tbody>
<tr>
<td>GU</td>
<td>GUb</td>
<td>GUL</td>
</tr>
<tr>
<td>(GULb)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### CSA A23.1 Types of Hydraulic Cements

<table>
<thead>
<tr>
<th>Portland cement</th>
<th>Blended hydraulic cement</th>
<th>Portland-limestone cement ***</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>GU</td>
<td>GUb</td>
<td>GUL</td>
<td>General use cement</td>
</tr>
<tr>
<td>MS</td>
<td>MSb</td>
<td>-</td>
<td>Moderate sulphate-resistant cement</td>
</tr>
<tr>
<td>MH</td>
<td>MHb</td>
<td>MHL</td>
<td>Moderate heat of hydration cement</td>
</tr>
<tr>
<td>HE</td>
<td>HEb</td>
<td>HEL</td>
<td>High early-strength cement</td>
</tr>
<tr>
<td>LH</td>
<td>LHb</td>
<td>LHL</td>
<td>Low heat of hydration cement</td>
</tr>
<tr>
<td>HS</td>
<td>HSb</td>
<td>-</td>
<td>High sulphate-resistant cement</td>
</tr>
</tbody>
</table>

*** Portland-limestone cements shall not be used in sulphate exposures as defined in Table 3 of CAN/CSA-A23.1 (even when mixed with SCMs)
Quality limits on limestone in CSA A3001
(based on EN197)

4.4.4 Limestone addition to portland-limestone cement
The limestone in portland-limestone cement shall meet the following requirements and shall be tested at least every 6 months:
(a) The calcium carbonate (CaCO₃) content calculated from the calcium oxide (CaO) content shall be at least 75% by mass.
(b) The methylene blue value, an indication of clay content, determined by CSA A3004-D1, shall not exceed 1.2 g/100 g.
(c) The total organic carbon (TOC) content, when tested in accordance with CSA A3004-D2, shall not exceed 0.5% by mass.

- These limits are only for limestone contents >5%
Clinker Requirements for PLC in CSA A3001

• 4.4.6 Cement and clinker requirements for use in portland-limestone cements
  – Where portland-limestone cement is produced from a combination of portland cement and limestone, the portland cement used shall meet the requirements of this Standard. Where the portland-limestone cement is produced by milling, the clinker used in the production of the portland-limestone cement shall be suitable for producing cement that meets the requirements of this Standard for portland cement.
A3001 PLC Performance Requirements

- In CSA A3000, the setting times and strength development limits are the same for PLC as for portland cements.
- Heat of hydration limits are also the same for MH and LH cements.
- In concrete, PLC also performs well with slag or fly ash at normal replacement levels.
Why PLC works: (Herford, 2008) Limestone and cement aluminates form Carboaluminates, which fill in porosity and increase strength + if get more aluminates from SCM, optimum will shift to higher % limestone.

Equal strength at 0 and 13% PLC.
PLC + Slag, Fly Ash, or Metakaolin
(more aluminates to form carboaluminate hydrates)

Research is currently underway at U of T to evaluate this
# Composition of Cementing Materials

<table>
<thead>
<tr>
<th></th>
<th>SiO₂ (%)</th>
<th>Al₂O₃ (%)</th>
<th>Fe₂O₃ (%)</th>
<th>CaO (%)</th>
<th>MgO (%)</th>
<th>SO₃ (%)</th>
<th>LOI (%)</th>
<th>Limestone (%)</th>
<th>Alkali equiv. (%)</th>
<th>Blaine (m²/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GU</td>
<td>19.59</td>
<td>5.36</td>
<td>2.36</td>
<td>62.43</td>
<td>2.37</td>
<td>4.45</td>
<td>1.8</td>
<td>3.5</td>
<td>0.96</td>
<td>391</td>
</tr>
<tr>
<td>PLC10</td>
<td>19.33</td>
<td>5.22</td>
<td>2.3</td>
<td>61.68</td>
<td>2.34</td>
<td>4.31</td>
<td>3.63</td>
<td>10</td>
<td>0.95</td>
<td>442</td>
</tr>
<tr>
<td>PLC15</td>
<td>18.6</td>
<td>5.09</td>
<td>2.23</td>
<td>60.03</td>
<td>2.26</td>
<td>4.21</td>
<td>5.9</td>
<td>15</td>
<td>0.93</td>
<td>507</td>
</tr>
<tr>
<td>Slag</td>
<td>38.14</td>
<td>7.18</td>
<td>0.74</td>
<td>39.95</td>
<td>10.57</td>
<td>2.71</td>
<td>-</td>
<td>-</td>
<td>0.63</td>
<td>-</td>
</tr>
</tbody>
</table>

Higher LOI with PLC: Higher Blaine needed
Limestone fineness in the interground product is significantly finer than the clinker fraction

L. Barcelo, Lafarge
<table>
<thead>
<tr>
<th>PLC in Sulfate Exposures</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Currently PLC is not allowed in sulfate exposures by CSA A3001 and A23.1 due to concern with potential for thaumasite sulfate attack (TSA) at cool temperatures.</td>
</tr>
<tr>
<td>• There is currently a CSA A3001 Amendment ballot out on this, but its outcome is not certain. Data is still being generated, so timing of the ballot is not the best.</td>
</tr>
<tr>
<td>• Research is underway.</td>
</tr>
<tr>
<td>• When sufficient data has been obtained, it will likely be possible to allow PLC + SCM (or blended cements) in sulfate exposures.</td>
</tr>
</tbody>
</table>
Thaumasite Form of Sulfate Attack

30-year-old bridge column exposed to wet oxidized sulfide clay in England

Thaumasite is not so common, but when it occurs, it attacks the whole matrix.
Thaumasite

- Thaumasite is **not** a normal product of the hydration of Portland cement.

  \[ \text{Ca}_3\text{Si(OH)}_6(\text{SO}_4)(\text{CO}_3) \cdot 12\text{H}_2\text{O} \]

- However, it can occur in chemically altered concrete especially in cool wet conditions.

- It requires calcium (\(\text{Ca}^{2+}\)), sulphate (\(\text{SO}_4^{2-}\)), carbonate (\(\text{CO}_3^{2-}\)), and silicate (\(\text{Si(OH)}_6\)), as well as a supply of water.

- Silicate is supplied by the decomposition of the calcium silicate hydrate, resulting in loss of cohesion.
Thaumasite Sulfate Attack

Turning Concrete Prisms Into Mush at 40 °F

These photos are not PLC
On-going Sulfate Resistance Research

- To investigate the sulfate resistance of PLC at normal temperatures
- To examine the resistance of PLC against TSA
- To study the effectiveness of combining PLC with SCMs to improve sulfate resistance
Phase I Lab Program

• Tested 5 PLCs (12% C$_3$A clinker) and different levels of slag

• ASTM C 1012 at 73 ° F (23 °C)

• Modified ASTM C 1012 at 40 °F (5°C) to test for TSA
1-year Expansion of GU and GUL Mortar Bars at 23 °C
(using 12% C₃A clinker)
1-year Expansion of 50% Slag-PLC Mortar Bars at 23 °C --- all in excellent condition

50% Cement + 50% Slag

Expansion (%) vs. Limestone Content (%)

- Expansion values range from 0.10 to 0.12%
- Limestone content varies from 0% to 21.8%

Graph showing expansion values for different limestone content levels.
Time to 0.10% Expansion of GU and GUL Mortar Bars at 5 °C---all failed and most formed Thaumasite

![Graph showing the time to 0.10% expansion of GU and GUL mortar bars at 5 °C for different limestone contents. The x-axis represents the limestone content (%) and the y-axis represents the failure time (days). The graph shows that as the limestone content increases, the failure time decreases.]
1-year Expansion of 50% Slag-GUL Mortar Bars at 5 °C
---all in excellent condition (as were 30% slag bars)
Conclusions on Sulfate Resistance

- Although not expected to be sulfate resistant due to 12% $C_3A$ clinker, Type GUL PLCs appear to be more susceptible to sulfate attack than a Type GU Portland cement.

- Both 30 and 50% slag prevents damage regardless of limestone content of PLC.

- When tested at 5 °C, thaumasite sulfate attack did occur with PLC, but it was prevented by both 30 and 50% slag.
New Tests

• Type V cements with 0, 3 and 10% interground limestone have been obtained from the Holcim plant in Utah.

• Sulfate resistance testing has started at both 73 and 40 °F using C1012 mortar bars and concrete prisms at 40 °F.
Alkali-Silica Reaction
### ASR: ASTM C1260 Accelerated Mortar Bar Expansions

<table>
<thead>
<tr>
<th>Length Change (%)</th>
<th>GU 100%</th>
<th>PLC10 100%</th>
<th>PLC15 100%</th>
<th>GU 70% SLAG 30%</th>
<th>PLC10 70% SLAG 30%</th>
<th>PLC15 70% SLAG 30%</th>
<th>GU 50% SLAG 50%</th>
<th>PLC10 50% SLAG 50%</th>
<th>PLC15 50% SLAG 50%</th>
</tr>
</thead>
<tbody>
<tr>
<td>14 Days</td>
<td>0.445</td>
<td>0.801</td>
<td>0.594</td>
<td>0.205</td>
<td>0.214</td>
<td>0.318</td>
<td>0.060</td>
<td>0.041</td>
<td>0.047</td>
</tr>
<tr>
<td>28 Days</td>
<td>0.685</td>
<td>1.155</td>
<td>0.784</td>
<td>0.377</td>
<td>0.410</td>
<td>0.630</td>
<td>0.218</td>
<td>0.163</td>
<td>0.187</td>
</tr>
</tbody>
</table>

Mortar bars, 25 x 25 x 250 mm (1 x 1 x 12 in.) stored in 1M NaOH at 80°C for **14 days**

**Typically used expansion limit is 0.10% at 14 days**
**ASR: ASTM C1293 Concrete Prism Expansions**

<table>
<thead>
<tr>
<th>Length Change (%)</th>
<th>GU 100%</th>
<th>PLC10 100%</th>
<th>PLC15 100%</th>
<th>PLC10 70% SLAG 30%</th>
<th>PLC15 70% SLAG 30%</th>
<th>PLC10 50% SLAG 50%</th>
<th>PLC15 50% SLAG 50%</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1 year</strong></td>
<td>0.182</td>
<td>0.218</td>
<td>0.241</td>
<td>0.036</td>
<td>0.027</td>
<td>0.023</td>
<td>0.016</td>
</tr>
<tr>
<td><strong>2 years</strong></td>
<td>0.201</td>
<td>0.228</td>
<td>0.248</td>
<td>0.055</td>
<td>0.041</td>
<td>0.036</td>
<td>0.013</td>
</tr>
</tbody>
</table>

- Concrete prisms
- 3 x 3 x 12 in.
- Stored over water at 38°C (100°F) and 100% RH in containers for 2 years
### ASTM C157 Drying Shrinkage

<table>
<thead>
<tr>
<th>Length Change (%)</th>
<th>GU 100%</th>
<th>PLC10 100%</th>
<th>PLC15 100%</th>
<th>GU 70% SLAG 30%</th>
<th>PLC10 70% SLAG 30%</th>
<th>PLC15 70% SLAG 30%</th>
</tr>
</thead>
<tbody>
<tr>
<td>28 days</td>
<td>0.036</td>
<td>0.037</td>
<td>0.037</td>
<td>0.026</td>
<td>0.027</td>
<td>0.025</td>
</tr>
<tr>
<td>1 year</td>
<td>0.069</td>
<td>0.061</td>
<td>0.062</td>
<td>0.058</td>
<td>0.052</td>
<td>0.053</td>
</tr>
<tr>
<td>2 years</td>
<td>0.067</td>
<td>0.068</td>
<td>0.065</td>
<td>0.062</td>
<td>0.06</td>
<td>0.067</td>
</tr>
</tbody>
</table>

- Shrinkage unaffected by PLC
- Reduced 28-day shrinkage with slag mixes
Rapid Index Test for Chloride Penetration Resistance

( ASTM C1202: commonly called RCP Test)

Resistance to electric flow is a function of the porosity and pore continuity of concrete---the same as permeability
56-day RCP Results

56 Day RCPT Results

CSA C-1 Exposure Limit

Cement-100%

Cement-70%+Slag-30%

GU
PLC10
PLC15
85-day RCP Results

85 Day RCPT Results

- GU
- PLC10
- PLC15

Coulombs

Cement-100%
Cement-70%+Slag-30%
Chloride Bulk Diffusion Test
ASTM C1556 (used in Life-365)

\[ \frac{C_x}{C_0} = 1 - \text{erf} \left( \frac{x}{2\sqrt{D_a \cdot t}} \right) \]

\( C_0 \) and \( D_a \) are found by curve fitting. Results are given in \( 10^{-12} \text{ m}^2/\text{s} \).
### ASTM C1556
Chloride Bulk Diffusion

<table>
<thead>
<tr>
<th>(Cs (% mass))</th>
<th>GU 100%</th>
<th>PLC10 100%</th>
<th>PLC15 100%</th>
<th>GU 70% SLAG 30%</th>
<th>PLC10 70% SLAG 30%</th>
<th>PLC15 70% SLAG 30%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.73</td>
<td>0.84</td>
<td>0.8</td>
<td>1.1</td>
<td>1.07</td>
<td>0.98</td>
</tr>
<tr>
<td>($D_a$ (m²/s * 10⁻¹²))</td>
<td>15.9</td>
<td>15.6</td>
<td>22.5</td>
<td>8.07</td>
<td>6.11</td>
<td>8.25</td>
</tr>
</tbody>
</table>

- Lowest diffusion values at 10% limestone with or without slag
- With 30% slag, 15% PLC ~no limestone GU cement
PLC Limitations of Use

- CSA A3000-08 and A23.1 both state that concretes made with PLC are not to be used in sulfate exposure (even when combined with SCMs).
- This was due to concerns in 2007 about mixed information in the literature, and to minimize any concern about Thaumasite sulfate attack, while research is on-going.
- (This same limitation is placed on concrete containing mineral fillers used as part of the aggregate)
- This issue is currently being addressed as part of 3 independent research programs by Day, Hooton, and Thomas and interim results show that SCMs prevent thaumasite formation in sulfate exposures at low temperatures.
- There will a ballot in 2010 which may lift these restrictions
Field Demonstration Projects

- To develop confidence in the use of PLC, the industry is undertaking demonstration projects across Canada.
- Mike Thomas presented 3 yesterday
Lafarge PLC Trials from 2008
(Concrete International Jan 2010)

BY MICHAEL D.A. THOMAS, DOUG Hooton, KEVIN CAIL, BRENTON A. SMITH, JOHN DE WAl, AND KENNETH G. KAZANIS

- 8 concrete slabs were cast in Oct 2008 at Lafarge, Gatineau QC
- 80-100mm slump, air-entrained, 30MPa, C-2 exposure (355kg/m³)
- GU and PLC with 0, 25, 40 & 50% mixed SCM (2 slag: 1 fly ash)
# Portland-Limestone Cement Demonstration Projects in Ontario

- May 2008: Pavement slabs at Holcim cement plant (GUL, GUL+ 25% Slag)
- Nov. 2009: Four pavement slabs with St. Marys Cement at the CBM Portlands plant (GUL, GUL+25% Slag)
- Nov. 2009: Two barrier walls on the QEW in Burlington with Holcim/Dufferin, in cooperation with the MTO (using GUL + slag rather than GU + slag).
PC+25% Slag vs PLC+25% Slag

Equal Properties:
Strength Development (35MPa @ 28days)
Drying Shrinkage (<0.04% at 28d)
Coulombs (<1500 at 56 days)
Freeze/Thaw
Scaling Resistance
PLC Barrier Walls on QEW
Nov. 4, 2009

GU Cement +
25% Slag

GUL Cement
+ 25% Slag

23 m³ of each mix placed, 30 MPa (4500 psi)
60-100 mm (2.5-4 in.) slump
Mix Details

267 kg/m$^3$ GUL (or GU)
88 kg/m$^3$ slag (25%)
355 kg/m$^3$ total cementitious
  (590 pcy)
w/cm = 0.40
Air-entrained
Temperature Profiles in Barrier Wall over first 6 days

Sections were ~ 1.0 m thick
## Nov. 2009 QEW Barrier Wall

<table>
<thead>
<tr>
<th>2009 QEW Barrier Wall</th>
<th>PC +25% SLAG</th>
<th>PLC + 25% SLAG</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Shrinkage (28d)</strong></td>
<td>0.038%</td>
<td>0.038%</td>
</tr>
<tr>
<td><strong>Strength (MPa)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>9.5</td>
<td>10.3</td>
</tr>
<tr>
<td>3</td>
<td>19.3</td>
<td>19.4</td>
</tr>
<tr>
<td>7</td>
<td>25.6</td>
<td>26.8</td>
</tr>
<tr>
<td>28</td>
<td>36.9</td>
<td>37.9</td>
</tr>
<tr>
<td>56</td>
<td>38.9</td>
<td>38.0</td>
</tr>
<tr>
<td>91</td>
<td>40.7</td>
<td>40.2</td>
</tr>
<tr>
<td><strong>Freeze/Thaw Durability</strong></td>
<td>94%</td>
<td>94%</td>
</tr>
<tr>
<td><strong>MTO LS-412 Scaling</strong></td>
<td>0.24 kg/m²</td>
<td>0.24 kg/m²</td>
</tr>
<tr>
<td><strong>RCP (Coulombs) 28 days</strong></td>
<td>2070</td>
<td>1490</td>
</tr>
<tr>
<td><strong>56 days</strong></td>
<td>1930</td>
<td>1340</td>
</tr>
</tbody>
</table>
## Field Trials Cylinders vs Cores Coulombs

<table>
<thead>
<tr>
<th></th>
<th>GU + 25% Slag</th>
<th>PLC10 + 25% Slag</th>
</tr>
</thead>
<tbody>
<tr>
<td>28 Day Cylinders</td>
<td>2071</td>
<td>1929</td>
</tr>
<tr>
<td>28 Day Cores</td>
<td>2127</td>
<td>2445</td>
</tr>
<tr>
<td>61 Day Cylinders</td>
<td>1488</td>
<td>1342</td>
</tr>
<tr>
<td>61 Day Cores</td>
<td>1417</td>
<td>1647</td>
</tr>
</tbody>
</table>
Field Trial Coulombs (Cylinders and cores)

RCPT

Charge Passed (C)

GU

PLC

Cement Type

28 Days-Cylinders
28 Days-Cores
61 Days-Cylinders
61 Days-Cores
28 days later
2010 Demonstration Projects

- Holcim, Lafarge, and St. Marys are all in the process of arranging further PLC demonstration placements on highway pavements, and barrier walls.
- MTO is receptive and is interested in the data that will be generated.
PLC will help make “Greener” Concrete