Specification Requirements and Environmental Performance of Portland-Limestone Cements

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*Minneapolis*  
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Portland-Limestone Cement

- What is a PLC?
- What are the spec requirements?
- What are the benefits?
- How does it work?
- Why?
ASTM and AASHTO
2012 Editions
AASHTO M240 & ASTM C595

- Same physical requirements as pre-existing C595/M240 cement types
- Chemical requirements – sulfate content, LOI
- Sulfate resistance – no MS or HS designation, initially
- Limestone requirements—CaCO$_3$, MBI, TOC
### Chemical Requirements for Blended Cements

<table>
<thead>
<tr>
<th></th>
<th>IS(&lt; 70), IT(P&lt; S&lt; 70), IT(L&lt; S&lt; 70)</th>
<th>IS(≥ 70), IT(S≥ 70)</th>
<th>IP, IT(P≥ S), IT(P&gt;L)</th>
<th>IL IT(L≥ S), IT(L≥ P)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>MgO, max, %</strong></td>
<td>. . .</td>
<td>. . .</td>
<td>6.0</td>
<td>. . .</td>
</tr>
<tr>
<td><strong>SO₃, max, %</strong></td>
<td>3.0</td>
<td>4.0</td>
<td>4.0</td>
<td>3.0</td>
</tr>
<tr>
<td><strong>S²⁻, max, %</strong></td>
<td>2.0</td>
<td>2.0</td>
<td>. . .</td>
<td>. . .</td>
</tr>
<tr>
<td><strong>Insol. res. max, %</strong>&lt;sup&gt;C&lt;/sup&gt;</td>
<td>1.0</td>
<td>1.0</td>
<td>. . .</td>
<td>. . .</td>
</tr>
<tr>
<td><strong>LOI, max, %</strong></td>
<td>3.0&lt;sup&gt;D&lt;/sup&gt;</td>
<td>4.0&lt;sup&gt;D&lt;/sup&gt;</td>
<td>5.0&lt;sup&gt;D&lt;/sup&gt;</td>
<td>10.0</td>
</tr>
</tbody>
</table>

<sup>C</sup> Insol res max does not apply to ternary blended cements.

<sup>D</sup> For ternary blended cements with limestone LOI max = 10%.
## Requirements for Limestone

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Test Method</th>
<th>Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCO₃ content</td>
<td>C114/T105</td>
<td>Min. 70%</td>
</tr>
<tr>
<td>Methylene blue index</td>
<td>See Annex A2</td>
<td>Max. 1.2 g/100g</td>
</tr>
<tr>
<td>Total organic carbon</td>
<td>See Annex A3</td>
<td>Max. 0.5%</td>
</tr>
</tbody>
</table>
Limestone Testing

A2. METHYLENE BLUE INDEX TEST FOR LIMESTONE

A2.1 Scope
A2.1.1 This annex describes the laboratory procedures for the quantitative determination of methylene blue dye adsorption index of limestone for use as an ingredient in blended cement.
A2.1.2 The text of this annex references notes and footnotes which provide (excluding those in tables and figures) shall not be considered as requirements of this annex.
A2.1.3 Unit—The values stated in SI units are to be regarded as standard.

A2.2 Summary of test
A2.2.1 The sample is reduced to a fine powder prior to testing. It is then suspended in the prepared test portion in water. The absorbance at each addition of solution by carrying out a blank test on filter paper plus the absorbency of the dye is confirmed, the methylene blue index value (MBI) is calculated and that of the sample tested.

A2.3 Significance and Use
A2.3.1 This annex provides a means to determine the amount of methylene blue index of limestone. Methylene blue index value (MBI) is determined by adsorption on the clay and content. Certain clays may increase the cement unless present in sufficient quantity to the limestone when used as an ingredient, the methylene blue index value of limestone permitted as an ingredient in blended cement.

A2.4 Apparatus:
A2.4.1 The equipment and materials, including the temperature and humidity control, shall meet the requirements of CS111, unless otherwise specified.
A2.4.2 The following equipment shall be included to perform this test:
(a) burette, with capacity of either 100 mL or 50 mL and graduation of either.
(b) micro-pipette,
(c) glass stir bar.

A3. TOTAL ORGANIC CARBON CONTENT OF LIMESTONE

A3.1 Scope
A3.1.1 This annex specifies the laboratory procedures for the quantitative determination of the total organic carbon content of limestone for use as an ingredient in blended cement.
A3.1.2 The text of this annex references notes and footnotes which provide explanatory material. These notes and footnotes (excluding those in tables and figures) shall not be considered as requirements of this annex.
A3.1.3 Unit—The values stated in SI units are to be regarded as standard. No other units of measurement are included in this annex.
A3.1.4 This annex does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

A3.2 Summary of test
A3.2.1 Total organic carbon is determined either on a sample from which the inorganic carbon has been removed through hydrochloric acid extraction or by difference of inorganic carbon from total carbon.

A3.3 Significance and Use
A3.3.1 This annex provides a means to determine the total organic carbon content of a sample of finely ground limestone. The organic carbon content of a limestone used as an ingredient in cement can increase the air entraining agent dosage required to achieve a specific air content in concrete. The specification places a limit on the total organic carbon content of limestone permitted as an ingredient in blended cement.

A3.4 Apparatus
A3.4.1 The equipment shall meet the requirements of Specification C 511, unless otherwise specified.
A3.4.2 The following equipment shall be included to perform this test:
(a) analytical balance, precision = 0.1 mg;
(b) volumetric flask, 50 mL;
(c) volumetric flask, 1000 mL;
(d) glass stirrer, 40 mm diameter, and porosity = C-4;
(e) magnetic stirrer;
(f) magnetic stir bar.
(g) oven, able to maintain a temperature of 45°C ± 5°C;
Summary of Provisions

• PLC: Type IL and Type IT with 5% to 15% limestone
• Same physical requirements
• Similar chemical requirements
• No provisions for sulfate resistance
• Min CaCO$_3$ content, MBI and TOC
Environmental Benefits
Environmental Benefits

[Bar chart showing CO₂ emissions per kg of cement for Portland and Portland-limestone cement at three different plants. The chart indicates lower emissions for Portland-limestone cement compared to Portland cement at all three plants.]

Portland cement
Portland-limestone cement

Schmidt 1992
## Environmental Benefits

<table>
<thead>
<tr>
<th></th>
<th>10%</th>
<th>15%</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Energy Reduction</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fuel (million BTU)</td>
<td>443,000</td>
<td>664,000</td>
</tr>
<tr>
<td>Electricity (kWh)</td>
<td>6,970,000</td>
<td>10,440,000</td>
</tr>
<tr>
<td><strong>Emissions Reduction</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO$_2$ (lb)</td>
<td>581,000</td>
<td>870,000</td>
</tr>
<tr>
<td>NO$_x$ (lb)</td>
<td>580,000</td>
<td>870,000</td>
</tr>
<tr>
<td>CO (lb)</td>
<td>104,000</td>
<td>155,000</td>
</tr>
<tr>
<td>CO$_2$ (ton)</td>
<td>189,000</td>
<td>283,000</td>
</tr>
<tr>
<td>Total hydrocarbon, THC (lb)</td>
<td>14,300</td>
<td>21,400</td>
</tr>
</tbody>
</table>

* Per million tons cement
Environmental Benefits

• Cement accounts for approximately
  – 95 % of concrete CO$_2$ emissions
  – 85 % of concrete energy consumed

• PLC is an option to implement proven technology to obtain desired performance and improve sustainability of concrete

Marceau et al. 2007
How Limestone Works

• Particle packing
  – Improved particle size distribution

• Nucleation
  – Surfaces for precipitation

• Chemical reactions
  – Only a small amount, but...
Why 15%?

Matschei et al. 2007
Brief History of PLC

• 1965 German standards include PLC (20%) specialty applications
• 1979 French standards include PLC
• 1990 PLC with 15±5% limestone routinely used in Germany
• 1992 UK standards reference PLC (20%)
• 2000 EN 197-1 creates CEM II/A-L (6-20%) and CEM II/B-L (21-35%)
• 2008 CSA A3001 defines PLC containing 5%-15% limestone
• 2012 ASTM C595 and AASHTO M240 include PLC
Summary

• PLC is a new (to US) cement type
• 5% to 15% limestone
• Performance similar
• Environmental benefits