Modified ASTM C359 Early Stiffening of Mortar to Anticipate Complex Cement-Admixture Interactions

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Outline

- Advantages/limitations of Predictive/Diagnostic Mortar Tests
- Applicability of the Modified ASTM C359 Test
- Modified ASM C359 Mortar Tests for Evaluating Cement-Admixture Interactions
- Case Studies
- Origins of Cement-Admixture Incompatibility
- A Few Fixes to Cement-Admixture Incompatibility
- Conclusions

Acknowledgement
The mortar test protocols and test data were produced by the Lab Technical Services and R&D groups of the W.R. Grace Co.
Inconsistent Cement-Admixture Performance

Water/cement ratio 0.5, 23 C, water only

Sulfate depletion

5 Cement Samples From Same Plant - with reported setting time problems - Tested Without Admixtures

Set Time Variations with OPC – with and without Chemical Admixtures

- 0.15% WRA [0.10% CS + 0.05% TEA]
- 0.20% MRWR [0.10% PC + 0.05% SG + 0.05% Ca(NO₃)₂]

Inconsistent Cement-Admixture Performance

With Admixtures

0.15% WRA [0.10% CS + 0.05% TEA]
0.20% MRWR [0.10% PC + 0.05% SG + 0.05% Ca(NO₃)₂]
Cement-Admixture Interaction: Impact on Variation in Mortar Spread

Investigating Variable Slump in Precast Production

Mortar mixes made with 50 grab samples cement
Admixtures: Control, MSFC, and PC
Measure mortar spread

Spread Variation
Control 20 mm
SP (MSFC) 112 mm
SSP (PC) 70 mm

Indications of Cement-Admixture Incompatibility

- Unexpected change in dose-slump response
- Excessive slump loss
- Excessive retardation
- Low strengths
- Unusually high or low AEA doses
- "Odd" loads - one truck slumps or sets ok, the next doesn't, even though you check the plant and it all looks consistent.
Applicability of a Modified ASTM C359 Early Stiffening of Mortar Test

◆ The C359 Mortar Test is a well established industry standard.

◆ Low cost and quick. Improved manpower efficiency.

◆ Ongoing quality control tool to verify lot-to-lot performance uniformity for various concrete material.

◆ Proactively screen possible relative performance differences between:
  ➤ Successive lots of same material
  ➤ Alternate sources of materials

◆ Troubleshoot unexpected performance issues.

◆ Proactively finding the edge of disaster.
What can the Modified ASTM C359 Test Indicate?

- Lack of Water Reduction by Water Reducing Admixture (WRA)
- Insufficient slump increase by WRA
- Rapid Slump Loss with WRA
- Increased water demand
- False and Flash setting tendency

Note: Absolute mortar performance may not proportionately correspond to concrete performance.
Expected Cement Dispersing Action of Superplasticizers

This is what should happen when you add a WR/HRWR to any Concrete

- Increased water demand
- Less than optimum strength development
- Higher particle surface area – increased strength
ASTM C359 Method Summary

1. Prepare mortar with specified amounts of cement, sand, and water.

2. Cast a bed of mortar

3. Make penetration measurements with modified Vicat apparatus at set intervals. Measure temperature with every penetration reading.

4. Remix mortar, re-cast bed, and continue penetration measurements.
Lab Set up for ASTM C359 Test
ASTM C359 Early Stiffening of Mortar Test
Detecting Cement – Admixture Incompatibilities

600g cement
600 g sand
w/c = 0.30*
* Revised procedure calls for variable w/c

50 mm
### Modified C 359 Procedure for Admixture Addition

<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
<th>Time Interval</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Add sand and cement, mix 10 sec slow speed</td>
<td>0-10 sec</td>
</tr>
<tr>
<td>2</td>
<td>Add water</td>
<td>10-15 sec</td>
</tr>
<tr>
<td>3</td>
<td>Mix medium speed</td>
<td>15 sec - 1:15</td>
</tr>
<tr>
<td>4</td>
<td>Stop and scrape, measure temp</td>
<td>1:15 - 2:00</td>
</tr>
<tr>
<td>5</td>
<td>Mix medium speed</td>
<td>2:00 - 2:15</td>
</tr>
<tr>
<td></td>
<td>Stop, fill ISC vial, place in ISC</td>
<td>2:15 - 3:00</td>
</tr>
<tr>
<td>6</td>
<td>Stop, fill container (trough)</td>
<td>2:15 - 3:00</td>
</tr>
<tr>
<td>7</td>
<td>Initial penetration</td>
<td>3:00</td>
</tr>
<tr>
<td>8</td>
<td>Penetration readings</td>
<td>5, 8, and 11 minutes</td>
</tr>
<tr>
<td>9</td>
<td>Remix</td>
<td>11:15</td>
</tr>
<tr>
<td>10</td>
<td>Sop, fill container</td>
<td>12:00</td>
</tr>
<tr>
<td>11</td>
<td>Penetration reading</td>
<td>13:00</td>
</tr>
<tr>
<td>12</td>
<td>Penetration reading</td>
<td>16:00</td>
</tr>
<tr>
<td></td>
<td>Penetration reading</td>
<td>19:00</td>
</tr>
</tbody>
</table>

#### Admixture Addition Modes

<table>
<thead>
<tr>
<th>Mix</th>
<th>Add’n</th>
<th>1 min</th>
<th>2 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wat</td>
<td>del.</td>
<td>Del.</td>
<td>1:15</td>
</tr>
<tr>
<td>10 sec</td>
<td></td>
<td></td>
<td>2:15</td>
</tr>
</tbody>
</table>
### ASTM C 359 Early Stiffening Results w/ Fixed Water Content

(W/C = 0.30, Original C359 Method)

<table>
<thead>
<tr>
<th>Cement →</th>
<th>006</th>
<th>017</th>
<th>051</th>
<th>133</th>
<th>143</th>
<th>170</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>3 / 24.1</td>
<td>31 / 24.8</td>
<td>50+ / 23.7</td>
<td>50+ / 24.7</td>
<td>50 / 23.4</td>
<td>50+ / 24.5</td>
</tr>
<tr>
<td>5 Minutes</td>
<td>1 / 25.6</td>
<td>1 / 25.2</td>
<td>45 / 23.7</td>
<td>50+ / 24.5</td>
<td>45 / 23.2</td>
<td>50 / 24.5</td>
</tr>
<tr>
<td>8 Minutes</td>
<td>1 / 25.6</td>
<td>1 / 25.1</td>
<td>29 / 23.5</td>
<td>50+ / 24.5</td>
<td>41 / 22.9</td>
<td>48 / 24.5</td>
</tr>
<tr>
<td>11 Minutes</td>
<td>1 / 25.2</td>
<td>0 / 24.6</td>
<td>6 / 23.2</td>
<td>47 / 24.2</td>
<td>10 / 22.8</td>
<td>48 / 24.0</td>
</tr>
<tr>
<td>Remix</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13 Minutes</td>
<td>2 / 23.6</td>
<td>46 / 23.5</td>
<td>50+ / 21.5</td>
<td>50+ / 23.0</td>
<td>48 / 22.2</td>
<td>50+ / 22.6</td>
</tr>
<tr>
<td>16 Minutes</td>
<td>2 / 23.6</td>
<td>38 / 23.5</td>
<td>50 / 21.4</td>
<td>50+ / 23.0</td>
<td>34 / 22.0</td>
<td>50+ / 22.6</td>
</tr>
</tbody>
</table>

**Issue**

- Water Demand: False Set
- False Set
- False Set

As can be expected, a wide range in mortar flow and stiffening can be expected as a function of cement source.
### ASTM C 359 Early Stiffening Results, Cement 006

#### Impact of W/C

<table>
<thead>
<tr>
<th>W/C Ratio</th>
<th>Penetration in mm / ºC</th>
<th>Current Approach</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.300</td>
<td>0.304</td>
</tr>
<tr>
<td>Initial</td>
<td>3 / 24.1</td>
<td>4 / 24.0</td>
</tr>
<tr>
<td>5 Minutes</td>
<td>1 / 25.6</td>
<td>4 / 24.5</td>
</tr>
<tr>
<td>8 Minutes</td>
<td>1 / 25.6</td>
<td>2 / 24.2</td>
</tr>
<tr>
<td>11 Minutes</td>
<td>1 / 25.2</td>
<td>1 / 24.1</td>
</tr>
<tr>
<td>Remix</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13 Minutes</td>
<td>2 / 23.6</td>
<td>3 / 22.8</td>
</tr>
<tr>
<td>16 Minutes</td>
<td>2 / 23.6</td>
<td>2 / 22.9</td>
</tr>
</tbody>
</table>

C359 test most effective when initial penetration starts 46-49 mm.
Impact of Chemical Admixture Addition Time on Stiffening of ASTM C359 Mortars

078 Cement

WRA 64 = LS/CS/TEA, 3 oz/cwt (195 ml/100 kg); 0.10% s/s

Admixture induced stiffening can be overcome by delaying time of addition after mixing of cement and water.
Isothermal Calorimetry on Mortars with Mix Water and Delayed Admixture Dosages

Note decrease in initial exotherm

Delayed Addition leaves increased amount of admixture to both disperse and retard silicate phases.
C359 Test with Water Cut  
Impact of Delayed Addition of Admixture on Early Stiffening  
Case #0388 0023 

<table>
<thead>
<tr>
<th>Mix</th>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Depth/Temp</td>
<td>10% water cut</td>
<td>Mix Water</td>
<td>1 min delayed</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Depth/Temp</td>
<td>Add’n NSFC/LS</td>
<td>add’n NSFC/LS</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10 oz/cwt</td>
<td>10 oz/cwt</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10% water cut</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Depth/Temp</td>
<td></td>
</tr>
<tr>
<td>Initial</td>
<td></td>
<td>50/79.1</td>
<td>43/79.9</td>
<td>50/79.5</td>
<td>50/79.9</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>50/79.0</td>
<td>9/79.8</td>
<td>50/81.5</td>
<td>50/80.0</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>50/78.4</td>
<td>7/79.5</td>
<td>12/81.6</td>
<td>50/80.0</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td>50/78.1</td>
<td>5/79.2</td>
<td>3/81.6</td>
<td>31/79.7</td>
</tr>
<tr>
<td>11</td>
<td></td>
<td>49/----</td>
<td>5/78.8</td>
<td>3/81.4</td>
<td>20/----</td>
</tr>
<tr>
<td>Remix</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td></td>
<td>50/76.0</td>
<td>10/77.7</td>
<td>30/78.4</td>
<td>15/77.7</td>
</tr>
<tr>
<td>16</td>
<td></td>
<td>50/76.1</td>
<td>4/77.7</td>
<td>10/78.7</td>
<td>5/77.7</td>
</tr>
<tr>
<td>19</td>
<td></td>
<td>50/76</td>
<td>4/77.5</td>
<td>5/78.6</td>
<td>5/77.7</td>
</tr>
</tbody>
</table>

Note improvement in early stiffening; however, hydrating cement seems to be “sulfate starved” with time.
Concrete with “C” cement exhibits satisfactory performance. Concrete with Cement “N” experiencing rapid slump loss.

Case #380-0220

Cement C looks “normal”, but all those “50s” don’t say much
N Cement

<table>
<thead>
<tr>
<th></th>
<th>Control</th>
<th>LS/CS/Amine</th>
<th>LS/CS/Amine</th>
<th>CS/LS</th>
<th>CS/LS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1 min 45 sec delay</td>
<td>1 min 45 sec delay</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>4 oz/cwt</td>
<td>4 oz/cwt</td>
<td>3 oz/cwt</td>
<td>3 oz/cwt</td>
</tr>
<tr>
<td></td>
<td>0.30 w/c</td>
<td>0.30 w/c</td>
<td>0.30 w/c</td>
<td>0.30 w/c</td>
<td>0.30 w/c</td>
</tr>
<tr>
<td>Initial</td>
<td>50/77.1</td>
<td>50/77.6</td>
<td>50/72.4</td>
<td>50/73.3</td>
<td>50/72.2</td>
</tr>
<tr>
<td></td>
<td>50/77.4</td>
<td>48/77.5</td>
<td>50/72.3</td>
<td>50/74.3</td>
<td>50/72.5</td>
</tr>
<tr>
<td></td>
<td>45/77.5</td>
<td>20/77.8</td>
<td>50/72.3</td>
<td>25/74.9</td>
<td>50/72.5</td>
</tr>
<tr>
<td></td>
<td>45/77.2</td>
<td>10/77.6</td>
<td>50/72.4</td>
<td>5/74.9</td>
<td>50/72.6</td>
</tr>
<tr>
<td>Remix</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>50/74.7</td>
<td>50/74.8</td>
<td>50/72.0</td>
<td>50/72.9</td>
<td>50/71.9</td>
</tr>
<tr>
<td>16</td>
<td>50/75.0</td>
<td>45/74.7</td>
<td>50/72.0</td>
<td>50/73.0</td>
<td>50/72.0</td>
</tr>
</tbody>
</table>

- Early stiffening with admixture eliminated with delayed addition
- “TEA effect” of C4AF not apparent.
- Admix seems to be “inducing” false set or delaying an inherent false set in the cement.
Isothermal Calorimetry with Cement “N”

Mix water vs delayed admixture addition alters early heat from aluminate hydration.
Delayed Addition often delayed main silicate exotherm
Impact of Delayed Addition

Relative impact of “aluminate control” with sulfate on dose-slump response.

Note impact of “delayed admixture addition.”

Excellent Aluminate Control

Poor Aluminate Control

Increase in Slump

Dosage

Delayed Addition

Mix Water Addition

Mix Water Addition

Delayed Addition

Poor Aluminate Control
Possible Causes of Admixture-Related Rapid Stiffening of Mortar

◆ Imbalance created with rate of aluminate reactivity and sulfate availability.
  Ø Admixtures decreases sulfate solubility
  Ø Admixture increases reactivity of aluminate through cement dispersion.
  Ø Admixture shifts false set to the time of penetration measurements.
  Ø Admixture accelerates ettringite formation

◆ Interestingly, early stiffening problems - whether false set or flash set – w/ and w/o admixtures – can occur with all concrete materials conforming to their respective specs.

◆ Concrete materials rarely, if ever, qualified with admixtures.
Basic Cement Hydration – Many Complex Chemical Reactions

Tricalcium silicate (Alite, C₃S) + water → Calcium silicate hydrate (CSH) + Ca(OH)₂
Dicalcium silicate (Belite, C₂S) + water → Calcium silicate hydrate (CSH) + Ca(OH)₂

Tricalcium aluminate (C₃A) + water/Ca(OH)₂ → Tetracalcium aluminate hydrate (BAD!!)
   (Arch enemy of water reducing agents)
   C₃AS₃H₃₀₋₃₂ ettringite, AFt

Tetracalcium aluminoferrite (C₄AF) + water/Ca(OH)₂ → Calcium aluminoferrite hydrate

C₃A: Continuous phase in cement. Reactivity must be balanced with sulfate availability, otherwise, severe setting problems can occur.
Abnormal Cement-Admixture Interactions: Possible Explanation

Aluminate hydrates

- Let’s assume the red line represents inter-ground sulfate on the surface of cement.

- It is believed that there are localized areas of C3A where insufficient available sulfate is available to eliminate direct C3A hydration.

- Consequences of direct C3A hydration in absence of sulfate:
  - Large exotherm
  - Rapid stiffening/hardening
  - Rapid/extensive chemi-adsorption of organic molecules/polymers

Low sulfate

No sulfate allowing C3A Hydrate formation

Adequate sulfate to form ettringite
Intercalation of Sulfonated Polymer in C₃A Hydrate

Fig. 15. Structural model proposed by Feron et al. [101] for C₄AH₆ with polynaphthalene sulfonate.

Synthetically Prepared C3A-PCE


$3\text{CaO} \cdot \text{Al}_2\text{O}_3$

$+ \text{H}_2\text{O}$

$+ \text{H}_2\text{O} + \text{Polycarboxylate (PC)}$

Ca-Al-OH-LDH

Main layer $[\text{Ca}_2\text{Al(OH)}_6]^+$

Interlayer or gallery height

0.48 nm

Basal spacing

d = 1.03 nm

Ca-Al-PC-LDH

Main layer $[\text{Ca}_2\text{Al(OH)}_6]^+$

0.48 nm

Basal spacing
Forms of Inter-ground Calcium Sulfate that can found in Portland Cement

Gypsum  \( \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \)
- normal additive to cement production
- dehydrates to plaster if mills are hot (most are)
- Controls aluminate well if aluminate has normal activity

Plaster  \( \text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O} \) “hemihydrate”
- only comes from dehydration of gypsum in mill – not added
- causes false set if too high
- best for control of very active aluminate

Anhydrite  \( \text{CaSO}_4 \)
- added to limit false set or lower cost
- poorest control of aluminate – implicated in flash set
- admixtures can depress rate of solubility
Orthorhombic C3A (sometimes called alkali-aluminate) is formed when alkalis are incorporated into the C3A crystal lattice.

The orthorhombic form of C3A is more reactive versus the cubic structure.

Changes in Ortho C3A/cubic C3A contribute to inconsistent admixture performance.

• (See http://www.springerlink.com/content/d63w6761l7l23559/fulltext.pdf)
Impact of Admixture on Anhydrite Solubility Rates

Certain dispersants can alter sulfate solubility!!

Effect of calcium lignosulfonate on the hydration of the tricalcium aluminate–anhydrite system

Xiaoping Wang, Yuxia Pang, Hongming Lou, Yonghong Deng, Xueqing Qiu*
Possible Approaches to Address Cement-Admixture Issues

- Delayed Addition - A Universal Fix?
  - Allows $SO_3$ to be available closer to aluminate reactivity
- Change Order of Addition with Multiple Admixtures
- Alternate Admixtures
- Work with cement producer to understand problem possibility modifying cement, especially adjusting $SO_3$. 
Summary

◆ The ASTM C359 test can be modified to accommodate admixtures, and potentially indicate cement-admixture incompatibilities.

◆ Low cost, efficient, and easy to perform.

◆ Useful for verifying cement lot-to-lot uniformity, with and without chemical admixture.

◆ Use of the C359 test in conjunction with isothermal calorimetry and cement mineral analysis have provide mechanistic understanding of good vs bad cement-admixture interactions.

◆ Modifications to the C359 test can include both admixture and SCM variations.
Thank you for your attention.
All questions most welcome.