Use of Chemical Admixtures to Enable Successful Manufacture of Concrete with Low Portland Cement Content

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Outline

- General Mix Design Strategy with HVFA
- The setting time and early strength challenge
- Chemical admixture options and approach
  - Flexing Polycarboxylate Technology
  - Mapping Set and Strength Accelerators
- Harnessing chemical admixture synergies to maximize early strength development

Acknowledgment
W.R. Grace R&D
General Mix Design Strategy for HVFA Concrete Mixtures

- Cementitious Content: 375-800 pcy (220-470) kg/m³
- Cement/SCM: 40-60%
- w/c: <0.40
- WR/MRWR/HRWR: Essential
- Set Accelerator: Req’d for set/early strength
- Air Entrainment: Freeze-thaw applications
Factors inhibiting increased cement replacement by SCMs

- Retarded set and strength development *
- Excessive retardation at cold temperatures *
- Inconsistent air entrainment *
- “Stickiness” *
- Prescription specified mix designs
- Spot shortages of quality materials

*Opportunity for Chemical Admixtures
SEM of 1-day Concrete with Cement and Fly Ash

- Fly Ash
- Cement
- Silica Fume
Impact of Fly Ash Replacement on Setting Time

BSA = 819 m²/kg, main particle size ~ 6 micron

Increasing SCM Content, increases initial and final set times

<table>
<thead>
<tr>
<th>Sample ash</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>K₂O</th>
<th>Na₂O</th>
<th>SO₃</th>
<th>Cl⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>48.2</td>
<td>30.31</td>
<td>5.57</td>
<td>3.85</td>
<td>1.05</td>
<td>1.34</td>
<td>0.60</td>
<td>0.30</td>
<td>0.009</td>
</tr>
</tbody>
</table>

Municipal Specifications Adjust Fly Ash Content as a Function of Temperature (Austin, TX)

<table>
<thead>
<tr>
<th></th>
<th>Hot Weather</th>
<th>Moderate Weather</th>
<th>Cold Weather</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement, lbs/cy</td>
<td>300</td>
<td>325</td>
<td>400</td>
</tr>
<tr>
<td>Fly Ash, lbs/cy</td>
<td>150</td>
<td>125</td>
<td>100</td>
</tr>
<tr>
<td>% Replacement</td>
<td>33%</td>
<td>28%</td>
<td>20%</td>
</tr>
</tbody>
</table>

http://www.ci.austin.tx.us/greenbuilder/fs_flyashconcrete.htm
Ash collected from precipitator and air classified into 3 fractions.

Increased Fineness favors more spherical morphology

Increased lubricating effect and packing density

Chemical Admixture Strategy for Early Strength

- Water Reduction with Polycarboxylate Technology
- Mapping/Selection Set and Strength Accelerators
- Harness Synergistic Interactions
Influence of W/C on strength and permeability

Power’s Equation:

Porosity or solid/space ratio, $x$, exponentially related to strength, $S$, and permeability.

$$S = kx^3,$$ where $k = 34,000$ psi (235 mpa)

Superplasticizer Selection

◆ Chose superplasticizer chemistry with maximum dose/slump efficiency.

◆ In general, the lower the dosage of water reducing admixtures to achieve a particular degree of concrete workability (slump), the less the impact on the rate of cement hydration.

◆ Maximize:

  \[
  \text{Workability Increase or Water Reduction} \quad \delta \text{ Set} \\
  \text{Early Strength Increase} \quad \delta \text{ Workability or Water Reduction}
  \]

◆ Correlate dispersant selection with “stickiness”
Mortar Mixtures Dosed with Various Water Reducers
Comparison of dose/slump efficiency

PCE most dose/slump efficient
Slump Increase as a Function of Set Time

Comparison of various water reducer technologies

517 lb/yd³ (305 kg/m³) cement, w/c = 0.50

PC provides most favorable slump/Δ set

Set Times when dispersant dosed for 3 → 7” (180 mm) slump:

PC – 4.5 hrs    NSFC - 5.5 hrs    Lignin - 8 hrs    Corn Syrup – 10.25 hrs
PCs can be designed for a Wide Range of Performance

PC can be designed for:

- high early strength
- quick slump gain
- long slump life without extended set
Paste Flow as a Function of Superplasticizer Structure and Dosage, 20°C

Nawa et. Al. Nice Conf. HRWR, 2000
Mix design: 708 lb/yd³, 40% Slag, w/cm = 0.45

Effect of Four PC on Set Time of Concrete with 40% Slag

Set time differences among PCs increases with both dosage and lower temperatures.
Rheological Measurements of PC-admixed Micromortar Mixtures. C=30g; Sand=54g; w/c = 0.5

- At same $t_0$, the micro mortar containing PC-1 has lower viscosity than the micromortar admixed with PC-2.
- Lower Viscosity is favored to help reduce “sticki-ness” factor with HVFA concrete.
Mapping Set and Strength Accelerators

Versus
Accelerators: Setting Time vs. Strength Gain

• Some accelerators may generally be more suitable for a particular performance.
• **Setting time** is primarily influences flatwork finishing and the timing for heat curing
• **Strength gain** is primarily impacts early form removal
Accelerators: Chloride vs Non-Chloride

- Calcium chloride is the most cost effective accelerator available but, adding chlorides to reinforced concrete can result in corrosion.
- In the presence of moisture and oxygen, chlorides initiate corrosion of reinforcing steel even in the high pH environment of concrete.
- Limits exist on the total permissible amounts of chloride in concrete.

Calcium Chloride is the “King of Accelerators”
Mapping Accelerator Technologies for Set and Strength

- Nano: 0.5 – 2%
- Calcium Chloride: 0.5 – 6%
- Sodium Thiocyanate: 0.02-0.05%
- Calcium Nitrite: 0.5 – 6%
- TEA: 0.02-0.05%
- TIPA: 0.02-0.05%
- Calcium Nitrate: 0.5 – 6%

Early Strength vs. Set
Isothermal calorimetry of C₃S dosed with 2% of various calcium salts

- Calcium Chloride most cost effective, most uniform response across wide range of cement chemistries

- Calcium nitrate is most common set accelerator platform. Normally, supplemented with other additives.
Relative Set/Strength Performance of Chloride, Nitrate, and Thiocyanate

- $\text{CaCl}_2$ effects both set and strength
- $\text{NaSCN}$ primarily effects strength
- $\text{Ca(NO}_3\text{)}_2$ primarily effects set.
Chemical Admixture Synergies with Polycarboxylates

$1 + 1 > 2$ !

Air and Strength
Concrete admixed with PC-HRWR and Calcium Nitrite
Prestressed Piles
Chowan River Bridge,
Edenton, NC
NSFC/Calcium Nitrite vs. Polycarboxylate/Calcium Nitrite

Plant Steam-Cured Concrete

390 kg/m$^3$ (658 lb/yd$^3$) Type II Cement, w/cm = 0.32

<table>
<thead>
<tr>
<th></th>
<th>NSFC+WR</th>
<th>PC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polycarboxylate</td>
<td>ml/100kg</td>
<td>--</td>
</tr>
<tr>
<td>NSFC</td>
<td>ml/100kg</td>
<td>1300</td>
</tr>
<tr>
<td>WR</td>
<td>ml/100kg</td>
<td>130</td>
</tr>
<tr>
<td>Calcium Nitrite</td>
<td>l/m$^3$</td>
<td>26.6</td>
</tr>
<tr>
<td>AEA</td>
<td>ml/100kg</td>
<td>78</td>
</tr>
<tr>
<td>Slump</td>
<td>mm</td>
<td>75</td>
</tr>
<tr>
<td>Air</td>
<td>%</td>
<td>5.4</td>
</tr>
<tr>
<td>Initial Set</td>
<td>Hr:Min</td>
<td>3:50</td>
</tr>
<tr>
<td>1-D Comp. Strength</td>
<td>MPa</td>
<td>32.4 (4700 psi)</td>
</tr>
</tbody>
</table>

Test Series I, Insulated Cure, Cement 051
Compressive Strength → 24hr

Strength (MPa)

5 10 15 20 25
Time (hrs)

Cement 051, Insulated Cure

- PCS .162%, ACC 2%
- NSFC .655%, ACC 2%
- PCS .151%, CANI 2%
- NSFC .658%, CANI 2%
Test Series I, Insulated Cure, Cement 051
Compressive Strength → 28-day (672 hr)
PC/Ca Nitrite vs. NSFC/Ca Nitrite @ 80°C

20-26% strength increase for PC/calcium nitrite vs. NSFC/calcium nitrite with comparable temp traces

Synergistic Strength Increase: 
PC/Calcium Nitrite vs NSFC/Calcium Nitrite

Why?
- Hydration kinetics?
- Microstructure development?
- ITZ?
- Pore size distribution?
- Other?
Effect of Chemical Admixtures on the Microstructural Development of Portland Cement Mortars and Concretes

<table>
<thead>
<tr>
<th>Materials</th>
<th>Concrete</th>
<th>Mortar</th>
<th>Cement paste</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement</td>
<td>420 kg/m³</td>
<td>420 kg/m³</td>
<td>200 g</td>
</tr>
<tr>
<td>Natural Sand, FM 6.61</td>
<td>830 kg/m³</td>
<td>861 kg/m³</td>
<td>-</td>
</tr>
<tr>
<td>Stone, ASTM C33, No.67</td>
<td>1040 kg/m³</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Water</td>
<td>180 kg/m³</td>
<td>180 kg/m³</td>
<td>56 g</td>
</tr>
<tr>
<td>15 μm quartz</td>
<td>-</td>
<td>-</td>
<td>10 g</td>
</tr>
<tr>
<td>w/c</td>
<td>0.43</td>
<td>0.43</td>
<td>0.28</td>
</tr>
<tr>
<td>PCS dosage (% s/c)</td>
<td>0.13%</td>
<td>0.13%</td>
<td>0.13%</td>
</tr>
<tr>
<td>NSFC dosage (% s/c)</td>
<td>0.6%</td>
<td>1.2%</td>
<td>1.2%</td>
</tr>
<tr>
<td>CANI dosage (% s/c)</td>
<td>1.0%</td>
<td>1.0%</td>
<td>1.0%</td>
</tr>
</tbody>
</table>

C. Porteneuve, A. Jeknavorian, F. Serafin, K.L Scrivener, E. Gallucci, G. Gal
American Ceramic Society Meeting, Baltimore, April 2005
### PC/CANI vs NSFC/CANI – Concrete Performance

<table>
<thead>
<tr>
<th></th>
<th>PCS + CANI</th>
<th>NSFC + CANI</th>
</tr>
</thead>
<tbody>
<tr>
<td>9-minute Slump (mm)</td>
<td>229</td>
<td>216</td>
</tr>
<tr>
<td>Air (%)</td>
<td>2.50%</td>
<td>2.20%</td>
</tr>
<tr>
<td>Initial setting time</td>
<td>3:47</td>
<td>4:15</td>
</tr>
<tr>
<td>(hh:mm)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**PC/CANI gave shorter set and higher strength than NSFC/CANI**

C. Porteneuve, A. Jeknavorian, F. Serafin, K.L Scrivener, E. Gallucci, G. Gal
American Ceramic Society Meeting, Baltimore, April 2005
Concrete Compressive Strength

PCS/CANI vs NSFC/CANI

Synergistic strength effect of PCS/CANI confirmed.
PC/CANI vs NSFC/CANI – Mortar & Paste Performance

PC/CANI consistently produced higher compressive strengths in both mortar and paste mixtures.

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American Ceramic Society Meeting, Baltimore, April 2005
Main exotherm occurs earlier with PC/CANI, but total heat comparable to NSFC/CANI.
Probing Concrete Microstructure with Backscattered Scanning Electron Microscopy (BSEM)

PC + Calcium Nitrite

NSFC + Calcium Nitrite

<table>
<thead>
<tr>
<th></th>
<th>PC + Ca(NO$_2$)$_2$</th>
<th>NSFC + Ca(NO$_2$)$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gap size, $\mu$m</td>
<td>0.1</td>
<td>0.7</td>
</tr>
<tr>
<td>C-S-H layer thickness</td>
<td>1.5</td>
<td>0.8</td>
</tr>
</tbody>
</table>
Statistical Analysis of BSEM of 1-day old concrete

<table>
<thead>
<tr>
<th>PCS/ CANI</th>
<th>Grain (μm)</th>
<th>C-S-H (μm)</th>
<th>Gap (μm)</th>
<th>Grain (μm)</th>
<th>C-S-H (μm)</th>
<th>Gap (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average</td>
<td>13.1</td>
<td>2.4</td>
<td>0.5</td>
<td>24.4</td>
<td>2.7</td>
<td>0.1</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>2.0</td>
<td>0.7</td>
<td>0.8</td>
<td>4.2</td>
<td>0.5</td>
<td>0.3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>NSFC/ CANI</th>
<th>Grain (μm)</th>
<th>C-S-H (μm)</th>
<th>Gap (μm)</th>
<th>Grain (μm)</th>
<th>C-S-H (μm)</th>
<th>Gap (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average</td>
<td>12.4</td>
<td>1.2</td>
<td>0.8</td>
<td>27.8</td>
<td>1.5</td>
<td>0.7</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>3.0</td>
<td>1.0</td>
<td>0.3</td>
<td>3.2</td>
<td>0.5</td>
<td>0.2</td>
</tr>
</tbody>
</table>

- For both grain sizes, the C-S-H layer is thicker with PCS/CANI.
- The NSFC/CANI sample exhibits a more significant gap between the anhydrous cement grain and the inner C-S-H.
### Effect of PCE/Calcium Nitrite for 60/40 OPC/Ash Concrete

420 kg/m³ total cementitious

<table>
<thead>
<tr>
<th>Mix</th>
<th>Fly Ash (Class F)</th>
<th>Water</th>
<th>Admixture</th>
<th>Slump</th>
<th>Air</th>
<th>Initial Set</th>
<th>Final Set</th>
<th>Comp. Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% replace</td>
<td>w/c</td>
<td>%solids/cm</td>
<td>mm</td>
<td>%</td>
<td>(hr:min)</td>
<td>(hr:min)</td>
<td>1-Day</td>
</tr>
<tr>
<td>Baseline</td>
<td>0</td>
<td>0.50</td>
<td></td>
<td>140</td>
<td>1.5</td>
<td>4:22</td>
<td>6:33</td>
<td>7.0</td>
</tr>
<tr>
<td>+ fly ash</td>
<td>40</td>
<td>0.50</td>
<td></td>
<td>215</td>
<td>0.9</td>
<td>9:20</td>
<td>13:01</td>
<td>3.1</td>
</tr>
<tr>
<td>+6% water cut</td>
<td>40</td>
<td>0.46</td>
<td></td>
<td>145</td>
<td>0.9</td>
<td>8:27</td>
<td>11:59</td>
<td>3.4</td>
</tr>
<tr>
<td>+18% water cut</td>
<td>40</td>
<td>0.38</td>
<td>0.13% PC-500</td>
<td>145</td>
<td>3.2</td>
<td>7:48</td>
<td>10:59</td>
<td>5.5</td>
</tr>
<tr>
<td>+CANI</td>
<td>40</td>
<td>0.38</td>
<td>0.13% PC-500 2.0% Ca Nitrite</td>
<td>165</td>
<td>3.6</td>
<td>5:20</td>
<td>8:15</td>
<td>6.0</td>
</tr>
</tbody>
</table>

- **24% water reduction with fly ash**
- **1 hr retardation from baseline**
- **1D strength = 86% of baseline**
- **7D strength > baseline**
Performance Map of HRWR/HES System

Reference  = 20% fly ash w/ HRWR. Test Mix = 50% fly ash w/ HRWR + HES
Strength target = 80% 1-day Ref.;  Set target = < 60 min Initial set

Cement Alkalinity
Low High

<table>
<thead>
<tr>
<th>Low</th>
<th>“F” Fly Ash Content</th>
<th>High</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5%</td>
<td>3.7%</td>
<td>4.8%</td>
</tr>
<tr>
<td>45 mins</td>
<td>105 mins</td>
<td>110 mins</td>
</tr>
<tr>
<td>63%</td>
<td>71%</td>
<td>62%</td>
</tr>
<tr>
<td>30 mins</td>
<td>100 mins</td>
<td>100 mins</td>
</tr>
<tr>
<td>63%</td>
<td>71%</td>
<td>62%</td>
</tr>
<tr>
<td>30 mins</td>
<td>100 mins</td>
<td>100 mins</td>
</tr>
</tbody>
</table>

Strength target performance met w/ low alkali cement + high CaO ashes
Set performance difficult to predict, fly ash-dependent.
Effect of Cement Alkali Content on Set Acceleration by Calcium Nitrate

Increasing alkali content means increased soluble sulfate and hydroxide, both of which precipitate calcium ions.

www.baustoffchemie.de/en/db/set-accelerators
In Summary……

- Proper selection of admixture systems (HRWRs and accelerators) can enable use of high volume cement replacement by SCMs.
- Polycarboxylate technology can be optimized for many diverse applications such as HVFA concrete mixes.
- Practical, cost-effective technologies for early activation of SCMs still needed.
- One cannot assume admixture systems will automatically work as usual when using high levels of SCMs.
- And just when you think, there is no hope to make that HVFA work for your application, remember…………
Thank you for your attention. All questions most welcome.