Innovations in Chemical Admixture Technology as Related to Sustainability

ACI Spring 2012 Convention
March 18 – 21, Dallas, TX

Ara A. Jeknavorian is a Research Fellow with the Construction Products Division of W.R. Grace in Cambridge, Massachusetts. Starting in 1979 with the Technical Service group, Dr. Jeknavorian conducted numerous investigations on the performance of concrete materials and chemical admixtures, and has developed numerous chemical and instrumental methods for troubleshooting cementitious systems. In 1995, he began product development for chemical admixtures, spearheading the introduction of polycarboxylate-based superplasticizers to N. America. He is an inventor on twelve (15) patents for concrete and masonry admixtures, and has authored over 30 publications in the field of analytical chemistry of cementitious systems and the application of chemical admixtures for concrete. Dr. Jeknavorian is a member of the American Chemical Society, American Concrete Institute, and the ASTM C09 Committee on Concrete, where he has chaired the Chemical Admixtures Subcommittee and has been recognized for outstanding service for his contribution to standards development for chemical admixtures. At the Sixth CANMET/ACI International Conference on Superplasticizers and other Chemical Admixtures (Nice 2000), Dr. Jeknavorian received recognition for outstanding contributions and achievements in the field of concrete admixture technology. Ara holds a Ph.D. degree in Analytical Chemistry from the University of Massachusetts.

Outline

- Recent Innovations in Admixture Technology
- Chemical Admixture Wish List
- Wonderful World of Polycarboxylates
- Dial-in Slump Retention with Time-Release PCE
- Admixtures For Aggregates
- “Nano” – Admixtures for Accelerated Strength Performance
- Admixture for Pervious Concrete

Consulting the Admix Genie

Ah...yes...
The Future of Chemical Admixtures........
Are you ready??

Role of Chemical Admixtures in Concrete Construction

- Chemical Admixtures of the Future: Opportunities and Challenges for Sustainable Concrete Production, Placement, and Service Life
- Ara A. Jeknavorian, Ph.D., Research Fellow
W.R. Grace & Co., Cambridge, MA, USA

*“Innovations in Chemical Admixture Technology as Related to Sustainability”* ACI Spring 2012 Convention - Dallas
ACI Committee 212 on Chemical Admixtures
Latest Innovations in Admixture Technology (over the past 10 years)
- Polycarboxylate-based Superplasticizers
- PCs for Self-Compacting Concrete
- Shrinkage Reducing Admixtures
- ASR Control Agents
- Admixtures for CLSM (Control Low Strength Material)
- Hydration Stabilizing Agents for Returned Concrete
- Antifreeze Admixtures (non-corrosive, alkali-free)
- Viscosity Modifying Admixtures
- Anti-washout Admixtures
- Slump Extending Admixtures
- Nano-Admixtures for High Early Strength
- Admixtures for Pervious Concrete
- Surface Enhancing Admixtures

Addressing Concrete Durability Issues
- Brittleness - cracking
- Dimensional stability
  - Thermal and hydration
- Permeability – water transport
  - ASR & DEF
  - Sulfate attack
  - Corrosion
  - Freeze/thaw
- Solution Strategies
  - Improve ductility – Macro fibers
  - Reduce shrinkage – SRA
  - Improve curing (self-curing) - Polycrylics
  - Reduce permeability
  - Admixtures to lower w/c - Superplasticizers
  - Reactive Void Fillers
    - Microsilica, limestone
    - Integral waterproofing - Stearates
  - QC of raw materials – Paste Calorimetry
  - Freeze-Thaw - Air entrainment w/ Surfactants, Wood Rosins, Tall Oil
  - Corrosion Inhibitor – Calcium Nitrite
  - ASR - Lithium Salts

Chemical Admixture Wish List
- A water reducing admixture that demonstrates uniform performance with all cements or cement/SCM combinations.
- An admixture which can perform as a normal, mid- and high range water reducer - “linear dose/slip response with neutral set.”
- A simple test that can alert concrete producers to a possible cement-admixture “incompatibility.”
- An admixture that “cools” concrete
- Admixture systems that allow higher replacement levels (50% +) of Portland cement with SCMs
- An admixture that facilitates production and significantly increases robustness of SCC – reduces concern for failed loads.
- Integral curing admixture.
- Dial-in slump retention without extended set and independent of cement chemistry and temperature.

Effect of Water Reduction on Concrete
Cement dispersion is the most important and extensively used technical capability chemical admixtures provide in producing sustainable quality concrete mixtures.

\[ \text{Compressive Strength or Permeability} = \frac{k}{(w/c)^3} \]

Particle Size Distribution, ASTM C 150 T-I Cement
The PSD for essentially all Portland Cements have a trade off for strength versus water demand.

Photomicrograph – Cement Dispersing Action of Superplasticizers

Will the slump cone be replaced by a hand-held rheometer??
**Technical Performance: Superplasticizers**

**Benefits of Superplasticized Concrete**

<table>
<thead>
<tr>
<th>Mix Proportions, kg/m³</th>
<th>Reference</th>
<th>High</th>
<th>Flowing</th>
<th>Reduced</th>
<th>Mix</th>
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<tbody>
<tr>
<td>Cement</td>
<td>356</td>
<td>356</td>
<td>356</td>
<td>267</td>
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<td>Sand</td>
<td>712</td>
<td>742</td>
<td>772</td>
<td>845</td>
<td></td>
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<td>Stage</td>
<td>1127</td>
<td>1216</td>
<td>1068</td>
<td>1187</td>
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<tr>
<td>Water</td>
<td>17</td>
<td>133</td>
<td>178</td>
<td>133</td>
<td></td>
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<tr>
<td>Superplasticizer, l/m³</td>
<td>0.9</td>
<td>0.9</td>
<td>0.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>WC</td>
<td>0.50</td>
<td>0.38</td>
<td>0.50</td>
<td>0.50</td>
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<tr>
<td>Slump, mm</td>
<td>115</td>
<td>125</td>
<td>240</td>
<td>125</td>
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</table>

**Compressive Strength, MPA**

<table>
<thead>
<tr>
<th></th>
<th>1-day</th>
<th>7-day</th>
<th>28-day</th>
</tr>
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<tr>
<td>1-day</td>
<td>9.7</td>
<td>28.3</td>
<td>35.3</td>
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<td>7-day</td>
<td>19.2</td>
<td>39.4</td>
<td>46.8</td>
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<tr>
<td>28-day</td>
<td>12.9</td>
<td>32.1</td>
<td>38.3</td>
</tr>
</tbody>
</table>

**Unexpected Performance Changes in Cementitious Systems**

- Cement Chemistry
  - Kiln fuels, interground additions, variable forms of gypsum
- Supplementary Cementitious Materials
  - Fly ash, slag, silica fume, metakaolin
- Chemical Admixture
  - More complex formulations
  - Multiple Admixtures (i.e. WRA, HRWR, AEA, Accel)

ASTM Sub-committee C01.90.02/C09.90 Joint Task Group on PASTE SYSTEM PERFORMANCE

**Portland Cement Clinker**

**Major Compounds in Portland Cement**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mineral</th>
<th>Phase</th>
<th>Chemical Formula</th>
<th>Notation</th>
<th>Mass Notation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tricalcium silicate</td>
<td>alite</td>
<td>3 CaO·SiO₂</td>
<td>C₃S</td>
<td>25 - 65</td>
<td></td>
</tr>
<tr>
<td>Dicalcium silicate</td>
<td>belite</td>
<td>2 CaO·SiO₂</td>
<td>C₂S</td>
<td>10 - 50</td>
<td></td>
</tr>
<tr>
<td>Tricalcium aluminate</td>
<td>aluminate</td>
<td>3 CaO·Al₂O₃</td>
<td>C₃A</td>
<td>3 - 12</td>
<td></td>
</tr>
<tr>
<td>Tetracalcium aluminoferrite</td>
<td>ferrite</td>
<td>4 CaO·Al₂O₃·Fe₂O₃</td>
<td>C₄AF</td>
<td>8 - 14</td>
<td></td>
</tr>
<tr>
<td>Sodium/potassium sulfate</td>
<td>Alkalis</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Inter-ground Calcium Sulfate – Gypsum, Plaster, and/or Anhydrite

**Probing Cement-Admixture Issues with Calorimetry**

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

**SCMs Can Provide a Multitude of Benefits for Concrete Properties**

- Decreased Permeability
- Reduced Sulfate Attack
- Reduced Efflorescence
- Reduced Shrinkage
- Reduced Heat of Hydration
- Reduced Alkali Silica Reactivity
- Increased Workability and Slump Retention
- Improved Finishing
- Reduced Bleeding
- Reduced Segregation

Then, why aren’t SCMs used consistently at 40-50% cement replacement **?
Exploiting the wonderful World of Polycarboxylates
Making flocculated hydrating cement particles disperse

Polycarboxylate Comb Polymer can be designed for:
- High early strength
- Quick slump gain
- Variable viscosity at same yield stress
- Long Slump life without extended set

Understanding Structure-Performance Correlation critical to Leverage Value of PC Technology

Polycarboxylates are to concrete as designer drugs are to medicine

Time Release PCs: Extending Slump Life without Retardation
PC4: Variable Dose Slump Retaining Polymer

Slump Retaining Admixture vs HSA (Hydration Stabilizing Admixture) for Extended Slump Life
Rapid Slump Loss Cement

HSA is an option to extend slump life, but with the capability of significantly extended set retardation.

Consequence of Retempering
Caution: If you retemper, the concrete will remember!

Changes:
- Adding 5 liters/m of water will:
  - Increase slump by 25 mm
  - Decrease strength by 1.4 MPa
  - Waste 11 kg cement
  - Increase shrinkage potential by about 10%
  - Decrease F/T resistance by 20%

Chemical “Admixtures” for Sand

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Effect of Manufactured Sands and Viscosity Modifying Admixture (VMA) on Pump Pressure

Mix Design, kg/m³:
- Cement: 248
- Fly Ash: 65
- Water: 178 – 186 kg/m³
- WRA: 260 ml/100 kg
- Slump: 115-127 mm

Effect of Manufactured Sands and Viscosity Modifying Admixture (VMA) on Pump Pressure

Limits on Clay in Concrete Aggregate (United States)
- ASTM C 33 Standard Specification for Concrete Aggregates
  - Material finer than 75 μm:
    - <3.5% for sand and gravel
    - <8.0% for manufactured sand
  - Clay lumps and friable particles:
    - ≤3% max
  - Sand Equivalent (ASTM D 2419) or Durability Index Test (ASTM D 3744 or California 227 and 229)
    - Typically requires lower clay than ASTM C33 limits
    - Does not distinguish effectively between clay and non-clay fines
  - Methylene Blue Value (not commonly specified)

Clays can be present in natural or manufactured sands.

CMA – Clay Mitigating Admixture
Impact on MBV Value

New UV-Methylene Blue Test
- Methylene blue is a function of clay content and clay activity
- A novel test method was developed to expedite and improve MBV results
  - Existing titration method (e.g. AASHTO TP 57): titration test to determine amount of methylene blue solution adsorbed by clay
  - New Grace UV-MBV method: UV-vis measurement of methylene blue solution to determine amount of methylene blue solution in presence of clay-bearing aggregates
    - One mixing of methylene blue solution rather than gradual titration enables fast results
    - Test is performed on entire sand sample, ensuring representative results

New UV Method

Concrete Recycling w/ Hydration Stabilizing Admixture

Slurry Density Meter Readings
Control HSA Dosage

A. Coarse aggregate screen
B. Sand separator
C. Spill storage
D. Admixture tank
E. Main water
F. Slurry density meter
G. Wash tank
H. Slurry storage tank
I. Mixer
J. Main

Concrete Admixtures for Pervious Concrete

- Maximize Compaction & Flowability
  - Strength related mainly to voids content (aggregate compacted voids content and paste volume), much less to paste strength (w/cm, silica fume)
  - High compactability needed for consistent performance (build compacting sometimes minimal)
  - High compactability expected to correspond to fast truck unloading
- Reduce Paste Drain & Water Sensitivity (HRWR/VMA)
  - Proper paste rheology needed to prevent paste collecting at bottom of section
  - Enable paste composition with less cement, more water
- Lengthen Curing Window (Retarder/VMA)
  - Increase water content
  - Retard cement hydration
  - Bind water

Impact of HRWR and VMA on Fluidity and Voids Content

- Increasing HRWR reduced void content but increased paste drain.
- Acceptable at a dose of 0.05% by cement content, but excessive at a dose of 0.1% by cement content.
- Paste drain was reduced by reducing w/c, but voids content is increased.

Chemical Admixtures based on Nano-particles

The reactivity associated with the increased surface area has a potent strength accelerating impact on cement hydration
Nano Seed/Particles for Concrete

Calcium silicates
Magnesium silicates
Lime, CaO
Hydrated Lime, Ca(OH)2
Calcium Carbonate, CaCO3
Titanium oxide, TiO2
Silica, SiO2
Iron Oxides
Carbon nanotube

All of these particles, when present in the nano-size range, have the ability to promote nucleation of cement hydration products, thus accelerating cement hydration process and strength gain.

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Nano Admixtures promote cement hydration in the pore volume to complement topochemical reactions on cement surface

Seeding schematic (Thomas et al. 2009)

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Compressive Strength Data (mpa), Effect of Nano-Admix

<table>
<thead>
<tr>
<th>Mpa</th>
<th>6 hr</th>
<th>9 hr</th>
<th>12 hr</th>
<th>24 hr</th>
<th>672 hr</th>
</tr>
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<tbody>
<tr>
<td>Blank</td>
<td>2.9</td>
<td>7.8</td>
<td>12.3</td>
<td>25.2</td>
<td>50.7</td>
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<tr>
<td>Nano-Admix</td>
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<td>11.8</td>
<td>17.7</td>
<td>30.3</td>
<td>52.2</td>
</tr>
<tr>
<td>Nano-Admix</td>
<td>7.3</td>
<td>15.4</td>
<td>21.3</td>
<td>31.5</td>
<td>51.9</td>
</tr>
</tbody>
</table>

Nucleating effect from Nano-admixture capable of 2X impact on early age compressive strengths (22 C).
Nano-admixtures have the capability of allowing increased use of SCMs, reduced heat curing, and reducing cement contents.

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Isothermal Calorimetry of Mortar Mixes with Nano-Admixture

Opportunities to reduce heat curing or increase use of SCMs

Position and intensity of main exotherm hydration peak significantly modified

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Automated Slump Control: In-Transit Water and Superplasticizer Adjustments

Batch slump used to ensure proper water content (strength)
Admixture adjusted to delivery slump target (contractor)
Some final thoughts:

Regardless of what new and exciting admixture technologies are introduced into the concrete industry, successful routine production of cost-effective, high quality, and sustainable concrete will greatly be facilitated by:

✓ Identify those parameters - materials, processes, structure design, and environment - that can transform in spec concrete construction into a case for litigation.

✓ Learn how to predict and control those parameters – keeping away from the edge of disaster.

Thank You!