Chemical Admixtures – Science, Technology and Applications over the Years

Dr. Bruce J. Christensen
Vice President
Global Technologies and Innovation Management
BASF Construction Chemicals
Ludwigshafen, Germany

The Institute of Concrete Technology - 40th Annual Convention
Warwickshire, UK
22 March 2012
PRE-HISTORIC TIMES
Pre-historic Times
First Known Uses of Chemical Admixtures

In the dawn of mankind is where it all began ...

**Cave painting:**
The prehistoric version of construction chemicals: architectural paints

**Opus Caementitium**
The precursor of concrete
burned lime stone, sand, aggregate and volcanic ash
plus the **first admixtures:**
milk, eggs, animal blood ➔ as organic binders
pig fat, wax, bitumen ➔ as waterproofing agents
PRIOR TO THE 1950's
Prior to the 1950’s Water Reducers

- First used in the 1920’s/1930’s
- Sulfonated lignin from the paper making industry was one of the first chemistries
- 5-10% water reduction possible
- Mechanism is deflocculating and dispersing the cement particles by electrostatic repulsion
- Main disadvantages are retardation of set and unintentional entraining of air at high dosages
Prior to the 1950’s
Air Entraining Admixtures

- First reported uses in the 1930’s
- Based upon wood resins (phenolics, carboxylic acids and other residues)
- Benefits for workability and freeze-thaw protection well documented
- Many factors that affect performance
  - Temperature
  - Gradation of fine aggregate
  - Alkali content in the concrete
  - Interactions with other admixtures (i.e. BNS superplasticizers)
Prior to the 1950’s
Accelerators

- First reported uses in the late 1800’s, making this class likely the first class of modern admixtures
- Calcium chloride is the best known, readily available, and inexpensive material
- Dosages of 2% by weight of cement typically used
- Main disadvantage is acceleration of steel corrosion, as well as some discoloration of the concrete when used at high dosages
1950 - 1980
From 1950 to 1980
Retarders / Water Reducers

- Despite the effects being known from the early water reducers, little is published on the topic until the 1960’s
- Hydroxylated polymers or carbohydrates (sugars) most widely used
- 0.05-0.2% dosage typical
- 5-8% water reduction possible with some materials
- Main issue is susceptibility to biological activity (need biocides)
From 1950 to 1980
Alkali-Silica Reaction Mitigation Admixtures

- Failure of concrete due to water-induced expansion of ASR gel
- First reports of chemical solutions in the early 1950’s
- Lithium salts the most common chemical admixture solution
- Main disadvantage is high cost
- Other potential solutions
  - Use alternative aggregates
  - Reduce alkali content
  - Use SCM’s like flyash
  - Combinations
From 1950 to 1980
Corrosion Inhibiting Admixtures

- Ingress of chloride into concrete causes corrosion of the steel, with subsequent expansion and spalling of the concrete.

- Many materials screened until the 1970’s, but not until then was calcium nitrite identified as one of the most suitable.

- Passive anodic corrosion inhibitor
  - Does not prevent chloride ingress, but increases the threshold until initiation.
  - Works on the anodic portion of the electrochemical cell.

- Best protection / durability achieved when combined with silica fume and a HRWR.
From 1950 to 1980
Superplasticizer/High Range Water Reducer

- One of the most significant developments in admixture history
- First introduced in Japan and Germany in the late 1950’s and early 1960’s
- Synthetic polymers that provide water reductions to 35% or more
- Mechanism is highly effective electrostatic dispersion
- BNS more widely used than SMF due to better slump retention, solution stability and cost
The 1980’s
The 1980’s
Mid-Range Water Reducers

- First introduced in North America in the last 1980’s
- Origins due to gap in performance between WR’s & HRWR’s
- Based upon lignosulfonates and set-balancing ingredients
- Water reductions over 15% (or slump increase to 100-125 mm)
- Normal setting (<1.5 hour delay)
- Finishing characteristics reported to be excellent
The 1980’s
Shrinkage Reducing Admixtures

- First introduced in Japan
- Mechanism believed to be reduction of surface tension in the capillary pores
- Based upon low weight alkoxylation adducts of low MW alcohols
- Reductions in drying shrinkage of >50% possible
- Requires use of synthetic AEA’s for adequate F/T protection
- ~10% reduction in early age compressive strength
The 1980’s
Hydration Control / Stabilization Admixtures

- First introduced in the mid 1980’s
- Based upon phosphor-containing acids and/or carboxylic acids
- Able to arrest the cement hydration for days, then be re-activated by addition of accelerator or waiting for “wear off”
- Mechanism is based upon retards all the clinker minerals, not just some
- Used for long hauls, wash-out slurries and overnight concrete stabilization
- Excellent for keeping mix drums clean

25 hours
The 1980’s
Cold Weather / Freeze Protection Admixtures

- Extensively research in Russia in the 1960’s
- First studied and used in the west in the mid1980’s
- Mixtures of inorganic salts, polymers and other ingredients
- Provide both freezing point depression and acceleration
- Concretes batched at 10-12 C and cast at < -10 °C set at normal times (before freezing) and gain strength

<table>
<thead>
<tr>
<th>CWA dosage (ml/kg)</th>
<th>Set (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No admixture</td>
<td></td>
</tr>
<tr>
<td>6.5 mL/kg</td>
<td></td>
</tr>
<tr>
<td>13 mL/kg</td>
<td></td>
</tr>
<tr>
<td>39 mL/kg</td>
<td></td>
</tr>
<tr>
<td>59 mL/kg</td>
<td></td>
</tr>
</tbody>
</table>

Concrete setting time, -11 °C curing

<table>
<thead>
<tr>
<th>Dosage (ml/kg)</th>
<th>Set (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CWA (39.1)</td>
<td>3.8</td>
</tr>
<tr>
<td>CWA (39.1) + HRWR (5.9)</td>
<td>3.4</td>
</tr>
<tr>
<td>CWA (58.7) + HRWR (5.9)</td>
<td>3.3</td>
</tr>
</tbody>
</table>
The 1980’s
Next generation Superplasticizers / HRWR’s

- First developed in Japan in the mid 1980’s; introduced in Europe / Americas in the late 1990’s

- Polycarboxylate ethers, which provide both electrostatic and steric dispersion - highly efficient

- Tunable chemistry

- Excellent slump retention, water reduction, strength development, setting time, finishing, …

- Can entrain unwanted amounts of air without formulation
The 1990’s
The 1990’s
Synthetic Air Entraining Agents

- First introduced in the early 1990’s
- Based upon tall oil fatty acids and other sulfonated hydrocarbons
- Typically generate finer, more stable air bubbles than resin/rosin type AEA’s
- Better for use in highly fluid concretes, using particularly BNS or SMF HRWR’s
- Excellent freeze-thaw durability
- Can give a slight compressive strength reduction in some materials
- May be some very fine bubbles not detectable by pressure methods
The 1990’s
Mixed Mechanism Corrosion Inhibitor

- Introduced in the early 1990’s
- Based upon amine esters
- Active-Passive Type
  - Reduces permeability of chloride ions into the structure
  - Increases the threshold level to initiate corrosion
- Highly effective at providing corrosion inhibition
- Requires synthetic AEA to achieve necessary air contents
- Slight early age strength decrease

Polar Group / Hydrocarbon (CH₂) Tail
The 2000’s
The 2000’s
Viscosity Modifying/Anti-Washout Admixtures

- Introduced decades ago in grout and mortar applications
- First significant use in concrete appears to be in anti-washout applications in the late 1990’s
- Popularized in the early 2000’s for use in low fines SCC, and in lean conventional slump mixtures
- Based upon starches, gums, cellulosics or synthetic polymers
- Latest versions have no impact on setting times or air entrainment
The 2000’s
Next Generation PCE Superplasticizers

- High Early Strength PCE
  - Accelerates the hydration by highly efficient dispersion
  - Combinations with conventional accelerators push it even further

- Super Slump Retaining PCE
  - Very little water reduction
  - Extend the slump life by 2-3 hours, even in 120 mm slump
  - Normal setting times
  - Excellent early strength
The 2000’s
Crystal Seed Hardening Accelerators

- First introduced in 2009
- Based upon specifically designed crystal seeds
- The rate of strength development can be further increased as compared to other conventional accelerators
- Acceleration achieved by nucleation of hydration products onto the seeding crystals
- Best performance in concretes using high sulfate cements
- No reversion in late age strength
A View of the Future
A View of the Future
What is next?

Meet the demands of sustainable construction
and to support the global mega trends

- Further reduction in clinker contents in cements and concretes
- Utilization of poor quality aggregates (high clay contents, alkali-reactive, etc.)
- Alternative binders for concrete
- Reduction of stickiness in high performance concrete mixtures
- Further use and modification of fibers as replacements for steel reinforcing