Today's Admixtures in Today's Concrete

Presented By: Katherine Chevrier
Topics:

1. Cement and Hydration
2. Water Reducers (WRA HRWR)
3. Air Entertainer (AEA)
4. Accelerators
5. Hydration Stabilizer & Retarder
7. Integral Waterproofing Admixture
Cement and Hydration
The cement particle and it’s hydration

Admixtures influence one thing for it’s performance – the hydration of cement

- Calcium Silicate Hydrate (CSH) gel forms on cement particle when the particle interacts with water – Ions are negatively and positively charged along the particle
- Crystals of Calcium Trisulfoaluminate called Ettringite form between cement particles
- The formation of the crystals densify and harden to form the paste in concrete
Fig. 8. SEM pictures of cement at different stages of hydration. a) Surface of unhydrated particle. b) Surface of particle hydrated for 15 s. c) Surface of particle hydrated for 120 min. d) Surface of particle hydrated for 240 min. e) Surface of particle hydrated for 480 min. f) Surface of particle hydrated for 480 min at larger magnification.
Water Reducers
### Table 3: Water-Reducing Admixture Uses, % Reduction and Slump Range

<table>
<thead>
<tr>
<th>Types</th>
<th>Uses</th>
<th>% Water Reduction</th>
<th>Slump Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low-range</td>
<td>Reduce w/c ratio, increase slump</td>
<td>5-10%</td>
<td>4-5 inches</td>
</tr>
<tr>
<td>Mid-range</td>
<td>Reduce stickiness, improve finishability, pumppability, placement and use with SCMs</td>
<td>10-15%</td>
<td>5-8 inches</td>
</tr>
<tr>
<td>High-range</td>
<td>Produce high-strength and/or high-performance concrete for heavily reinforced members or where consolidation is difficult</td>
<td>12-30+%</td>
<td>8 inches or greater, SCC</td>
</tr>
</tbody>
</table>

### Table 4: Water-Reducing Admixture Chemistries

<table>
<thead>
<tr>
<th>Type</th>
<th>Typical Materials Used</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low-range</td>
<td>Lignosulfates, Hydroxylated carboxylic acids, Carbohydrates</td>
</tr>
<tr>
<td>Mid-range</td>
<td>Lignosulfates, Polycarboxylates</td>
</tr>
<tr>
<td>High-range</td>
<td>Sulfonated melamine formaldehyde condensates, Sulfonated naphthalene formaldehyde condensates, Lignosulfates, Polycarboxylates</td>
</tr>
</tbody>
</table>

Type A Water-reducing admixtures
Type D Water-reducing & retarding admixtures
Type E Water-reducing & accelerating admixtures
Type F Water-reducing, high range admixtures
Type G Water-reducing, high range & retarding admixture

---

0 5 10 15 20 25 30

% Water Reduction

Type
A-F

WR
WR-MID-RANGE
WR-ACCEL
E
D

HR, WR
HR, WR-RET
Mechanism:

- Cement dispersion by Steric or Electrostatic repulsion

- Acidic groups within the polymer neutralize the surface ion charges on the cement particles bound to positive ions to a negative when coating the layer of the cement particle

- Negative charge and layer of absorbed compounds create a combination of steric and electrostatic repulsion dispersing the particles – releasing the water tied up in amalgamation that reduces the viscosity in the paste of concrete, thus increasing slump

- As hydration continues more positive ions are introduced into the mix, over running the ability of the polymer
Water Reducers separate flocs into individual grains. Trapped water is released and the grains slip by each other like ball bearings, improving the workability of the concrete.
New Age Technology – Polycarboxylates

- Newest generation of water reducers by applying a new mechanism – Steric Hindrance vs Repulsion

- Not affected by introduced Ions due to it being a physical mechanism – longer acting

- Polymers are comprised of a main carbon chain using carboxylate and ployethelen oxide chains that stem out from cement particles

- Chains hold the cement particles apart and water surrounds the cement grains

- The end of the chain emits a negative charge that causes the cement particles to repel one another

- Cement hydration eventually wears the chains down
### Polymers Types and Mechanisms

<table>
<thead>
<tr>
<th>Type</th>
<th>Mechanism</th>
</tr>
</thead>
</table>
| Ligno Sulphonates | - electrostatic inter particle repulsion  
                      - reduced surface tension  
                      - retarding  
                      - water reduction up to 10% |
| Gluconates      | - electrostatic inter particle repulsion  
                      - better setting behavior  
                      - water reduction up to 20% |
| Naphthalenes    | - electrostatic inter particle repulsion  
                      - better setting behavior  
                      - water reduction up to 20% |
| Melamines       | - electrostatic inter particle repulsion  
                      - water reduction up to 25% |
| Vinyl copolymers | - electrostatic inter particle repulsion  
                      - steric hindrance  
                      - water reduction up to 40% |
| PCE             | - electrostatic inter particle repulsion  
                      - steric hindrance  
                      - water reduction up to 40% |
Added Benefits of Water Reducers

All water reduces increase strength development as a result of better cement dispersion – no matter the method of dispersion.

Dispersion increases the exposed area of the cement grain for effective hydration of the entire particle.

Plain  With HRWR
Why Use Water Reducers?

Low/Mid Range Water Reducer

- Lower water cement ratio
- Increases strength of concrete
- Reduces concrete permeability
- Increases concrete durability
- Helps to control working time of concrete (retarding effect)
- Increase slump to enhance workability

High Range Water Reducer

- In thin section placements
- In areas of closely spaced and congested reinforced steel
- In tremie pipe (underwater) placements
- In pumped concrete to reduce pump pressure, and hence, increase lift and distance capacity
- In areas where conventional consolidation methods are impractical or cannot be used – SCC
- For reducing handling costs
- To create high strength concrete
Water Reducers – Precautions

- Type D can retard between 1–4hrs depending on dose
- Type E will accelerate quickly depending on dose – flash set
- Ligno based WR can test higher air contents of 1–2%
- Some high range water reducers can entrain larger air bubbles with farther spacing
- Some can cause air instability
- Some can cause segregation with low cementitious packages
- Changes in raw materials can greatly affect performance
Air Entrainers
Air Entrainers – Mechanism

- Surfactants at the air and water interface reduce surface retention encouraging the formation of microscopic bubbles during mixing.
- The negative charged head (hydrophilic) attracts water with a hydrophobic tail that repels water and is attracted to the air within the bubble.
- The tail end orients itself within the bubble while the head remains in the water forming a tough water repelling film adding strength, elasticity and stabilization to the air bubble to keep the water out.
- Mixing disperses the bubbles negative charges and repulsion orients the air bubbles for spacing.
- The positive and negative ions of other raw materials aides the guidance of the bubbles for adherence and cohesion for stability.
- Anionics tend to produce smaller bubbles (using ions for electrostatic attraction).
- Nonionics a coarser distribution (using emulsifying sulphactants not dissociating into ions in aqueous solution).

- Some AE will use a blend of both.
As water freezes it expands up to 9% causing pressures that can rupture concrete and cause scaling.

Air entrained concrete has microscopic bubbles that provide reservoirs which relieve pressure as excess water is forced into them, preventing damage to the concrete.

Air entrainment is added to concrete to improve its resistance to freezing when exposed to water and deicing chemicals.

- Improves Workability
- Reduces Segregation
- Reduces Bleeding
Entrained Air – 10 to 100 um
Entrapped air – 1000 um or 1 mm

One cubic meter of 5% air entrained concrete contains:

~13 Billion Bubbles
Air Entrainer Types

- **Wood derived acid salts or Vinsol™ Resin**
  - Quick air generation
  - Minor air gain with mixing – air loss with prolonged mixing
  - Mid-sized bubbles
  - Compatible with other admixtures

- **Wood Rosin (Tricyclic Acids)**
  - Same as above

- **Tall Oil (Fatty Acids)**
  - Slower air generation
  - May increase with prolonged mixing
  - Small air bubbles
  - Compatible with other admixtures

- **Vegetable Oil Acids**
  - Coconut fatty acids
  - Slower air generation
  - Moderate air loss with mixing
  - Coarser air bubbles
  - Compatible with other admixtures

- **Synthetics**
  - Quick air generation
  - Minor loss with mixing
  - Coarser air bubbles
  - May be incompatible with some HRWR
  - Compatible with other admixtures
Air Entrainers – Precautions

- Reduction in strength (5–6% for every 1% entrained)
- Air stability/instability with many different raw materials
  - FA and organics in aggregates
- Some AE’s incompatible or unstable with some admixtures
- Dosage affected by many variables
  - Temperature, concrete and ambient
  - Sand gradation
  - Cement
  - Fly Ash
  - Water supply
  - Slump
- Different AE will be affected differently by mixing
  - Some may cause air loss – some air gain
- Different efficiencies affected by many variables
  - Batching methods – wet/dry plant
  - Transporting – fins of truck
- Effects type of finishing
  - Power trowelling
  - Finishing tools
Accelerators
Accelerators speed up the rate of cement hydration by increasing the rate at which tricalcium silicate reacts with water – chemically intervening the hydration process. This increases the rate of growth of calcium hydroxide crystals – thus increasing set and early strength in the first 24 hrs.
Accelerators – Types

- Rapid – sets concrete in minutes, not commonly used
- Normal/Standard – Decreased set times by 1/2 hr intervals or by %

Chemistry is based on 3 groups

- Soluble inorganic salts – Calcium Chloride
  - Not for use in applications using steel or rebar
- Soluble organic compounds – Calcium Nitrate
  - Better known as NCA – safe for steel or rebar applications
- Misc. solid materials – Calcium Nitrite
  - Used in corrosion inhibitor
Accelerators – Why Use Them

- For every 5° C change in concrete temperature: set time decreases by $\frac{1}{3}$rd
- Better scheduling, Fewer cold weather delays, Faster construction
- Typically used in high early mix designs – 20MPa in 24hrs (especially important for early form removal or post tensioning)
- Reduces the amount of heating and hoarding required
- Saves labor due to reduced setting times
Accelerators – Precautions

- Reduced slump retention
- Increased chloride concentration with chloride based accelerators
- Reduced sulphate resistance with chloride based accelerators
- Chloride based accelerators when mixed with lignosulfonate base WR can cause retardation
- Reduced time for placement and finishing
- If overdosed can cause delayed set
- Concrete temperatures must be maintained at > 10°C after placing or affects of accelerators will not be realized
- Do not use water to re-adjust slump. This will kill the accelerating affect. Use Plasticizer
- For best results – max slump should be 80mm before Plasticizer
Hydration Stabilizers – Retarders
Retarders – Mechanism

- Slow the early stages of hydration by reducing the rate at which tricalcium silicate reacts with water
- This decreases the rate of growth of calcium hydroxide crystals – thus decreasing set and early strength in the first 24hrs

Cement Grain

Dosed retarder, Sugar or lignin based

Figure 4: Effect of Concrete Temperature and Retarder on Setting Time

Source: PCA, “Design and Control of Concrete Mixtures,”
Retarders – Types

- Sugar – 0.2 to 1.0% weight of cement
- Lignosulfonic acids and salts
- Hydroxycarboxylic acids and salts
- Phosphonates and salts
- Salts of amphoteric metals – Zinc/Lead/Tin

Two main types
- Set Retarders
  - Component of many NRWR
  - Typically corn syrup and sugar acid based
- Hydration Stabilizers
Retarders – Why Use Them

- Hot weather concreting
- Large pours with no cold joints
- Flatwork during the summer months
- Long hauls
- High cementitious mixes
- Longer workability time
- Reduces permeability & cracking
- Delay initial set by 1–8 hours
- Benefit of higher final strength
Retarders – Precautions

- Some retarders are not compatible with other admixtures – extended delay
- Does not inhibit surface moisture loss
  - Evaporation loss at the surface of the placement will cause the surface to “crust” and make finishing difficult – use of evaporation retarders an asset
- Never pour concrete after sugar has been added to the load!!!
Shrinkage Reducing Admixtures / Workability Retaining Admixtures / Corrosion Inhibitors
SRA – What You Need To Know

- Propylene Glycol and alkaline polymers are typically the base chemical used
- Lowers capillary pressure by reducing surface tension
- As water evaporates curved upper surfaces form at the interfacial area of the capillaries which increases the internal pressure
- SRA’s manipulate the curvature lessoning capillary tension

Precautions:
- Can impact air stability and increase air content
- Potential high air contents in non air mixes
- Can increase set times
Corrosion Inhibitors – What You Need To Know

- Typical chemical bases are Nitrates some use organic materials
- Chemically arrest corrosion by adding nitrite–ions to neutralize the ferric oxide caused by the high PH of concrete creating a passive film around the steel, thus preventing chloride–ions from penetrating the steel
  - Organic inhibitors based by amines and esters penetrate the steel acting as a water repellent, restricting ingress of water soluble chlorides
- Offset any corrosive effects from chloride materials within the design constituents – or permeating through the concrete from outside influences

Precautions:
- Some will greatly accelerate set times
- Some not compatible with some LRWR/NRWR and will have the opposite affect on set – retardation
Workability Retaining Admixtures – What You Need To Know

- Maintains workability retention of concrete farther than what just WR could do alone – 90min to 120min
- Does not retard or provide stabilizing of hydration
- Does not work as a water reducer
- Does not create slump

**Batch**
- 60min
- 90min

**Reference**
- Ref 180mm
- Ref 65mm
- Ref 30mm

**WRA**
- WRA 190mm
- WRA 155mm
- WRA 150mm

Reference Mix lost 5.75 in. (145mm)
Integral Waterproofing Admixture
Integral Waterproofing Admixture – Mechanism

- Calcium Hydroxide and other soluble by-products from cement hydration dissolve in water introduced in capillaries and micro/macro cracks within the concrete surface, while unhydrated cement and non soluble materials remain lines on the capillary walls.

- Interaction of admixture reacts with the capillary water mixture and forms crystals starting on the concrete surface with the unhydrated cement – filling the capillary.

  \[
  \text{Cement} + \text{Water} + \text{Crystalline Product} \rightarrow \text{CSH} + \text{CH} + \text{Needle Shape Crystals}
  \]
Integral Waterproofing Admixture – Visual of Mechanism
Integral Waterproofing Admixture – Crystals

Crystals fill the pores and capillaries in concrete.

Normal Concrete
Bleed Canal

Treated Concrete
Bleed Canal

Regular Concrete
ICW Concrete
Integral Waterproofing Admixtures – Why Use Them and Precautions

- Lowers permeability and increases durability
- Maintains water tightness in structures within the water table, structures containing water or in hydrostatic conditions when cracks form – self healing
- Removes physical applications of waterproofing membranes
- Is integral – cannot be punctured or damaged and is not affected by UV’s

Percautions:
- Most products increase set times – care is needed when using retarders or hydration stabilizers
- Retardation will occur in some products when combined with WR’s – especially LR/NR
- Can effect air and slumps
  - Some companies supply products that include AE – make sure you know the product your using
Some contents contained in this presentation came from PCA Design and Control of Concrete Mixtures

Thank you to the following Admixture Supply companies who provided some of the material in this presentation:

• Euclid – Bert Almedia
• Sika – Jason Jessome
• BASF – Chris Sandhu & Chris Lecuyer (AKA the Chris’s)
• Xypex (with an X) – Brad Pope
• Kryton – John Anderson
• Grace – Richard Horth
The End

Thank You