Chemical Admixtures

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What are Admixtures?

• Admixtures are chemicals, added to concrete, mortar or grout at the time of mixing, to modify the properties:
  ➢ either in the wet state immediately after mixing
  ➢ or after the mix as hardened.

• Admixtures are usually defined as being added at less than 5% on the cement in the mix but the majority of admixtures are used at less than 2% and the typical range is 0.3–1.5%.
Reason for Use of Admixture

• To reduce the **cost** of concrete construction

• To achieve **certain properties** in concrete more effectively than by other means

• To maintain the **quality of concrete** during the stages of mixing, transporting, placing, and curing in adverse weather conditions

• To overcome **certain emergencies** during concreting operations
Cost-effective

- Making placing easier
- Compaction easier
- Permeability
- Freeze/thaw (air content)
- Consistence and sustainability
- Density
- Strength development
- Bond of concrete to...
- Colored concrete
- Durability
- Handling properties
- Impact and abrasion resistance
- Reduce segregation
- Capacity for bleeding
- Prevent shrinkage
- Bond of concrete to...
Admixture’s Classification

1. Plasticizers & Super plasticizers
2. Retarding admixtures
3. Accelerating admixtures
4. Air-entraining admixtures
5. Corrosion inhibitors
Admixture’s Classification

- Hydration-control admixtures
- Shrinkage reducers
- Alkali-silica reactivity inhibitors
- Colouring admixtures
- Miscellaneous admixtures such as workability, bonding, damp proofing, permeability reducing, grouting, gas-forming, and pumping admixtures
# Brief history of admixture use

<table>
<thead>
<tr>
<th>Romans</th>
<th>Retarders</th>
<th>Urine</th>
<th>Air entrainment</th>
<th>Blood</th>
<th>Fibres</th>
<th>Straw</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plasticizers</td>
<td>1932</td>
<td></td>
<td>Patent for sulphonated naphthalene formaldehyde plasticizers (but not available in commercial quantities)</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>193?</td>
<td></td>
<td>Lignosulphonates used as plasticizers</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>193?</td>
<td></td>
<td>Hydroxycarboxcilic acid salts used as plasticizers and retarders</td>
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</tr>
</tbody>
</table>
### Brief history of admixture use

<table>
<thead>
<tr>
<th>Category</th>
<th>Year</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water proofers</td>
<td>193?</td>
<td>Fatty acids, stearates and oleates</td>
</tr>
<tr>
<td>Air entrainers</td>
<td>1941</td>
<td>Tallow and fatty acid soaps for frost resistance</td>
</tr>
<tr>
<td>Superplasticizers</td>
<td>1963</td>
<td>Sulphonated naphthalene formaldehyde commercially available</td>
</tr>
<tr>
<td></td>
<td>1963</td>
<td>Sulphonated melamine formaldehyde patent and available</td>
</tr>
<tr>
<td></td>
<td>1990–1999</td>
<td>Polycarboxylate ether development and introduction</td>
</tr>
</tbody>
</table>
# Admixtures performance

**Table 1: Principal performance requirements for admixtures given in BS EN 934–2**

<table>
<thead>
<tr>
<th>Type of admixture</th>
<th>Performance requirement</th>
<th>Value in BS EN 934–2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water reducing/plasticizing</td>
<td>Water reduction at equal consistence</td>
<td>Reduction ≥ 5%</td>
</tr>
<tr>
<td>High-range water reducing/superplasticizing</td>
<td>Water reduction at equal consistence</td>
<td>Reduction ≥ 12%</td>
</tr>
<tr>
<td></td>
<td>Increase in consistence at equal w/c ratio</td>
<td>Slump increase ≥ 120 mm</td>
</tr>
<tr>
<td>Water retaining</td>
<td>Reduction in bleeding</td>
<td>Reduction ≥ 50%</td>
</tr>
<tr>
<td>Water resisting</td>
<td>Reduction in capillary absorption</td>
<td>Reduction ≥ 50% by mass</td>
</tr>
<tr>
<td>Air entraining</td>
<td>Air void characteristics in hardened concrete</td>
<td>Spacing factor ≤ 0.200 μm</td>
</tr>
<tr>
<td>Set accelerating</td>
<td>Reduction in initial setting time</td>
<td>Reduction ≥ 40% at 5°C</td>
</tr>
</tbody>
</table>
## Admixtures performance

| Hardening accelerating | Compressive strength at 1 day  
|                        | Compressive strength at 2 days  
|                        | Increase ≥ 20% at 20°C  
|                        | Increase ≥ 30% at 5°C  
| Set retarding | Increase in initial and final setting times  
| Set retarding/water reducing/plasticizing | Water reduction at equal consistency  
|                        | Increase in initial and final setting times  
|                        | Reduction ≥ 5%  
|                        | Initial increase ≥ 90 min.  
|                        | Final increase ≤ 360 min.  
| Set retarding/high-range water reducing/super plasticizing | Water reduction at equal consistency  
|                        | Increase in consistence at equal w/c ratio  
|                        | Increase in initial and final setting times at equal consistency  
|                        | Reduction ≥ 12%  
|                        | Slump increase ≥ 120 mm  
|                        | Initial increase ≥ 90 min.  
|                        | Final increase ≤ 360 min.  
| Set accelerating/water reducing/plasticizing | Water reduction at equal consistency  
|                        | Reduction in initial setting time  
|                        | Reduction ≥ 5%  
|                        | Reduction ≥ 30 min. at 20°C  
|                        | and ≥ 40% at 5°C  

Dose of admixture

• BS EN 934–2 advises that “trial tests should be carried out with the materials to be used on site to find the dosage necessary to achieve the desired result”.

• The concrete producer may well have the results of such tests, which should be obtained before specifying the type and dose of admixture for a specific concrete mix.

1. Admixtures of the same type from different manufacturers may well require different doses to achieve the desired effect;

2. The effect of admixtures is dependent on the particular cement, additions and aggregates used in the concrete.
Plasticizers
(water reducers)
Plasticizers (water reducers)

• A material, which:
  − Either increases workability of freshly mixed concrete without increasing water cement ratio
  − or maintains workability with a reduced amount of water, is termed as water reducing admixture.

• Reduction in water depends on dose of:
  − Admixtures
  − Cement content
  − Type of aggregate
  − ratio of cement ,fine and coarse aggregate
Plasticizers (water reducers)

Chemical composition

- Lignosulfonic acids, derivatives and their salts.
- Hydroxylated carboxylic acids, their salts and derivatives.
- Naphthalene sulphonic acid based
- Sulfonated melamine polycondensation products
- Inorganic material like:
  - borates,
  - phosphates,
  - amines and their derivatives,
  - carbohydrates,
  - sugar and certain polymeric compounds like cellulose, ethers etc.
Plasticizers (water reducers)

Advantages

• Increase the workability of the concrete without reducing the compressive strength

• High strength can be obtained with the same cement content by reducing water cement ratio.

• Saving in the quantity of cement (approx. upto 10%) can be achieved keeping the same water/cement ratio and workability.
Plasticizers (water reducers)

Effect on Cement Particles

All surface of cement particles are not available for hydration

Release of trapped water from cement flocs by the action of plasticizers
### Plasticizers (water reducers)

**Use of plasticizers: Example**

<table>
<thead>
<tr>
<th>Description of Mix</th>
<th>Dosage ( % cement)</th>
<th>Cement (kg/m³)</th>
<th>W/C</th>
<th>Slump [cm]</th>
<th>Compressive strength [Mpa]</th>
</tr>
</thead>
<tbody>
<tr>
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<td>1 d</td>
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<tr>
<td><strong>Reference</strong></td>
<td>--</td>
<td>300</td>
<td>0.6</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td><strong>Plasticizes</strong></td>
<td>0.2%</td>
<td>300</td>
<td>0.6</td>
<td>10</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>0.3%</td>
<td>300</td>
<td>0.6</td>
<td>12</td>
<td>6</td>
</tr>
<tr>
<td><strong>Strength increase</strong></td>
<td>0.2%</td>
<td>300</td>
<td>0.56</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>0.3%</td>
<td>300</td>
<td>0.54</td>
<td>7</td>
<td>8</td>
</tr>
<tr>
<td><strong>Cement saving</strong></td>
<td>0.2%</td>
<td>280</td>
<td>0.6</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>0.3%</td>
<td>270</td>
<td>0.6</td>
<td>7</td>
<td>6</td>
</tr>
</tbody>
</table>
Plasticizers (water reducers)

Initial workability of concrete and typical workability loss with time

![Graph showing initial workability and workability loss over time for different types of plasticizers.](image)

- **Control**
- **Retarded plasticized**
- **Retarded superplasticized**
- **Plasticized**
Plasticizers (water reducers)

**Effects of Plasticizer:**

- Fluidize the mortar or concrete.
- Reduces water requirement by 5-15%.
- Improves workability. Increase in slump from 30-150 mm.
- May entrain air at a small percentage (1-2%).
- Likely to retard setting and hardening.
- Increase in concrete strength 10 – 20%.
- Rapid slump loss.
- Small effect on drying shrinkage.
Super plasticizers
(high-range water reducers)
Super plasticizers (high-range water reducers)

- Super Plasticizers are water reducers, chemically different from the plasticizers or normal water reducer
- capable of reducing water content by about 30% or increasing slump upto 200mm without causing segregation or bleeding in concrete.

![Diagram](image.png)

*Fig. 9. Repulsion of adsorbed superplasticiser disperses the cement particles.*
Super plasticizers (high-range water reducers)

Types of superplasticizer action:

a) Creating “grease” layer
b) Surrounding grains of cement with negative charge
c) Decreasing of surface water tension
d) Long chain of polymer, physically precluding the grains of cement to approach each other
Super plasticizers (high-range water reducers)

Chemical composition:

- Sulfonated melamine formaldehyde condensates
- Sulfonated naphthalene formaldehyde condensates
- Modified lignosulfonates
- Others such as sulfonic acid esters and carbohydrate esters
Super plasticizers (high-range water reducers)

**Amount used:**

- Based on various types of superplasticizers different amount is used.
  - Lignosulphonates – not more than 0.25% cem
  - Carboxylic acids – 0.1% cem
  - Sulphonated maleic-aldehyde condensates (SMF) – 0.5 to 3% cem
  - Sulphonated naphthalene-formaldehyde condensates (SNF) – 0.5 to 3% cem
Super plasticizers (high-range water reducers)

Advantages:
• Cement content can be reduced to a greater extent keeping the same W/C ratio. This will lead to economy.

• Permits reduction of water content about 30% without reducing the workability

• Water-cement ratio can be reduced significantly keeping same cement content and workability. This will lead to increase in strength.
  • It is possible to use w/c ratio as low as 0.25 or even lower and yet to make flowing concrete to obtain strength of order 120 MPa or more.
Super plasticizers (high-range water reducers)

Advantages:

- Higher workability at very low water cement ratio like casting concrete with heavy reinforcement.

- Reduction in permeability

- Super plasticizers are used where early strength development is required in prestressed concrete or casting of floor, where early access for finishing equipment is required.
Super plasticizers (high-range water reducers)
Super plasticizers (high-range water reducers)

Fig. 5.26. The influence of addition of superplasticizer on the early strength of concrete. Cement content 370 kg/m³. All concrete of same workability. Cement: Type III (Rapid hardening)
Super plasticizers (high-range water reducers)

Superplasticizer is practiced for:

• Production of flowing, self levelling, self compacting concrete
• Production of high strength and high performance concrete.
Retarders
Retarders

• Retarding admixtures are used to **delay the rate of setting of concrete**.

• A retarder is an admixture that **slows down the chemical process of hydration** so that concrete remains plastic and workable for a longer time than concrete without the retarder.

1. Retarders are used to **overcome the accelerating effect of high temperature** on setting properties of concrete in **hot weather concreting**.

2. Very useful when concrete has to be placed in very **difficult conditions and delay may occur** in transporting and placing.
Retarders

• Retard setting time of concrete. Retardation of up to 10 hours is possible.
• Help obtain architectural finishes.
• Reduce slump loss.
• Offset effects of hot weather.
• Reduction in early strength expected.
• Affects on shrinkage unpredictable.
Retarders

Chemical Composition

- Lignosulphonic acids and their salts. e.g. Na (Sodium), Ca, etc.
- Hydro-carboxylic acids and their salts.
- Carbohydrates including sugar.
- Inorganic salts based on floururates, phosphates, oxides, borax and magnesium salts.
- Gypsum and Calcium Sulphate are well known retarders.
## Retarders

### Amount used and effects

<table>
<thead>
<tr>
<th>Admixture addition litres/50 kg cement.</th>
<th>Setting time hrs.</th>
<th>W : C ratio</th>
<th>Compressive Strength MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial</td>
<td>Final</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>4.5</td>
<td>9</td>
<td>0.68</td>
</tr>
<tr>
<td>0.14</td>
<td>8.0</td>
<td>13</td>
<td>0.61</td>
</tr>
<tr>
<td>0.21</td>
<td>11.5</td>
<td>16</td>
<td>0.58</td>
</tr>
<tr>
<td>0.28</td>
<td>16.0</td>
<td>21</td>
<td>0.58</td>
</tr>
</tbody>
</table>
Advantages of Retarders

• Improves workability, cohesion and extends setting time, provides protection against delays and stoppages and facilitates keeping workable concrete for extended period.

• In the large construction, good workability of the concrete throughout the placing period and prevention of cold joints is ensured by adding retarders in the concrete.

• Extended setting time minimise risks of long distance delivery in hot weather, improves pumpability of concrete by extended setting period and improved workability of concrete.

• Reduces bleeding and segregation where poor sand grading are unavoidable.

• Reduces adverse environmental effects of various nature on concrete and embedded steel by considerable reduction in permeability.
Accelerators
Accelerators

Accelerating admixtures are added to concrete to increase the rate of early strength development

Why accelerators?

1. Permit earlier removal of formwork
2. Reduce the required period of curing
3. Advance the time that a structure can be placed in service
4. Partially compensate for the retarding effect of low temperature during cold weather concreting
5. In the emergency repair work.
Accelerators

Commonly used materials as an accelerator:

- Calcium chloride
- Some of the soluble carbonates
- Silicates fluosilicates (Expensive)
- Some of the organic compounds such as triethenolamine (Expensive)
Accelerators

Benefits of Accelerators

• Accelerators are so powerful that it is possible to make the cement set into stone hard in a matter of five minutes are less.

• With the availability of such powerful accelerator, the under water concreting has become easy.

• Similarly, the repair work that would be carried out to the waterfront structures in the region of tidal variations has become easy.

• The use of such powerful accelerators have facilitated, the basement waterproofing operations.
Accelerators

**Calcium Chloride**

- Calcium chloride (CaCl₂) is the chemical most commonly used in accelerating admixtures, especially for non-reinforced concrete.
- Should not exceed 2% by mass of cementing material.
- An overdose can result in placement problems and can be detrimental to concrete.
- It may cause: rapid stiffening, a large increase in drying shrinkage, corrosion of reinforcement, and loss of strength at later ages.
Air-entraining Admixture
Air-entraining admixtures

**Function**

- Air Entraining admixtures are surface active chemicals which cause small stable bubbles of air to be formed uniformly through a concrete mix.
- The bubbles are mostly below 1 mm diameter with a high proportion being below 0.3 mm.

**Materials**

- Air entraining admixtures have traditionally been based on:
  - Abietic acid salts (Vinsol Resin).
  - Fatty acid salts
Air-entraining admixtures

- **Entrapped air:**
  - By chance
  - As large as 3mm

- **Entrained air:**
  - On purpose
  - Size: 50 to 300 μm
Air-entraining admixtures

Air entraining agents lower the surface tension of the water to facilitate bubble formation. Uniform dispersion is achieved by blending surfactants to increase the stability of the interfacial layer between air and water, preventing bubbles from coalescing.
Air-entraining admixtures

- Improved workability --- air bubble as lubricant
- Improved ductility --- more deformation from small hole
- Reduced permeability --- isolated air bubble
- Improved impact resistance --- more deformation
- Improved durability --- freezing and thawing (release ice forming pressure)
Disadvantages of adding air entraining admixtures

- Strength loss of 10-20%

Effect of entrained air on durability
Air Entraining Admixtures

Effect on freezing and thawing

- **Specimens Cured - I**
  - Day in Moulds 27
  - Days in Fog Room

- **Plain Concrete**
  - Unit Wt.: 2360 kg/m³

- **Air-entrained Concrete**
  - Unit Wt.: 2245 kg/m³

Graph showing percent loss in weight against cycles of freezing and thawing.
Air Entraining Admixtures

Effect on bleeding

![Graph showing the effect of different admixtures on bleeding](image-url)
Corrosion-inhibiting admixtures
Corrosion-inhibiting admixtures

• Reinforcing **steel corrosion** is a major concern with regard to the durability of reinforced concrete structures.

• Each year, numerous bridges, parking garages, and other concrete structures undergo extensive **repair and rehabilitation** to restore their structural integrity as a result of corrosion damage.

• There are **several ways** of combating chloride-induced corrosion, one of which is the use of corrosion-inhibiting admixtures

• they protect embedded reinforcement by **delaying the onset of corrosion** and also by reducing the rate of corrosion after initiation

• **TYPES**: inorganic materials such as **calcium nitrite**, and organic materials such **as amino alcohols and esters**
Corrosion-inhibiting admixtures

• **Calcium nitrite** resists corrosion by stabilizing the passive layer in the presence of chloride ions

• Organic inhibitors function by **forming a protective film at the surface of the steel** to help resist moisture and chemical attack
Corrosion-inhibiting admixtures

• Some available corrosion inhibitors will accelerate the time of set in concrete and therefore retarding admixtures may be necessary to improve working time

• corrosion resistance can also be increased by reducing the permeability of the concrete through the use of low w/c or with a permeability reducing admixture
Corrosion-inhibiting admixtures

The corrosion inhibitor can extend the time to onset of corrosion as indicated by the following example:

Concrete spec.
PC 400 kg/m³   w:c 0.40
Reinforcement at 40 mm
Chloride diffusion coeff. 1 × 10⁻¹² m²/s

No corrosion inhibitor
Chloride corrosion threshold 0.4% on cement
Threshold reached after 20 years

Calcium nitrite added at 10 litres/m³ (30% soln)
Chloride corrosion threshold raised to 0.8% on cement
Threshold reached after 50 years
References

• Chemical admixtures: [http://www.ce.berkeley.edu/~paulmont/241/chemical_admixture.pdf](http://www.ce.berkeley.edu/~paulmont/241/chemical_admixture.pdf)

• John Dransfield, Admixtures for concrete, mortar and grout. Chapter 4 of “Advanced Concrete Technology” Book.