Admixtures for improving the concrete performance with special reference to polycarboxylates

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Our Corporate Journey
Established in 1867 by two Scotsmen

George Stephen BALMER

Alexander LAWRIE
THE MATURING YEARS (1900 - 1936)
Private Limited Co. - 1st. January 1924
Public Limited Co. - 6th. January 1936

THE GROWTH YEARS (1937 - 1969)
Foray into manufacturing

THE GOVT. ERA (1972 ONWARDS)
BALMER LAWRIE & CO. LTD.

- Industrial Packaging
- Specialty Containers
- Tea
- Engineering & Tech. Services
- Joint Ventures
- Greases & Lubricants
- Performance Chemicals
- Travel & Tours
- Logistics Services
- Container Freight Stn.
Manufacturing Facilities – Lubricant & Chemicals
Function of Admixtures

- Improve concrete workability
- Improve concrete / mortar strength and other physical properties
- Reduce cement consumption or substitute special cement
- Regulate setting and hardening rate and air entraining for air content
- Reduce water bleeding to improve performance
- Improve concrete pumping performance
- Improve adhesion between aggregates and other materials.
Types of Admixtures

- High Performance Water Reducers (HPWR)
- High Range Water Reducers (HWR)
- Conventional Water Reducers (WR)
- Air Entraining Water Reducers (AEWR)
- Pumping Aids (PA)
- Accelerators (Ac)
- Retarders (Re)
- Air Entrainer (AE)
How SP* works?

- SPs’ are high molecular long chain anionic polymers
- Initial added water get entrapped within cement particles.
- SP gets adsorbed on cement particles thus creating negative charge.
- Anionically charged cement particles repel each other and move apart thus releasing entrapped water and disperse cement particles.
- Dispersion improves fluidity of cement paste.
- SNF – belongs to this category

*SP-Super plasticizer
Sulphonic group negatively charged

Sulphonic group responsible for electrostatic repulsion

Sulphonic group - adsorption

Cement grain
Hydration products of cement

- Calcium silicate hydrate (C-S-H)
- Calcium Hydroxide
- Afm (C₃A·3CaSO₄·32H₂O) and Aft C₃A·3CaSO₄·12H₂O phases

Intercalation of Super plasticizer in C₃A layers

Intercalation of SNF is favored inside C₃A layers on direct addition resulting in more organo mineral phases (OMP).
How HPSP* works?

*HPSP - High performance super plasticizer

- HPSPs’ are anionic polymers with long side chains of varying lengths.
- In addition to the charging of cement particles long side chain of HPSP produces steric hindrance effect keeping the cement particles further apart compared to SP.
- Hence HPSPs’ provide enhanced performance and at lower dosage.
- Polycarboxylates are under this class.

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(a) Electrostatic Repulsion  
(b) Steric Repulsion
Polycarboxylates superplasticizer:

Polycarboxylates are new generation of concrete admixtures, have more water reducing rate than naphthalene based superplasticizer with better slump retention.

Chemical structure of polycarboxylate superplasticizer and its reaction with cement:

The main chain of polymer molecule has absorption group of carboxylic group, On the lateral chain it has PEO providing sterically hindrance to cement layers.

Zeta potential measurement of cement particles in aqueous suspensions of different PC’s are in the ranges of 1-5 mV indicating dispersion of cement particles occur mainly via dispersion mechanism.

Side chain lengths, chain densities, ion charges can be altered.
Fundamental mechanism of PC intercalation in C$_3$A phases

Compressed adsorption layers in cement by the action of PC generation elastic repulsive energy

- **worm type** with 8.5 EO
- **worm type** with 17 EO
- **star type** with 111 EO
- **brush type** with 45 EO

**8.5PC6**
MCL: 44.4 nm; SCL: 2.37 nm

**17PC6**
MCL: 87.0 nm; SCL: 4.74 nm

**111PC6**
MCL: 16.3 nm; SCL: 30.9 nm

**45PC6**
MCL: 29.4 nm; SCL: 12.5 nm

刷型和星型—无插层

蠕虫型—有插层

**AlO, CaO polyhedra**

**sulfate anion**

**water**
Preparation of PC

It involves two steps

1. Preparation of macromonomer
   This process is tedious

2. Copolymerization of macromonomer with acrylic monomers in different mole ratios

**In-House Technology**

Our indigenous technology is unique and can produce PC with ease without any tedious steps. It can be functionalized
• This technology helps us to achieve mix designs of concrete with a W/C ratio of 0.32 and a high slump retention up to 3 hrs. This is a requirement for making diapharm walls of 75MPa for Metro Rail tunnels.
Advantages of PC

- Low Dosages
- High slump retention
- Water reduction up to 25%
- Good compatibility with cements
- Environmental friendly products

Different types of PC

- Slump retention
- For highly early strength
- To reduce Shrinkage
- Sulphate ion interference free
- Less tacky for better pumping
- For self consolidating – SCC
Hydrolysis of Crosslinked points by alkaline water during setting of cement releases carboxylate ion and it increases progressively resulting low slump loss.

Schematic trend in slump loss behavior with Different acrylic superplasticizer.
The second method involves blending of PC/PE with slump loss controlling agents (SLCA).

Hydrolysis of SLCA occurs in alkaline condition.
Branched PC – less tacky

- Concrete with low W/C and high powder content will be viscous in nature
- A more branched type PC will be less tacky

Low viscous concrete- better pumping
Hyperbranched polymers are under the class of Dendritic macromolecules. Hyperbranched polymers, are typically obtained in a one-pot reaction and as a result can be easily prepared also in larger quantities.
Hyperbranched PC – less sulphate interference
Controlling sulphate ion concentration and PC adsorption by Ca salts

- PC adsorption is significantly affected by the presence of soluble sulphates suggesting the competitive adsorption with sulphate ion.
- This can be counteracted by using the solubility equilibrium of gypsum.

\[ [Ca^{2+}][SO_4^{2-}] = 2.4 \times 10^{-5} \]

Increase in calcium reduces the soluble sulphate ion

PC adsorption increases with calcium ion concentration
The moisture gets evaporated through the small pores of concrete.

The surface tension of water causes a loss in volume as it pulls the pores together.
PC – Self Consolidating Concrete (SCC)

Viscosity modifying agents incorporated in PC reduces the yield stress of concrete and its flows even with a low shear force.
## Our Product Range

<table>
<thead>
<tr>
<th>Product Code</th>
<th>Application Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>UNF5</td>
<td>Used for M20-M30 designs in batching plants with a water reduction of 12-15%</td>
</tr>
<tr>
<td>FDN</td>
<td>For M30-M40 designs in batching plants; water reduction – 15%</td>
</tr>
<tr>
<td>200 R</td>
<td>For RMC’s in M20-M30 design &amp; water reduction of 12% with a slump retention of 120 mm for 2 hrs</td>
</tr>
<tr>
<td>500 R</td>
<td>Suitable in M30-M40 designs; water reduction- 15% with a slump retention of 120 mm for 2 hrs</td>
</tr>
<tr>
<td>500 CR</td>
<td>Special product for RMC’s and developed for challenging mix design with a water reduction of 15%; A slump retention of 110 mm for 2 hrs is achieved</td>
</tr>
<tr>
<td>PCE</td>
<td>Will be launched shortly with our in-house developed technology</td>
</tr>
<tr>
<td>SPF</td>
<td>Under development and will be launched shortly</td>
</tr>
</tbody>
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Conclusions

**Admixtures helps in**

- for better workability of concrete at low W/C ratios
- Achieve high and early strength with energy savings
- to save cement
- To avoid shrinkage, heat development & aids in pumpability of concrete

**Challenges**

- Admixtures intercalate inside $C_3A$ layers depending on the sulphate contents.
- Intercalation of admixtures is a unwanted phenomenon and leads higher dosages of these admixtures.
- It is unlikely that cement manufactures will adjust their products
- It is essential to develop admixtures especially PC which will less sensitive to different sulphated cements and more robust in their applications
References


2. M. Collerpadi & M. Valente in 8th CANMET/ACI International Conference on Superplasticizers and Other Chemical Admixtures in Concrete

3. Lectures of Dr. Caijun Shi College of Civil Engineering, Hunan university


5. Cement and Concrete Research 31 (2001) 1169-1176