

Admixtures for improving the concrete performance with special reference to polycarboxylates

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Balmer Lawrie & Co. Ltd.

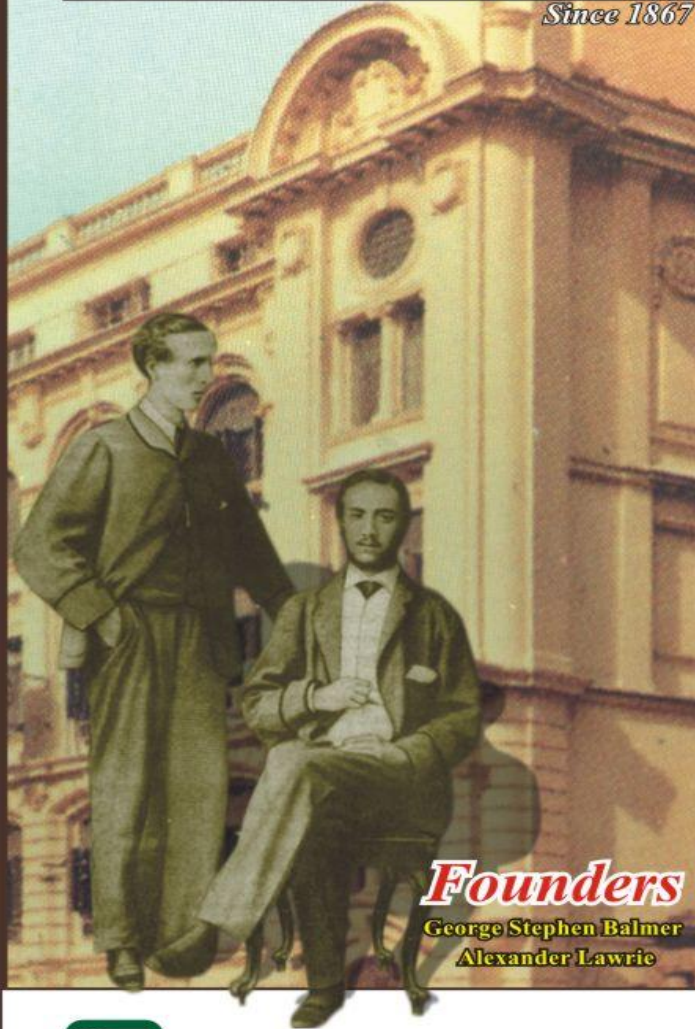
SBU- Performance Chemicals

Our Corporate Journey



Business through ethics

Since 1867



Founders

George Stephen Balmer
Alexander Lawrie

Established in 1867 by two Scotsmen

George Stephen **BALMER**

Alexander **LAWRIE**



Balmer Lawrie & Co. Ltd
LEATHER CHEMICALS DIVISION

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)

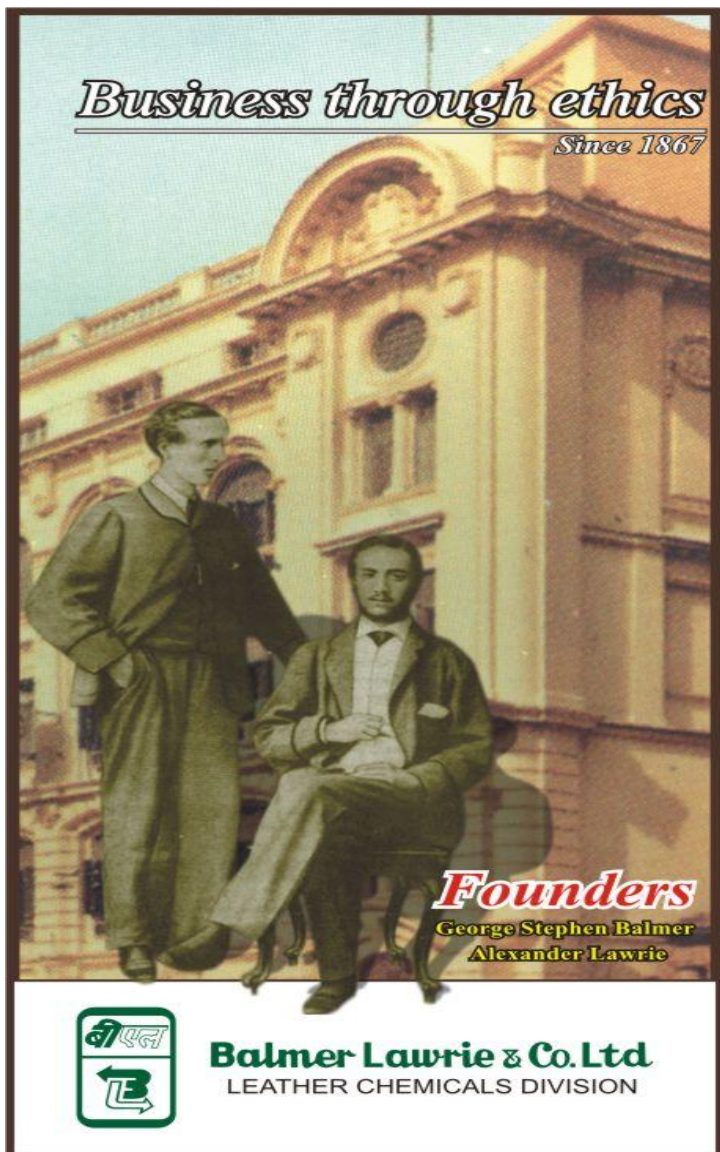




SINCE 1867

Balmer Lawrie & Co. Ltd, Kolkata

Business Profile...



BALMER LAWRIE & CO. LTD.

Industrial Packaging

Greases & Lubricants

Specialty Containers

**Performance
Chemicals**

Tea

Travel & Tours

**Engineering &
Tech. Services**

Logistics Services

Joint Ventures

Container Freight Stn.

Manufacturing Facilities – Lubricant & Chemicals

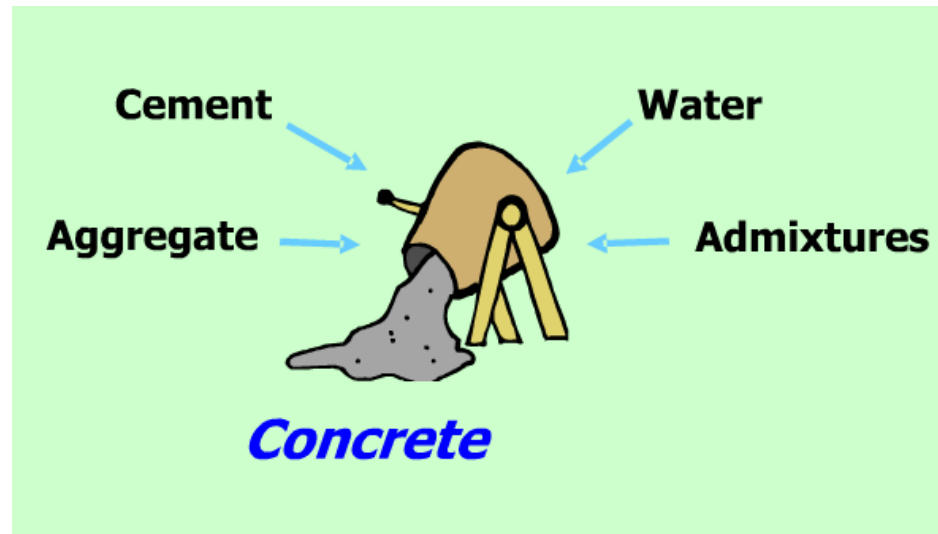


- SEWREE
- SILVASSA
- TALOJA
- CHENNAI
- KOLKATA



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)**
- **Acclerators (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

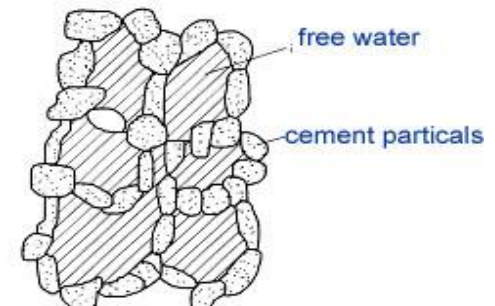


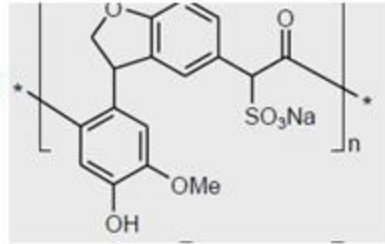
Fig 1 Schematic of concrete flocculation

*SP-Super plasticizer

Working principle – Charge repulsion

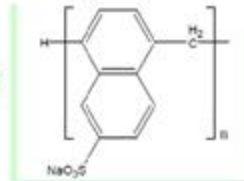
1920

Lignosulphonates



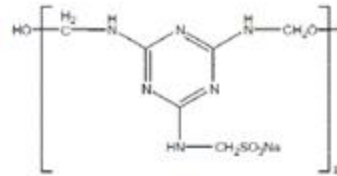
1960

Naphthalenesulphonates



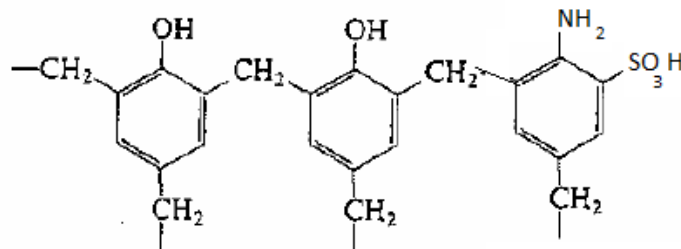
1970

Melaminesulphonates



1990

Sulphanilic acid based condensates

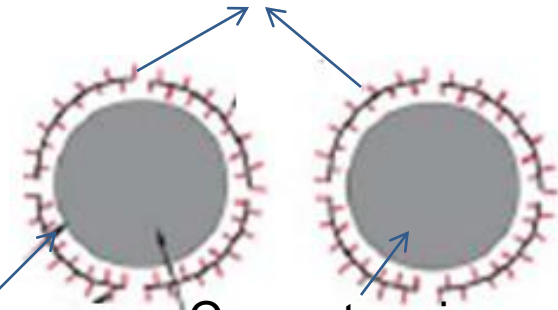


Sulphonic group negatively charged



Main Polymer Chain

Sulphonic group responsible for electro static repulsion

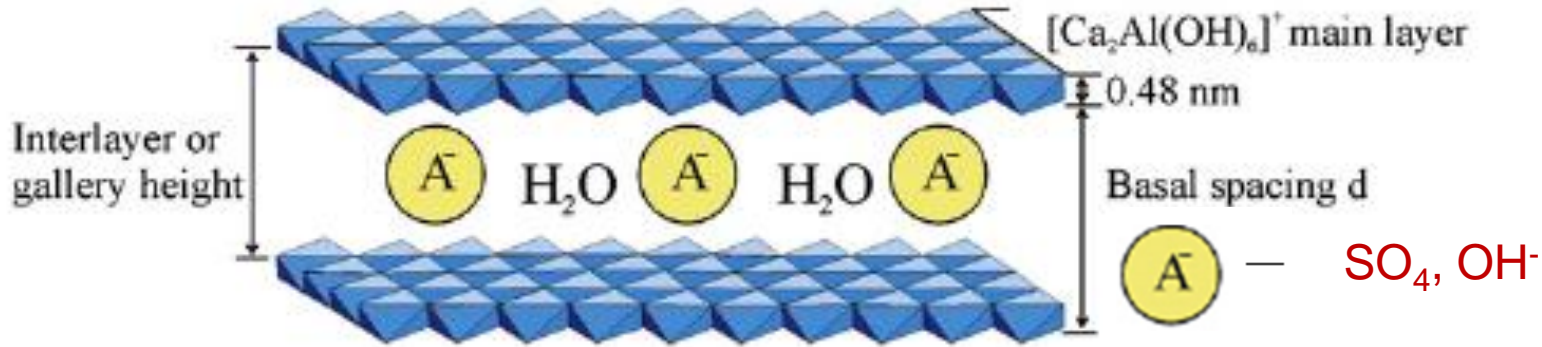


Sulphonic group - Cement grain adsorption

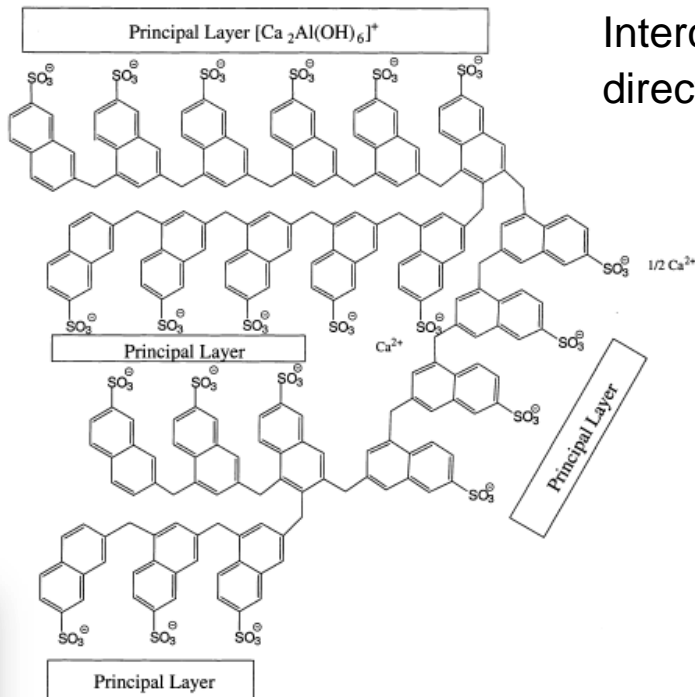


Hydration products of cement

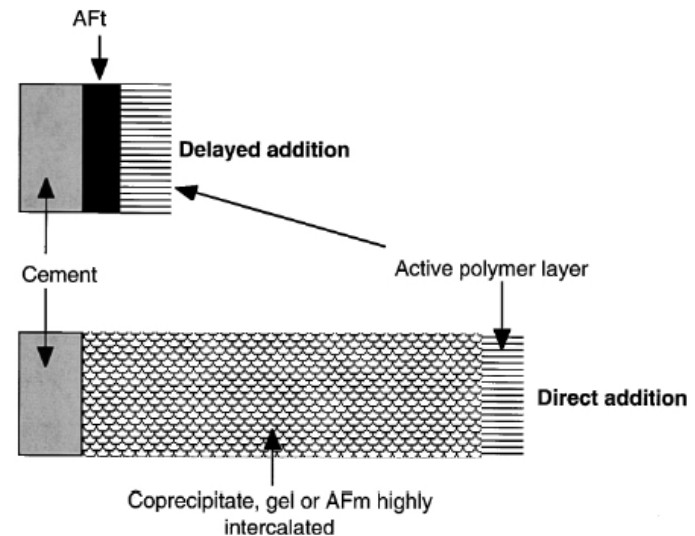
- ❖ Calcium silicate hydrata- C-S-H
- ❖ Calcium Hydroxide
- ❖ Afm ($C_3A \cdot 3CaSO_4 \cdot 32H_2O$) and Aft ($C_3A \cdot 3CaSO_4 \cdot 12H_2O$) phases



Intercalation of Super plasticizer in C_3A layers



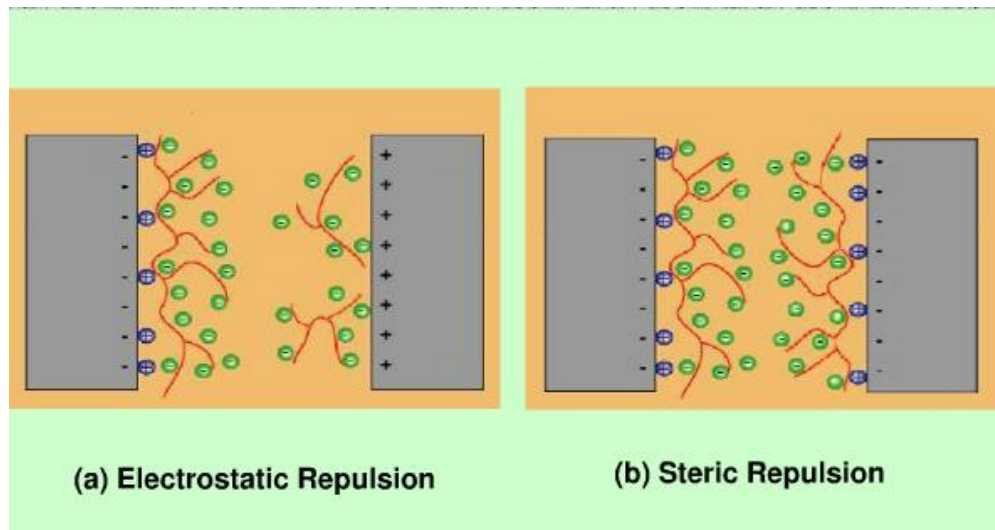
Intercalation of SNF is favored inside C_3A layers on direct addition resulting in more organo mineral phases **OMP**.



How HPSP* works?

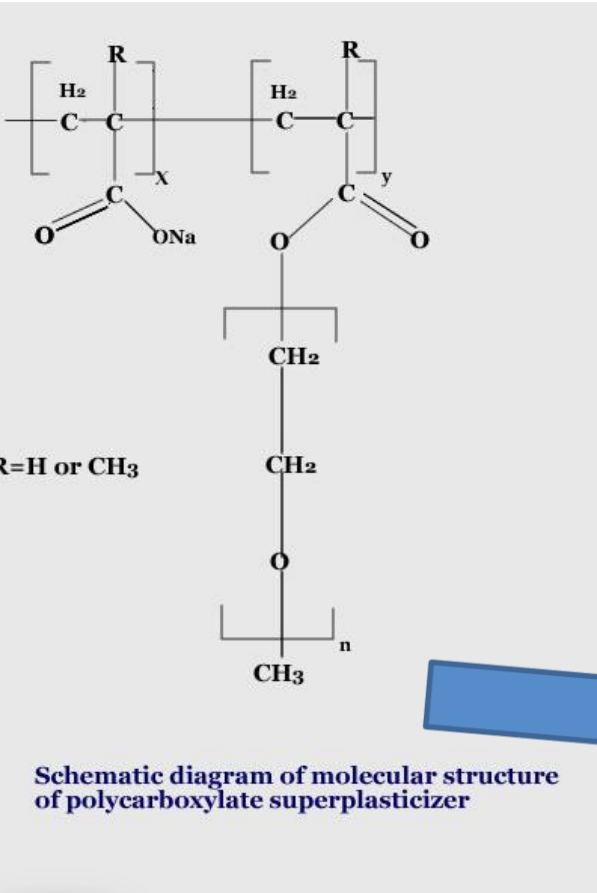
*HPSP-High performance super plasticizer

- 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 .



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 .

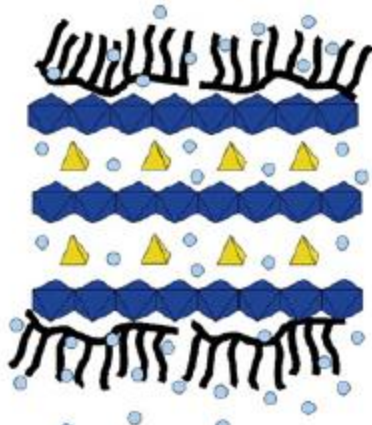
Zeta potential measurement of cement particles in aqueous suspensions of different PC 's are in the ranges of 1-5 mV indicating dispersion of cement particles occur mainly via dispersion mechanism.



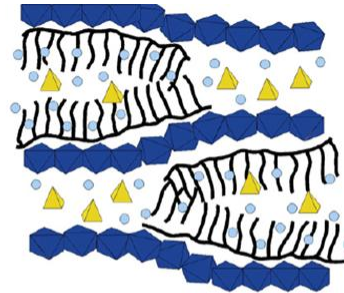
Side chain lengths , chain densities , ion charges can be altered



Fundamental mechanism of PC intercalation in C₃A phases



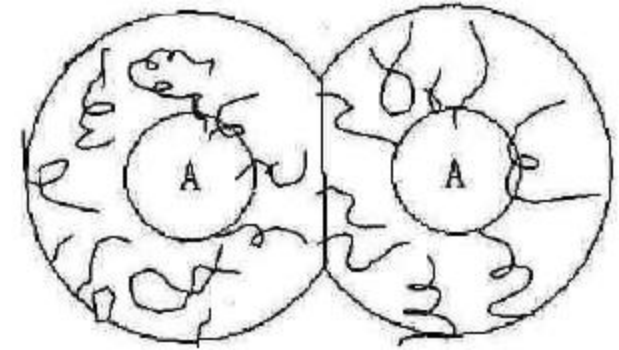
brush and star type-
no intercalation



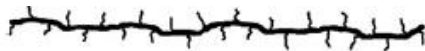
worm type-
with intercalation

● AIO, CaO polyhedra

▲ sulfate anion ● water

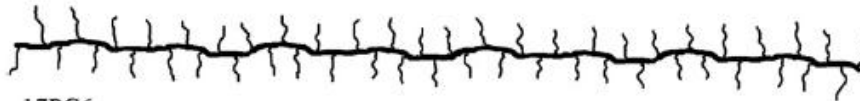


Compressed adsorption layers in cement
by the action of PC generation elastic
repulsive energy



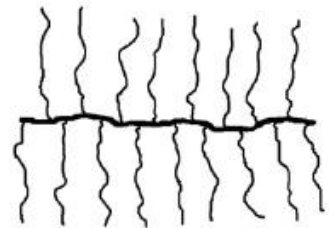
8.5PC6
MCL: 44.4 nm; SCL: 2.37 nm

worm type with 8.5 EO

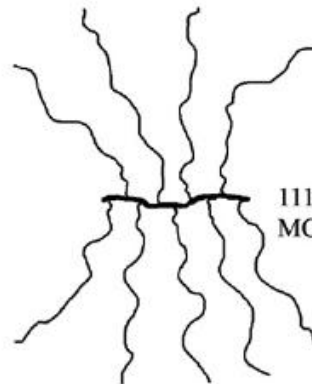


17PC6
MCL: 87.0 nm; SCL: 4.74 nm

worm type with 17 EO



45PC6
MCL: 29.4 nm; SCL: 12.5 nm



111PC6
MCL: 16.3 nm; SCL: 30.9 nm

star type with 111 EO

brush type with 45 EO



Preparation of PC

It involves two steps

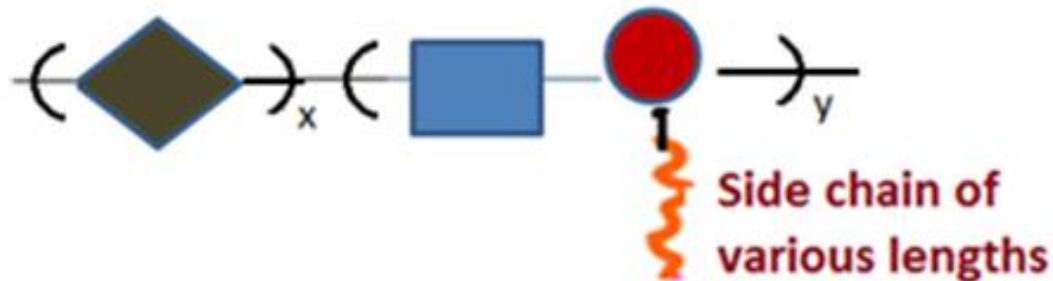
1. Preparation of macromonomer

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 diaphragm walls of 75MPa for Metro Rail tunnels



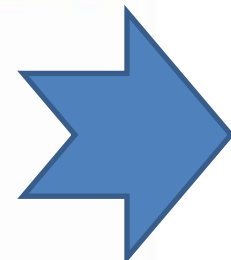
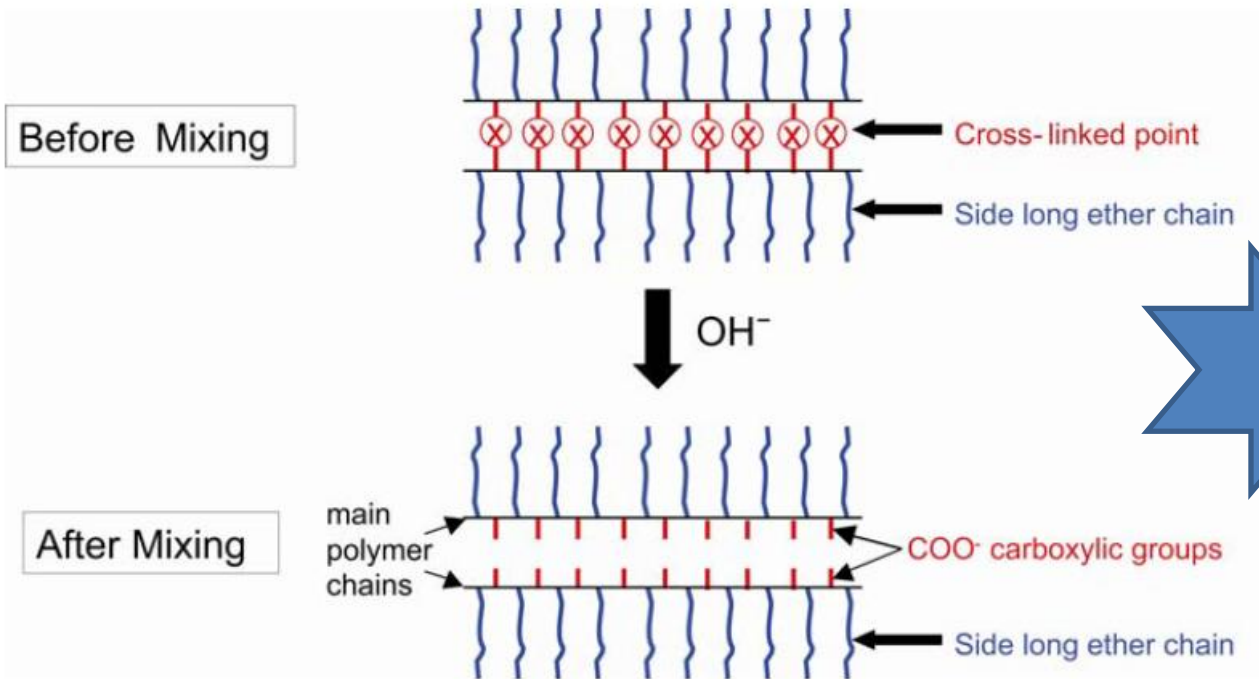
Advantages of PC

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

Different types of PC

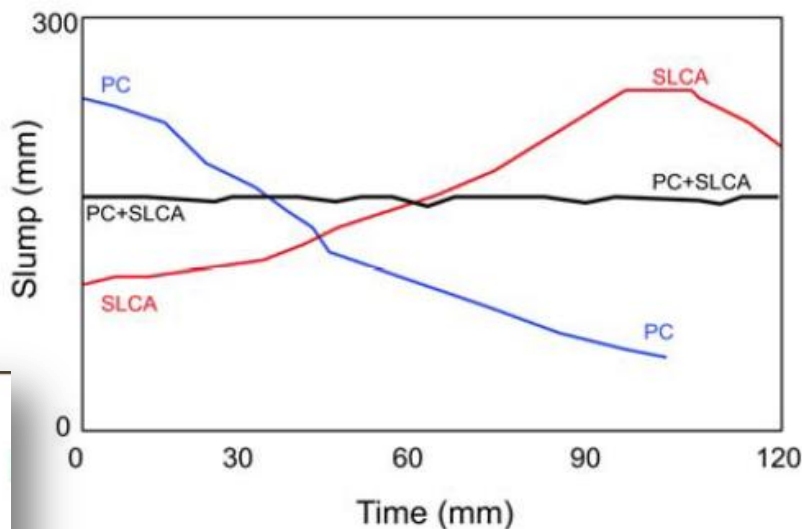
- Slump retention
- For highly early strength
- To reduce Shrinkage
- Sulphate ion interference free
- Less tacky for better pumping
- For self consolidating –SCC





One way to design PC for long slump retention

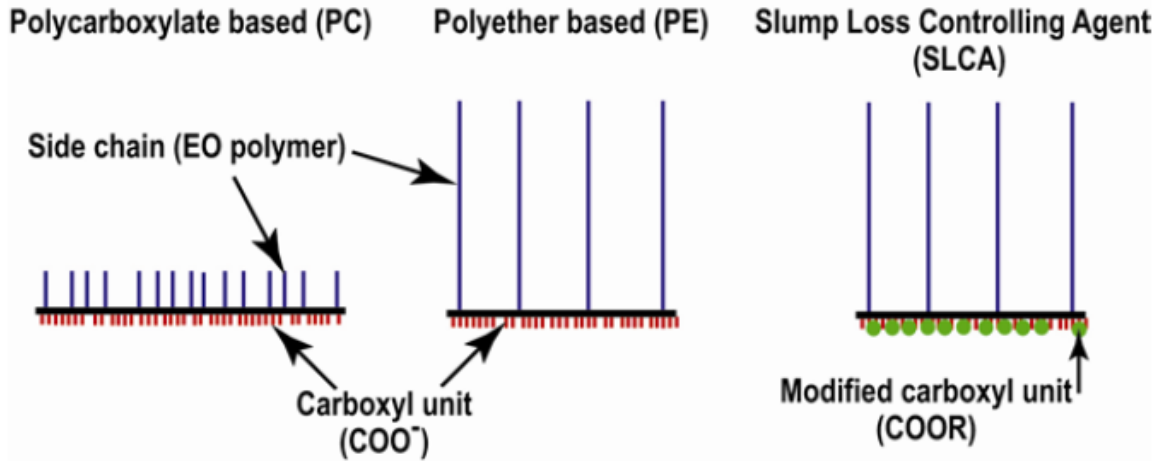
Hydrolysis of Crosslinked points by alkaline water during setting of cement releases carboxylate ion and it increases progressively resulting low slump loss



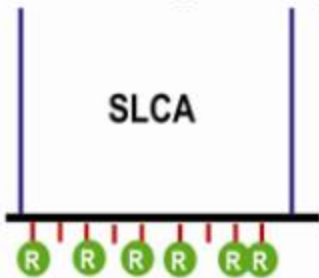
Schematic trend in slump loss behavior with Different acrylic superplasticizer



The second method involves blending of PC /PE with slump loss controlling agents (SLCA)



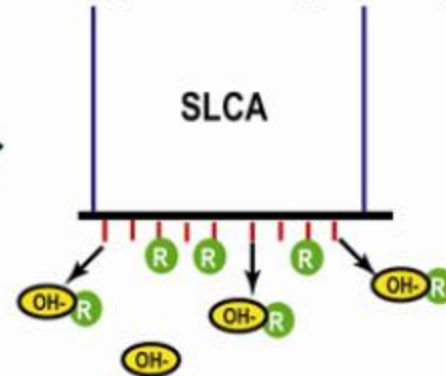
no adsorption initially
no initial dispersability



Hydrolysis in
alkaline condition



adsorption onto cement and
development of dispersability



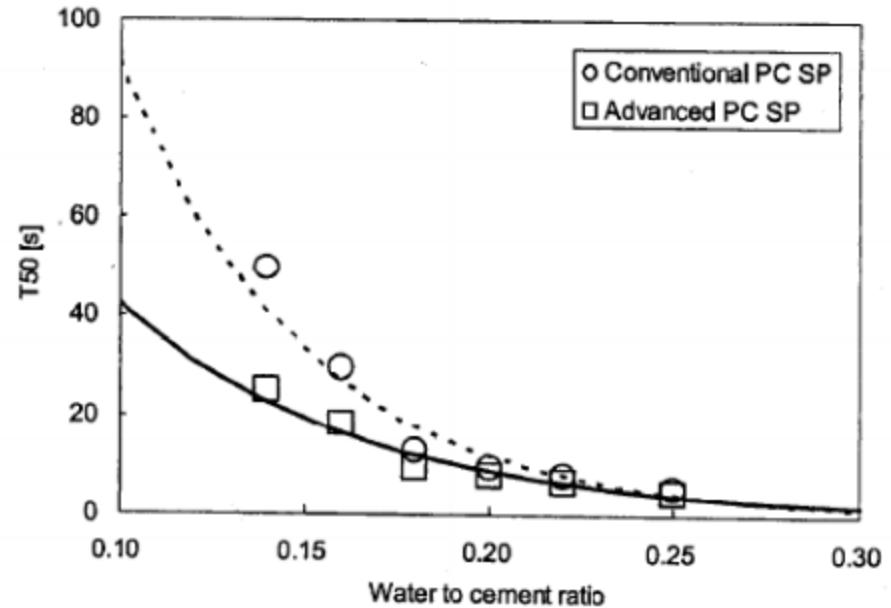
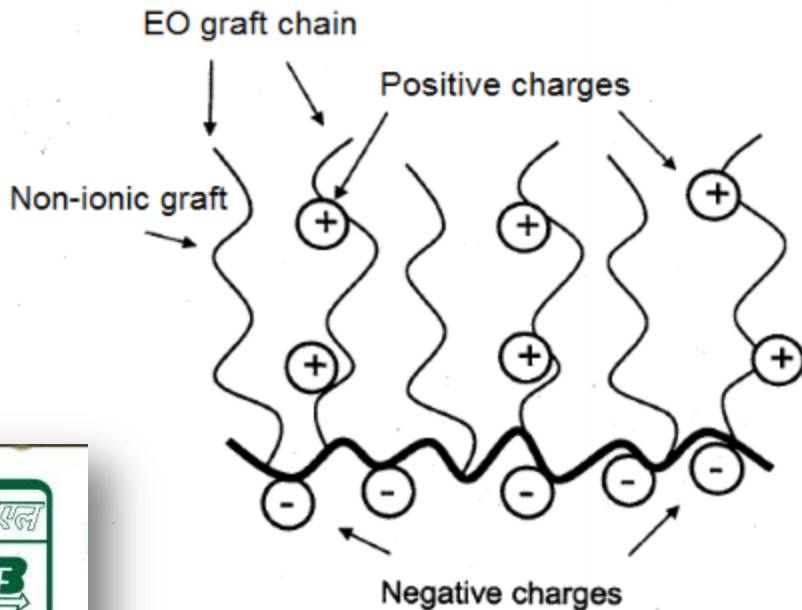
Hydrolysis of SLCA occurs in alkaline condition



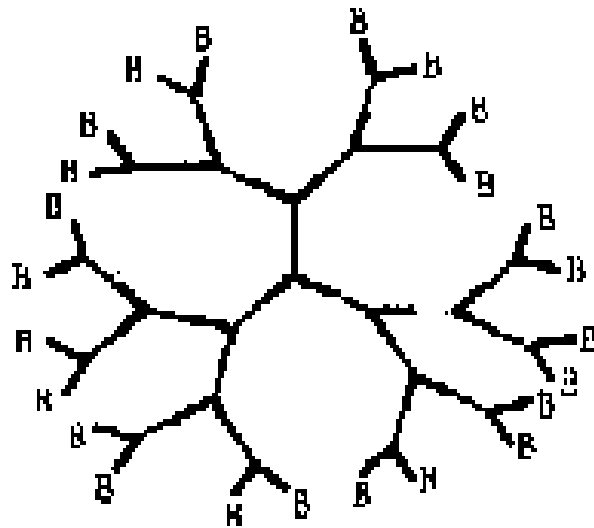
Branched PC – less tacky

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

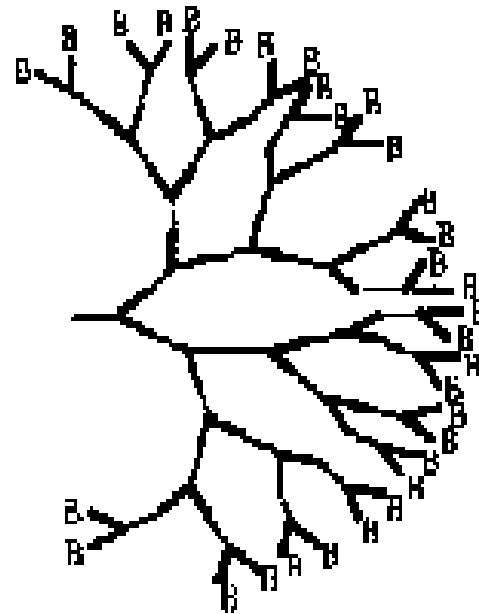
Low viscous concrete- better pumping



Structural representation of Hyperbranched polymers



dendrimers

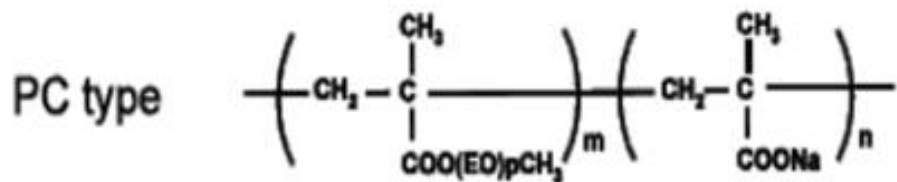


Hyperbranched polymer

Hyper branched 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.

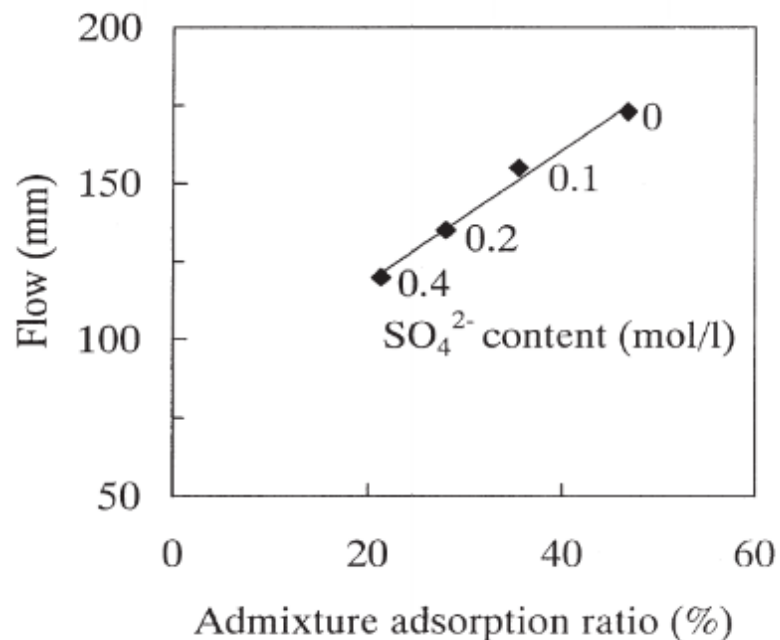
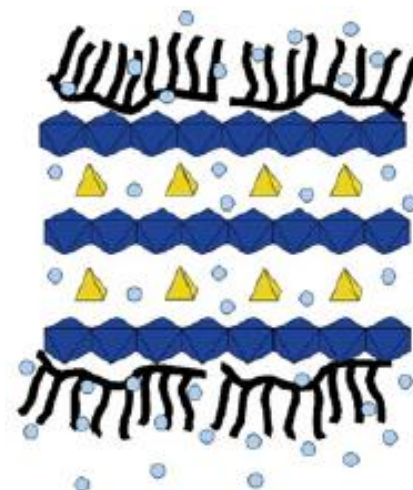
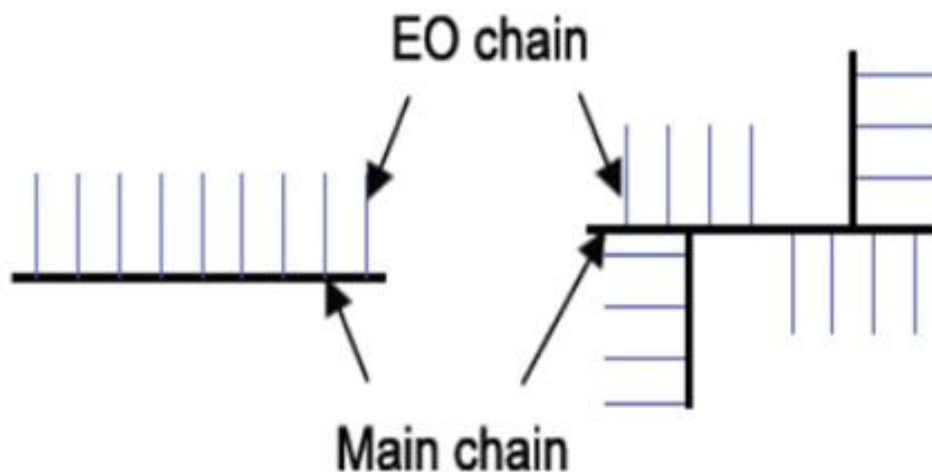


Hyperbranched PC – less sulphate interference



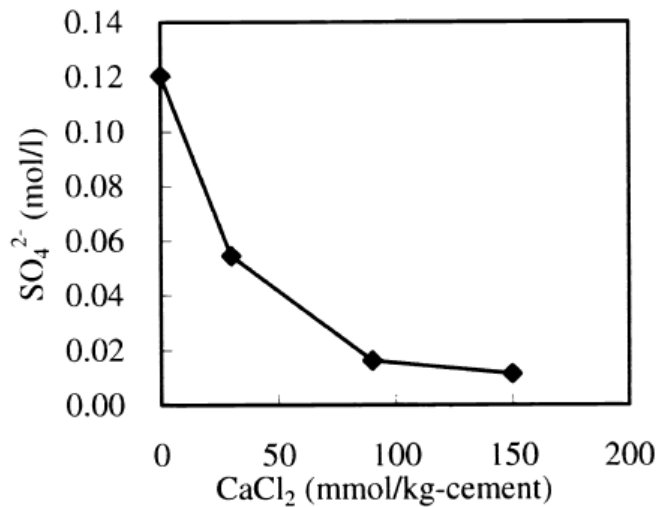
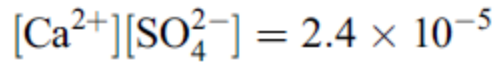
PC type

NHBP type

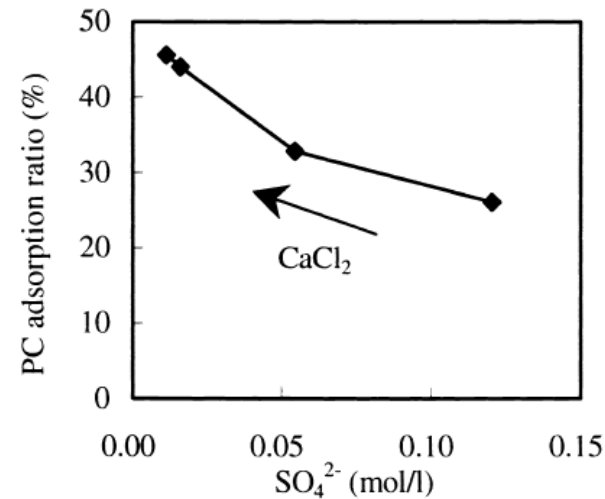


Controlling sulphate ion concentration and PC adsorption by Ca salts

- 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



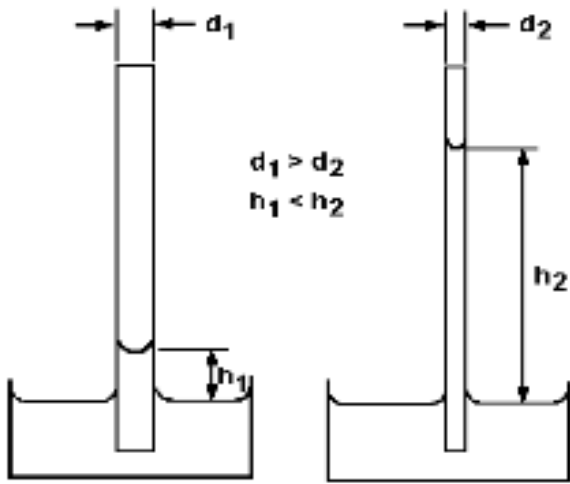
Increase in calcium reduces the soluble sulphate ion



PC adsorption increases with calcium ion concentration



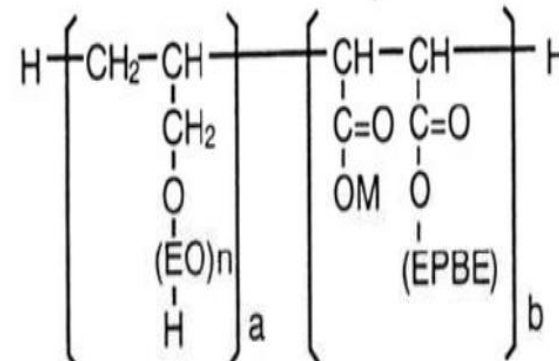
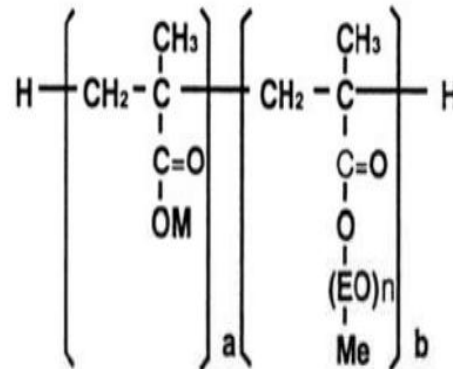
PC – for less shrinkage



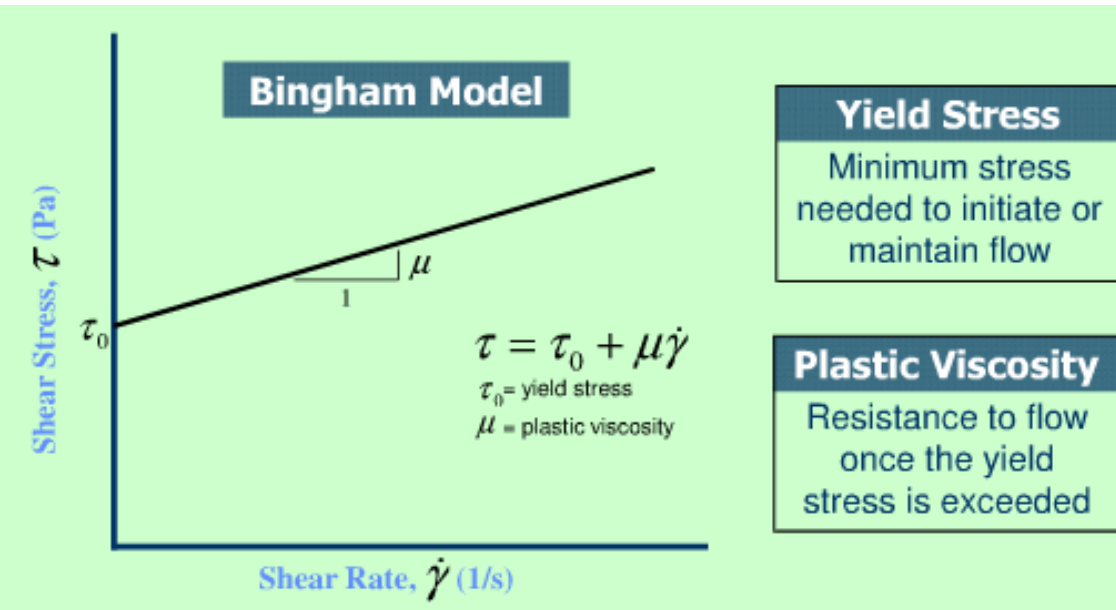
$$h = \frac{2\gamma \cos \theta}{\rho g r}$$



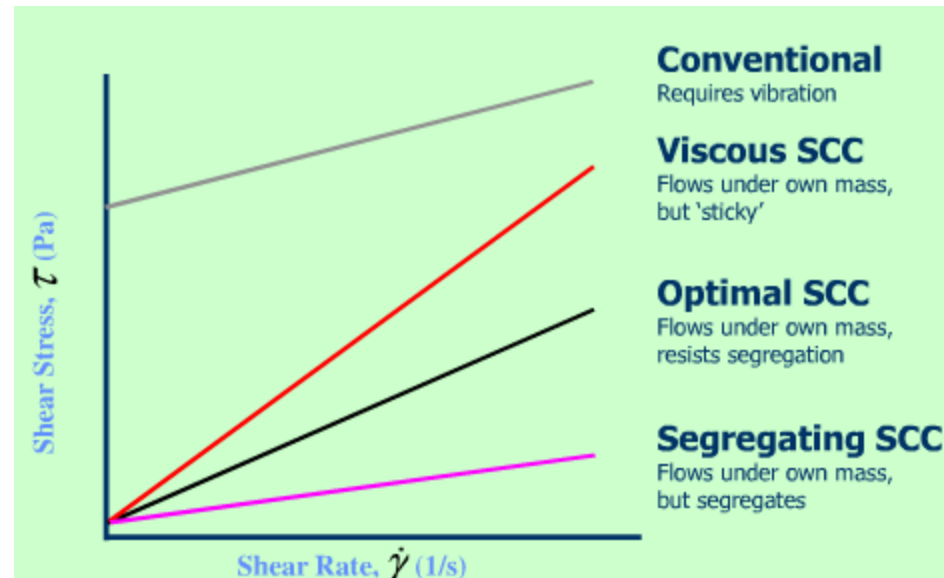
- The moisture gets evaporated through the small pores of concrete .
- The surface tension of water causes a loss in volume as it pulls the pores together



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



- UNF5 ----- Used for M20-M30 designs in batching plants with a water reduction of 12-15%
- FDN ----- For M30-M40 designs in batching plant ; water reduction – 15%
- 200 R ----- For RMC's in M20-M30 design & water reduction of 12 % with a slump retention of 120 mm for 2 hrs
- 500 R ----- Suitable in M30-M40 designs ; water reduction- 15%with a slump retention of 120 mm for 2 hrs
- 500 CR ----- 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
- PCE ----- will be launched shortly with our in-house developed technology
- SPF ----- Under development and will be launched shortly

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

1. Cement and Concrete Composites 29, (2007) 251-262
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
4. Cement and Concrete Research 40 (2010) 45-57
5. Cement and Concrete Research 31 (2001) 1169-1176

