**CHEMICAL ADMIXTURES FOR CONCRETE**

**Definition: what are chemical admixtures?**

The definition of RILEM (International Union of Testing and Research Laboratories for Materials and Structures) is:

- Admixtures for concrete, mortar or paste are inorganic or organic materials.
- These are added to the normal components of a mix not normally exceeding 5% by mass of cement or cementitious materials.
- Admixtures interact with hydrating cement by physical, chemical or physico-chemical actions.
- They modify one or more properties of concrete, mortar or paste either in fresh or hardened state.
- Admixtures are usually very complex compounds chemically excepting a few.
- They are unlikely to be pure compounds but associated with some other minor chemical compounds or they may be mixed formulations.
- It is rather difficult for a civil engineer to understand them through their chemical nature.
- Their effect on cement concrete, mortar or paste can be assessed by (the usual) simple tests on cement, mortar and concrete.
- In most advanced countries, admixtures have become as essential ingredient of concrete as cement, aggregate and water themselves.

**Why admixtures? The need.**

- If we are pouring a low grade concrete, say M20, If we are not unduly concerned about its water content nor its water-cement ratio,
- If the cost of materials and labour are paid entirely by the owner (or some one else) at whatever rates we have quoted, then, Admixtures will make the concrete more expensive. But then our concrete will be an indifferent one,
- Its durability, water tightness and consistent strength will be suspect.
- If we have a problem later on, there is little we can do to rectify it.
- But, in many other situations we cannot get away with such concrete or such an attitude.
- We may have to observe strictly a low w/c ratio as per design requirement
- We may have to transport concrete over large distances or to great heights
- We may need high flowability either due to reinforcement congestion or narrowness of sections or the inability to use vibrators
• We then need chemical admixture.
• All major bridges in India require admixtures for their concrete.
• Cost of admixtures is often compensated by savings in labour costs, placing costs and/or cement costs.

Usual admixtures:
• For our country, the most common chemical admixtures are plasticizers and Super-plasticizers. These are also known as water reducers and high-range water reducers, respectively.
• Retarders are likely to be needed, especially for hot weather concreting, ready mixed concrete or for special continuous pours.

Other types of admixtures are:
• Accelerators
• Air-entraining agents
• Pumping aids
• Shot Crete/ Guniting aids
• Corrosion inhibitors, and some others.

How do they act?
• The chemical, physical or physico-chemical actions of admixtures in cement concrete are quite complex.
• In fact, cement itself is an extremely complex compound with major compounds such as calcium silicates, calcium aluminates, gypsum.
• Besides it contains many alkali and other calcium salts.
• The action of admixtures can, however, be simplified for the sake of Understanding, as:
  (i) adsorption
  (ii) De-flocculation or dispersion
  (iii) Chemical absorption or interaction

Often, all the three take place. We should know a little about these so that we can choose admixtures for our job more correctly.

PHYSICO-CHEMICAL ACTIONS OF ADMIXTURES
• The most important compounds of cement that react very early when water is added are:
  • Tricalcium silicate (C₃S), and
  • Tricalcium Aluminate (C₃A)
Gypsum moderates the otherwise flash setting tendency of C₃A

Adsorption
- The admixed chemicals adsorb, at a molecular level, on the compounds of cement or cement grains and on the products of hydration of the cement compounds, notably C₃A.
- Thus, they inhibit their normal rapid hydrating mechanism.
- Adsorption inhibits premature stiffening of the hydrating compounds.
- However, it is relatively a transient phenomenon

Chemical absorption and Interaction
Some of the admixed chemical can also combine chemically with the compounds of cement (notably C₃A) or with their hydrated products.
- This modifies the usual kinetics of reaction of the cement compounds
- This mechanism also inhibits very early stiffening (with in the first 4 or 5 minutes of water addition).
- Though chemical absorption and interaction is relative more stable than adsorption they do not vitiate setting and long-term hydration.

De-flocculation / Dispersion
- Cement grains being small and hygroscopic tend to stick to each other and flocculate.
- The flocculate trap considerable amounts of water
- Certain admixtures adsorb on individual grains, create a sort of repulsive forces and cause deflocculation and cement grains are dispersed.
- Trapped water is released and becomes available for workability and flowability.
- More sites become available for hydration

More Facts
- All chemicals do not do the same in their actions. Cement composition, especially its compound composition, influences a lot on the physico-chemical actions of admixtures
- We should not blindly follow the experiences of a neighbouring contractor as his cement may differ from ours. We should not take that every brand of admixture will be suitable for our job and our cement.
- We should be ready to test the admixture with our cement and in our site before use.
We should remember that cement itself is a highly variable material as there are significant differences from factory to factory and even from batch to batch from the same factory.

Despite standardization, same variations are inevitable caused both by raw material differences and process control variables.

**Plasticizers/ water reducers**

- Of all the admixtures, these are the most commonly used. They are used basically in two ways.
- One, as a plasticizer, to increase flowability of concrete. Flowability or high workability helps in rapid placement, easy compaction, complete filling of deep and narrow formwork, avoidance of honeycombing in congested and/or difficult sections.
- Two, as a water-reducer, to decrease the water content (or water-demand) of a mix without changing its workability.
- If the W/C Ratio is not also changed, reduced water content would mean reduced cement content thus saving on cement costs.
- The saving is likely to be more than the cost of plasticizer addition. If cement content is not changed, then W/C ratio will decrease. Strength will increase. For the same cement content higher grade of concrete can be produced.
- Plasticizer can be used partly for plasticizing and partly for water-reducing in a manner of our choice.

**Chemicals of water reducers**

- Usually salts of lignosulphonic acid or hydroxylated carboxylic acids (e.g. citric acid)
- Plasticizing action is related to their adsorption and dispersing effects.

**Lignosulphonates**

- They retard the initial rapid hydration of C₃S and C₃A. Of these two, C₃A adsorbs relatively larger amounts of admixture.

**Hydroxylated Carboxylic Acids**

- They adsorb relatively more on the already hydrated products of the cement compounds than on the cement grains themselves.
- This causes the inter-layer water between the silicate hydrates and that between aluminate hydrates to be more mobile. Many water reducers are also
retarders to a certain extent. But they are unlikely to delay the setting times beyond the permitted limits

- Some water reducers can accelerate setting. Care is needed with such chemicals in hot weather

SUPER PLASTICIZERS / HIGH RANGE WATER REDUCERS

- They are also used either as plasticizers or as water reducers.
- They are used in larger doses than plasticizers and are effective in reducing water demand more than 12% and even up to 35 percent. If water reduction is not the criterion super plasticizers help in achieving a flowing concrete i.e. a concrete of very high slump.
- Alternately, a very high strength concrete can be obtained by reducing the W/C ratio drastically, even as low as 0.30.
- In a way they are ‘wonder’ admixtures that have revolutionized concrete technology.
- They have facilitated the use of large volume of fly ash and similar fine pozzolans and yet obtain high performance concrete.

CHEMICALS FOR SUPERPLASTICIZERS

These are, usually:

(i) Sulphonated melamine formaldehyde (SMF)
(ii) Sulphonated naphthalene formaldehyde (SNF)
(iii) Modified lignosulphonates (MLS)
(iv) Poly Carboxylated Ethers (PCE)

PHYSICO-CHEMICAL ACTIONS OF SUPER-PLASTICIZERS

- SMF (or SNF) is quickly adsorbed on C₃A and C₄AF phases of cement as soon as they are added to a wet concrete mix
- In case of lignosulphonates, not only they get adsorbed on the C₃A and C₄AF phases but they also get linked to the hydrated products of C₃A by absorption and interaction.
- This adsorption is the main cause for de-flocculation and dispersion of cement and increased flowability. Some cements are better off than others in this regard.
- Sulphate Resisting Portland Cement (Type V ASTM) is better than Ordinary Portland Cement (Type I ASTM) which in turn is better than Rapid hardening Portland cement (Type II ASTM).
• The dependence seems to be on the ratio of $C_3A / SO_3$. Choice of superplasticizer and its dosage thus depend upon the potential compound composition of cement and the quantity of gypsum added.

• Carboxylated Ether (CE) has a co-polymer which acts after the alkalinity of cement paste builds up and thus keeps the dispersion of cement grains effective longer. The workability is also retained longer.

Mix modifications with plasticising admixtures

SLUMP LOSS

• It is a common experience that slump of concrete decreases with an increase in delay of placement. This decrease is normally gradual.

• The decrease in slump compared with that obtained immediately after mixing is called slump loss.

• When plasticizers or superplasticizers are added the slump loss-time behaviour can change drastically.

Slump loss can be very significant after about 30 minutes of mixing.
METHODS TO OVERCOME SLUMP LOSS

- Slump loss is a severe problem with Ready mixed concrete
- It is also a problem when placement is done at great heights or at large distances from the mixer.
- Slump loss is obviated by some of the following measures though they may not be fully satisfactory.
- Adding a retarder in addition to superplasticizer done with SMF or SNF. Adding a part of superplasticizer later at the site before discharging or just before arrival at site – control will be with truck operator- accurate control of dosage may become difficult. Dosage tends to be more in two-part addition.

CAN CHEMICAL ADMIXTURES BE TRusted?

- An usual question. Especially when the marketing pressures are high. The answer is yes, but.
- The ‘but’ arises from a need of the user to ensure compatibility of a commercial product with the cement he has at hand. This is done not only by going through chemical manufacturer’s technical information but also testing.
- Testing is done on cement, mortar and concrete with and without chemical admixture. IS 9103 prescribes physical requirements.
- The bigger the job the more elaborate can be the tests, including chemical tests on the cement itself.

Release of Trapped Water from Cement Flocs by the action of superplasticizer
Flocculated cement particles (left) in the absence of superplasticizer & Deflocculated (right) in the presence of superplasticizer

Illustration of Physical Dispersion Effect

Reference:
4. Current Literature...