

Chapter 5: Admixtures for Concrete

5.1 Definition

Admixtures are those ingredients in concrete other than Portland cement, water, and aggregates that are added to the mixture immediately before or during mixing.



Concrete should be workable, finish-able, strong, durable, watertight, and wear resistant. These qualities can often be obtained easily and economically by the selection of suitable materials rather than by resorting to admixtures (except air-entraining admixtures when needed).

Admixtures are not a solution for poor mix design nor sloppy concrete practice. They are aimed at providing a more economical solution and enhanced concrete properties.

The major reasons for using admixtures are:

1. To reduce the cost of concrete construction.
2. To achieve certain properties in concrete more effectively than by other means.
3. To maintain the quality of concrete during the stages of mixing, transporting, placing, and curing in adverse weather conditions.
4. To overcome certain emergencies during concreting operations.

The effectiveness of an admixture depends upon several factors such as **type, brand, amount of cementing materials; water content; aggregate shape, gradation, and proportions; mixing time; slump; and temperature of the concrete.**

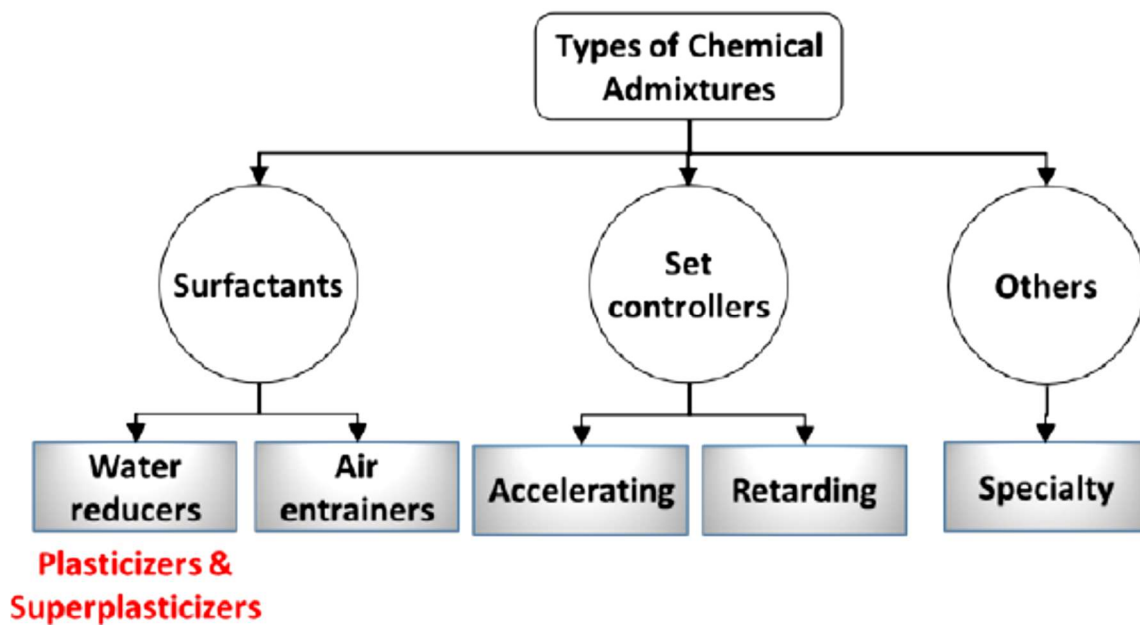
There are two general groupings of admixtures' namely:

- ❖ Chemical admixtures.
- ❖ Mineral admixtures.

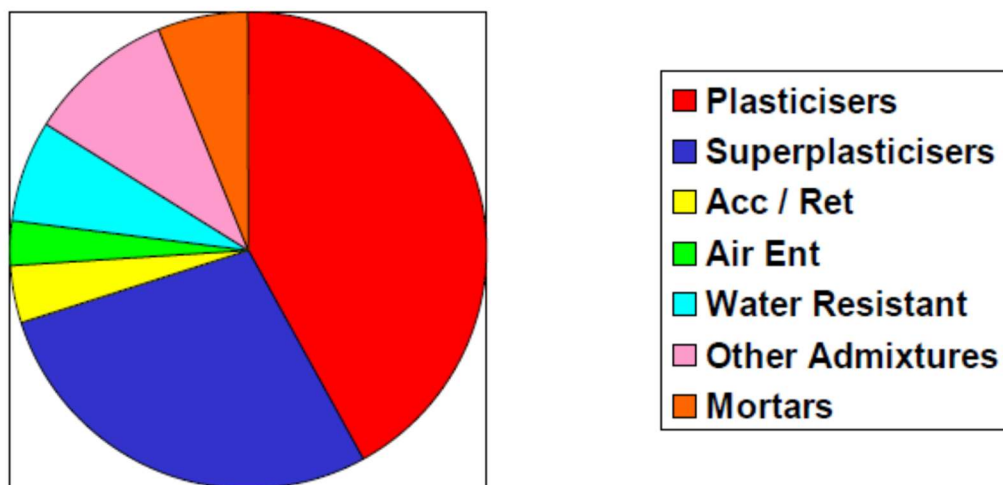
First: Chemical Admixtures

5.2 Definition

They are water soluble compounds added primarily to control setting and early hardening of fresh concrete or to reduce the water requirements. Chemical admixture classification is as follows:



Admixture sales by type for 2006



Therefore, the chemical admixtures include:

1. Air entraining admixtures.
2. Water reducing admixtures.
3. Retarding admixtures.
4. Accelerating admixtures.
5. Specialty admixtures.

Hydration-control admixtures, corrosion inhibitors, shrinkage reducers, alkali-silica reactivity inhibitors, coloring admixtures, miscellaneous admixtures such as workability, bonding, damp-proofing, permeability reducing, grouting, gas-forming, anti-washout, foaming, and pumping admixtures.

Type of admixture	Desired effect	Material
Accelerators (ASTM C 494 and AASHTO M 194, Type C)	Accelerate setting and early-strength development	Calcium chloride (ASTM D 98 and AASHTO M 144) Triethanolamine, sodium thiocyanate, calcium formate, calcium nitrite, calcium nitrate
Air detrainers	Decrease air content	Tributyl phosphate, dibutyl phthalate, octyl alcohol, water-insoluble esters of carbonic and boric acid, silicones
Air-entraining admixtures (ASTM C 260 and AASHTO M 154)	Improve durability in freeze-thaw, deicer, sulfate, and alkali-reactive environments Improve workability	Salts of wood resins (Vinsol resin), some synthetic detergents, salts of sulfonated lignin, salts of petroleum acids, salts of proteinaceous material, fatty and resinous acids and their salts, alkylbenzene sulfonates, salts of sulfonated hydrocarbons
Alkali-aggregate reactivity inhibitors	Reduce alkali-aggregate reactivity expansion	Barium salts, lithium nitrate, lithium carbonate, lithium hydroxide
Antiwashout admixtures	Cohesive concrete for underwater placements	Cellulose, acrylic polymer
Bonding admixtures	Increase bond strength	Polyvinyl chloride, polyvinyl acetate, acrylics, butadiene-styrene copolymers
Coloring admixtures (ASTM C 979)	Colored concrete	Modified carbon black, iron oxide, phthalocyanine, umber, chromium oxide, titanium oxide, cobalt blue
Corrosion inhibitors	Reduce steel corrosion activity in a chloride-laden environment	Calcium nitrite, sodium nitrite, sodium benzoate, certain phosphates or fluosilicates, fluoaluminates, ester amines
Dampproofing admixtures	Retard moisture penetration into dry concrete	Soaps of calcium or ammonium stearate or oleate Butyl stearate Petroleum products
Foaming agents	Produce lightweight, foamed concrete with low density	Cationic and anionic surfactants Hydrolized protein
Fungicides, germicides, and insecticides	Inhibit or control bacterial and fungal growth	Polyhalogenated phenols Dieldrin emulsions Copper compounds
Gas formers	Cause expansion before setting	Aluminum powder

Grouting admixtures	Adjust grout properties for specific applications	See Air-entraining admixtures, Accelerators, Retarders, and Water reducers
Hydration control admixtures	Suspend and reactivate cement hydration with stabilizer and activator	Carboxylic acids Phosphorus-containing organic acid salts
Permeability reducers	Decrease permeability	Latex Calcium stearate
Pumping aids	Improve pumpability	Organic and synthetic polymers Organic flocculents Organic emulsions of paraffin, coal tar, asphalt, acrylics Bentonite and pyrogenic silicas Hydrated lime (ASTM C 141)
Retarders (ASTM C 494 and AASHTO M 194, Type B)	Retard setting time	Lignin Borax Sugars Tartaric acid and salts
Shrinkage reducers	Reduce drying shrinkage	Polyoxyalkylene alkyl ether Propylene glycol
Superplasticizers* (ASTM C 1017, Type 1)	Increase flowability of concrete Reduce water-cement ratio	Sulfonated melamine formaldehyde condensates Sulfonated naphthalene formaldehyde condensates Lignosulfonates Polycarboxylates

Superplasticizer* and retarder (ASTM C 1017, Type 2)	Increase flowability with retarded set Reduce water-cement ratio	See superplasticizers and also water reducers
Water reducer (ASTM C 494 and AASHTO M 194, Type A)	Reduce water content at least 5%	Lignosulfonates Hydroxylated carboxylic acids Carbohydrates (Also tend to retard set so accelerator is often added)
Water reducer and accelerator (ASTM C 494 and AASHTO M 194, Type E)	Reduce water content (minimum 5%) and accelerate set	See water reducer, Type A (accelerator is added)
Water reducer and retarder (ASTM C 494 and AASHTO M 194, Type D)	Reduce water content (minimum 5%) and retard set	See water reducer, Type A (retarder is added)
Water reducer—high range (ASTM C 494 and AASHTO M 194, Type F)	Reduce water content (minimum 12%)	See superplasticizers
Water reducer—high range—and retarder (ASTM C 494 and AASHTO M 194, Type G)	Reduce water content (minimum 12%) and retard set	See superplasticizers and also water reducers
Water reducer—mid range	Reduce water content (between 6 and 12%) without retarding	Lignosulfonates Polycarboxylates

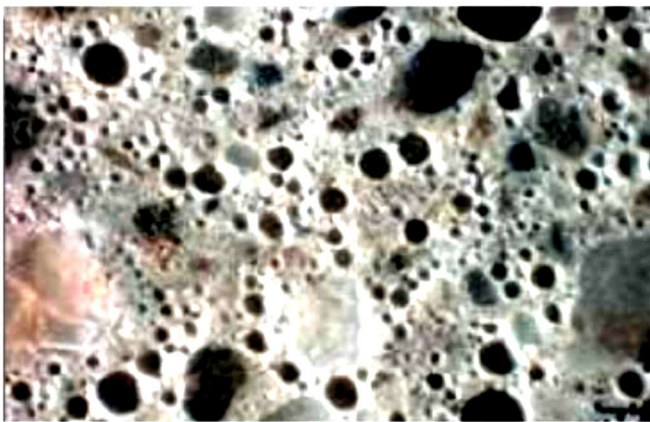
5.3 Air-Entraining Admixtures.

Air-entraining admixtures are used to purposely introduce and stabilize microscopic air bubbles in concrete (air bubbles predominately between 0.25—1 mm diameter). Air entrainment will dramatically improve the durability of concrete exposed to cycles of freezing and thawing. Furthermore, the workability of fresh concrete is improved significantly, and segregation and bleeding are reduced or eliminated.

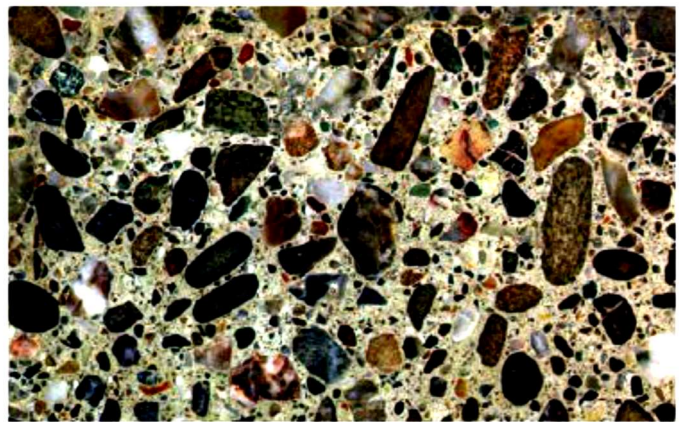
5.3.1 The Air-Void System

As un-reacted water freezes it expands 9 % by volume on phase change. This internal volume expansion causes internal stresses in the matrix. It can generate cracks in the concrete, which may allow water to infiltrate and the process can get progressively worse. It can lead to significant degradation of the concrete.

Further, the formation of ice in the pore spaces generates pressure on any remaining unfrozen water. Introducing a large quantity of air bubbles provides a place for this water to move in to relieving the internal pressure.



Air-Entrained concrete



Non Air-Entrained concrete

The **air void parameters** that need to be determined for the concrete are:

- 1- **Total Entrained Air**;
- 2- **Spacing Factor** distance between voids (not more than 200 micron =0.2mm).

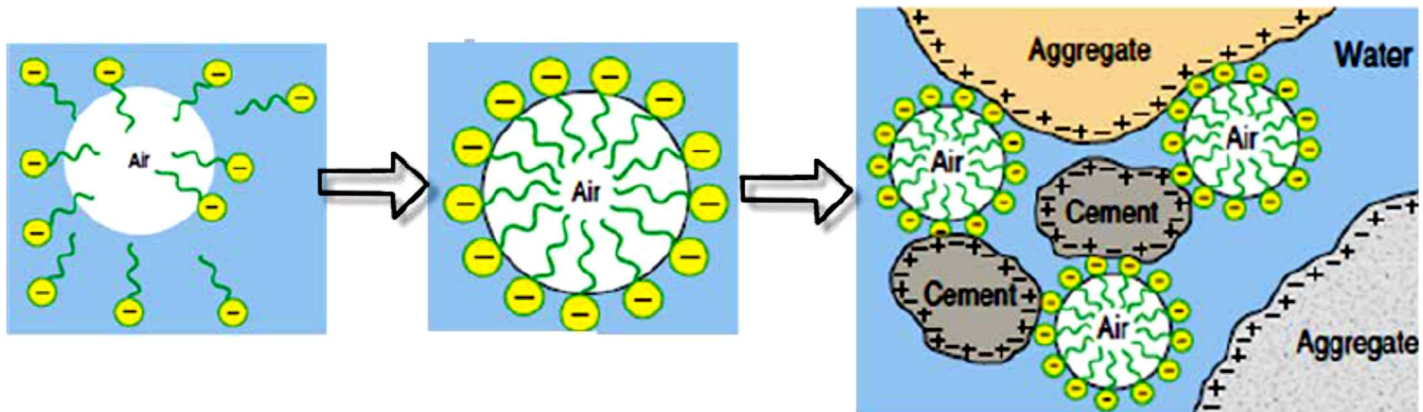
Entrapped air is different from **entrained air**. Entrapped air consists of irregular voids that are produced through the compaction process. Some amount of entrapped air is always present in concrete, and the mix design codes generally stipulate the assumption of the amount of entrapped air based on the coarse aggregate size in concrete. In general, about 1 – 2% of entrapped air is

present inside concrete. Entrained air, on the other hand, is generated using the admixture, and consists of small and spherical voids.

Air-entrained concrete contains stable tiny air bubbles that are distributed uniformly throughout the cement paste. Entrained air can be produced in concrete by use of an air-entraining cement, introduction of an air entraining admixture, or by a combination of both methods.

5.3.2 Air Entraining Materials

What is needed is an agent that causes the water to foam into a very small matrix of very small bubbles. The admixtures are of the same family as household detergents, but these do not generate small enough bubbles and are not stable enough. Air entraining agents contain surface-active agents or surfactants. These lower the water surface tension so bubbles can form, and stabilize the bubbles once they are formed.



5.3.3 Effect of Air on Other Concrete Properties

Air entrainment will affect directly the following three properties of concrete:

1. – Increased resistance to freezing and thawing.
2. – Improvement in workability and cohesiveness of fresh concrete.
3. – Reduction in strength.

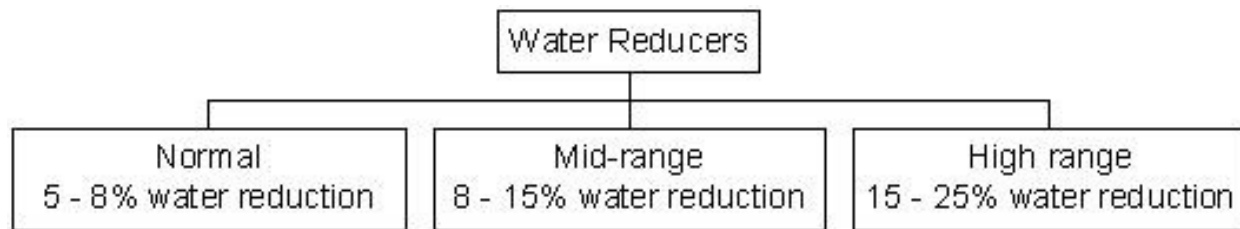
Incidentally, air entrainment will affect the properties in following ways:

1. – Reduces the tendencies of segregation and bleeding.
2. In addition, the **lower w/c ratio** that can be used the **better compaction** characteristics results, which give **more impermeable concrete** and a **better overall resistance to aggressive agents** (i.e. sulfates).

5.4 Water-Reducing Admixtures

Water-reducing admixtures are used to (1) reduce the quantity of mixing water required to produce concrete of a certain slump, (2) reduce water-cement ratio, (3) reduce cement content, (4) improve durability, (5) improve water tightness, or (6) increase slump.

Various types of Water Reducers can reduce the water content by approximately 5% to 25%. Adding a water-reducing admixture to concrete without reducing the water content can produce a mixture with a higher slump. The **rate of slump loss**, however, is not reduced and in most cases is increased. Rapid slump loss results in reduced workability and less time to place concrete.



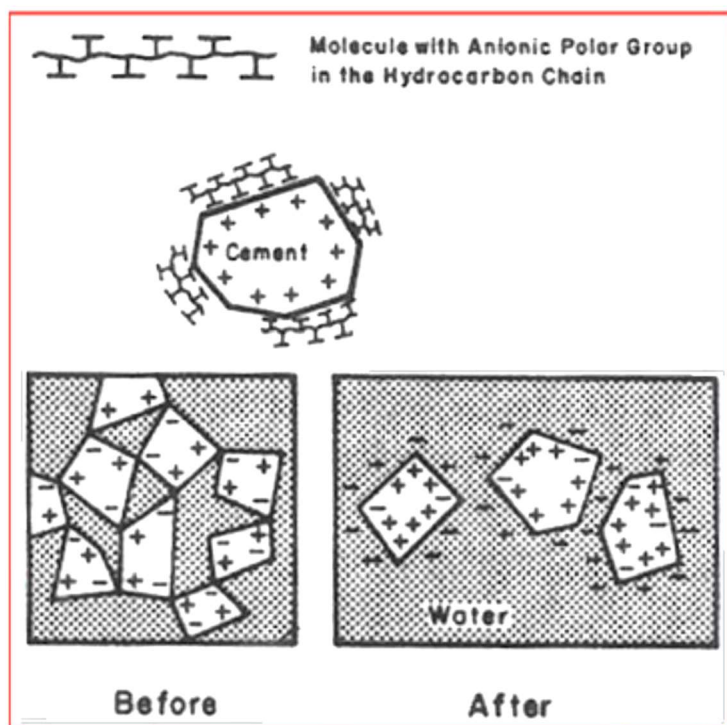
An increase in strength is generally obtained with water-reducing admixtures as the water-cement ratio is reduced.

It can be said that Water Reducers can be used in three ways:

1. For a given workability, they can reduce the water demand, thus resulting in higher strength and durability.
2. For a given w/c and strength, they can increase the workability.
3. For a given w/c, strength and workability, the quantity of cement can be reduced.

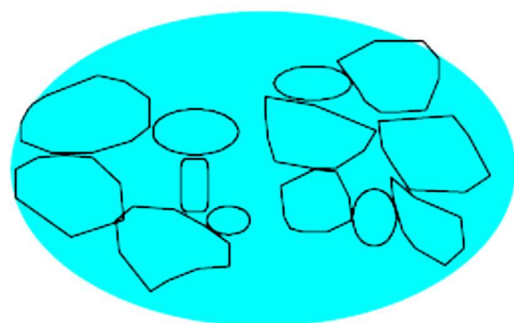
Water reducers belong to a group of chemicals known as '**dispersants**'. The action of the dispersant is to prevent the **flocculation** of fine particles of cement. These dispersants are basically **surface-active chemicals**.

In the mix, the cement grains absorb the plasticizers molecules which results in changing the surface charge of the same sign. This causes repulsive forces and makes the dispersion which increases plasticity and workability. The plasticizers are available in market in various brands with specifications for composition, dosages etc. With the progress of hydration, the electrostatic charge diminishes and flocculation of the hydrating product occurs.

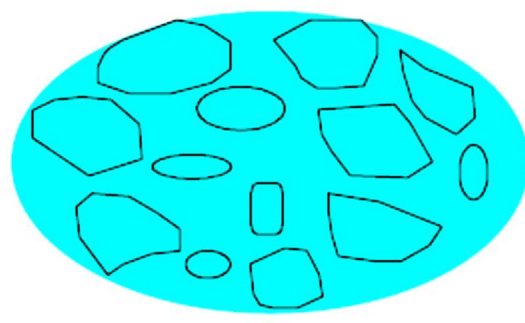


cement flocs
reduce fluidity

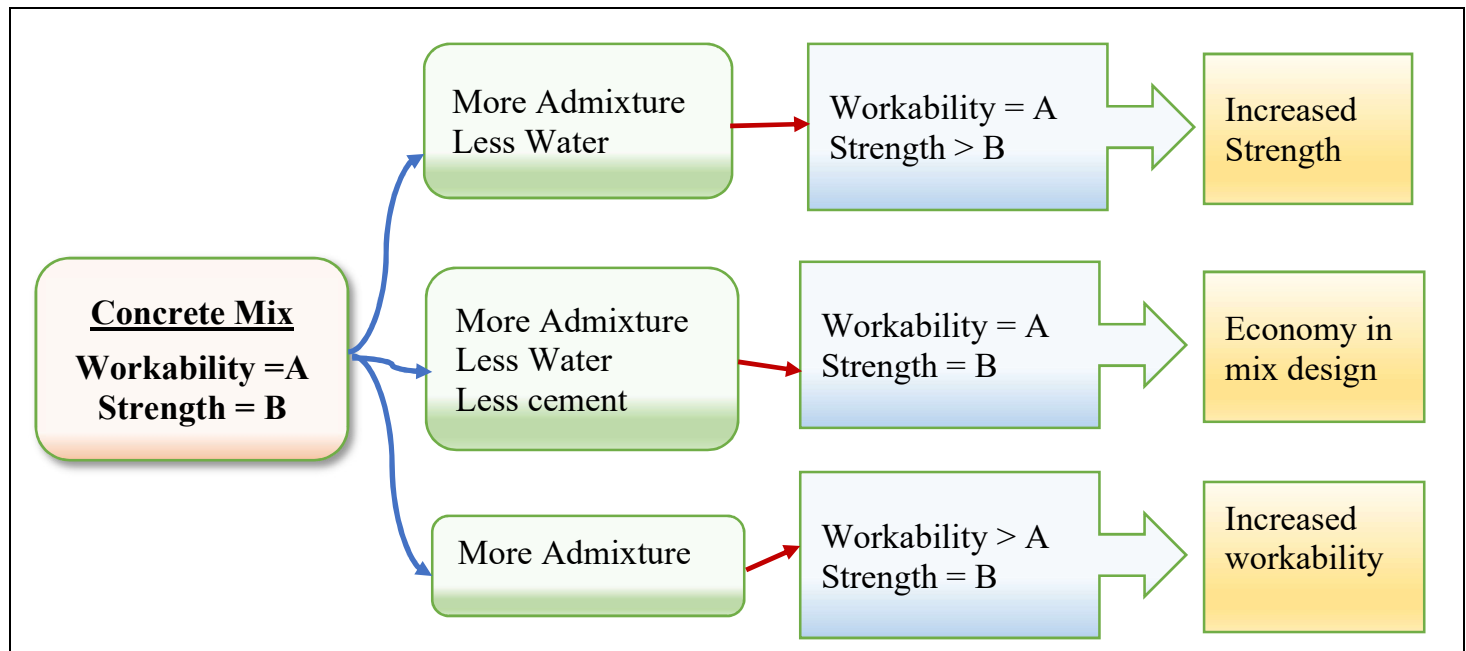
cement is uniformly dispersed
increasing fluidity



add a plasticising
admixture



This effect of water-reducing admixtures on concrete mixtures can be utilized in three ways as shown in Figure below:



Function of the water reducing admixtures.

High-Range Water-Reducing (Super-plasticizers) - HRWR

Super-plasticizers, also called **High Range Water-Reducing Admixtures** (HRWR) because of their ability to reduce three to four times the mixing water in a given concrete mixture compared to normal water-reducing admixtures, were developed in the 1970s and have found wide acceptance in the concrete construction industry.

Super-plasticizer materials

There are four types of super plasticizers that are generally used for concrete as given below:

1. Sulphonated melamine formaldehyde condensates – It is suitable in low temperature areas, dosage: 0.5 - 3% by weight of cement.
2. Sulphonated naphthalene formaldehyde condensates – It is more suitable in high temperature areas, dosage: 0.5 - 3% by weight of cement.
3. Modified Ligno sulphates – It is suitable for Indian conditions where temperature variation is high, dosage not more than 0.25% by weight of cement.
4. Carboxylated admixture – It is suitable where workability is required to be retained for large duration.

The superplasticizer is adsorbed onto the cement particles, thereby lowering inter-particle attraction and producing a more uniform dispersion of cement grains as with a normal water—reducer. Basically, the dispersion mechanism of concrete based Superplasticizers is mainly due to Steric hindrance effect.

The advantages of Super-plasticizers are:

- Significant water reduction.
- Reduced cement contents.
- Reduce water requirement by 12-30%.
- Increased workability of concrete.
- Reduced effort required for placement.
- More rapid rate of early strength development.
- Increased long-term strength.
- Reduced permeability of concrete.

The disadvantages of Super-plasticizers are:

- Additional admixture cost (the concrete in-place cost may be reduced)
- Slump loss greater than conventional concrete
- Less responsive with some cement

5.5 Set controlling admixtures.

Set-controlling admixtures are used in concrete being placed and finished in other than optimum temperatures. Set-controlling admixtures **alter the rate of the cement's hydration** and, therefore, the rate of setting (hardening) of the paste. Set-controlling admixtures include **accelerating** and **retarding** admixtures.

5.5.1 Accelerating admixtures

Accelerating admixtures are water **soluble chemicals** which increase the rate of reaction between cement and water and thereby accelerate the setting and early strength development of concrete.

Accelerators materials

Most accelerators are based on one of the following chemicals:

- Soluble inorganic salts (CaCl, carbonates, aluminates, fluorides, and ferric salts).
- Soluble organic compounds (triethanolamine, calcium formate, calcium acetate).

Calcium chloride is the most popular choice due to low cost and high rate of acceleration for a given dosage.

The **purposes of using accelerators** and the advantages resulting from the use of accelerators are many, among them are:

- Allow an earlier finishing of the concrete surfaces,
- Earlier removal of forms
- Reduction of the required period of curing and protection
- Earlier placement in service of a structure or a repair.
- Partial or complete compensation for the effects of low temperatures on strength development.
- Reduced bleeding and segregation and increase density of concrete,

Precautions of using accelerators

- High dosage rates or, occasionally, normal dosage rates with high cement content mixes may cause rapid stiffening and considerable heat evolution with consequent risk of thermal and shrinkage cracking. Calcium chloride in particular should be used with care in hot weather.
- Calcium chloride or admixtures containing calcium chloride are restricted in structural concrete which contains embedded metal.

5.5.2 Retarding admixtures.

Retarding admixtures are used where setting time of concrete need to be delayed. Retarder delays the hydration process but doesn't affect the eventual process. Initial setting time can be delayed by more than 3 hours. The main application of retarding admixtures is in controlling the setting time of concrete.

The retarders slow the rate of early hydration of C3S by extending the length of the dormant period. They also tend to retard the hydration of C3A phases.

The main purposes of retarders are:

- To offset the accelerating effect of high ambient temperature (hot weather) and thereby lowering the maximum temperature to a level where thermal cracks give less problems.
- To keep the concrete workable throughout the entire transport, placing and finishing periods. Particularly important when transporting concrete over large distances.
- To prevent setting of the concrete in the truck in case of delay.

5.6 Retarder Materials

1. salts and derivatives of lignosulfonates.
2. salts and derivatives of hydroxycarboxylic acids.
3. sugars and their derivatives (a bag of sugar mixed in a truck of concrete can stop the set in case of emergency).
4. inorganic salts.

Note: 1&2 are also water reducers.

5.7 General Precautions in use of admixtures:

Admixtures are required to conform to relevant specifications (such as ASTM, BS, EN), where applicable. **Technical data** should include:

- a. Main effect of admixture.
- b. Any additional influences admixture may have.
- c. Physical properties of the material.
- d. Concentration of active ingredient.
- e. Presence of any potentially detrimental substances such as chlorides, sulphates etc.
- f. Potential occupational hazards for users.
- g. Conditions for storage and shelf life.
- h. Instructions for preparation of admixture and procedures for introducing it into the concrete mix.
- i. recommended dosage under identified conditions, max permissible dosage, and effects of over-dosage.

Second: Mineral Admixtures

5.8 Mineral Admixtures

Mineral admixtures (Also called ‘Supplementary Cementing Materials’) are **inorganic materials** that also have **pozzolanic properties**. Mineral admixtures are very fine-grained materials which added to the concrete mix to **improve** the properties of concrete and make it more economical, or as a **replacement** for Portland cement (blended cements). The designation **pozzolana** is derived from one of the primary deposits of volcanic ash used by the Romans.

It should be said that most of the mineral admixtures have lesser specific gravity than the other constituents of concrete, therefore more volume is expected when one of these mineral admixtures replaces OPC by mass.

Mineral admixtures are added to concrete in different amounts in order to:

- Enhance the workability of fresh concrete;
- Improve resistance of concrete to thermal cracking,
- Resist alkali-aggregate expansion, and sulfate attack;
- Enable a reduction in cement content.”

The American Concrete Institute (ACI) defines pozzolans as “a siliceous or siliceous and aluminous material that in itself possesses little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically reacts with calcium hydroxide at ordinary temperatures to form compounds having cementitious properties.”

Commonly used mineral admixtures are:

1. Ground granulated blast furnace slag (GGBFS)
2. Type F fly ash (F-FA),
3. C-FA: Type C fly ash (C-FA),
4. SF: Silica fume (SF)
5. Metakaolin (MK)
6. Glass powder (GP)
7. Rice husk ash (RHA)

8. Can you find others. (Student activity)

Comparison of composition between OPC and Mineral admixtures:

Table compositions of cement and supplementary cementing materials

% By Mass	OPC	GGBFS	F-FA	C-FA	SF
Lime (CaO)	65	40	1	20	-
Silica (SiO ₂)	21	35	50	35	90
Alumina (Al ₂ O ₃)	5	8	25	20	2
Iron oxide (Fe ₂ O ₃)	2	3	10	5	2

5.8.1 Ground granulated blast furnace slag

Blast furnace slag is a by-product of the extraction of iron from iron ore. Coal and limestone are added inside the blast furnace. The impurities in iron ore combine with the lime and rise up to the surface of the blast furnace, while the molten iron, which is heavier, stays at the bottom.

The use of blast-furnace slag as a cementitious material is very old. In 1892, it was the first time that Portland-blast furnace slag cement was manufactured.

The reactivity of slag depends on the rate of cooling. In increasing order of reactivity, the cooling processes may be ranked as: Slow cooling (in air), Rapid cooling (by water spray), and Quenching (dipping in water).

Amongst mineral admixtures, slag possesses the highest specific gravity (2.8 – 3.0). Because it is a processed material, the fineness can be controlled to any desired degree. However, for most typical applications, slag fineness is only slightly higher than cement fineness.

Types of slag

- Air cooled slag: Low reactivity slag that finds use as aggregate. The strength and toughness of this aggregate makes it a very suitable material for railroad ballast.
- Expanded or foamed slag: Low reactivity slag that is foamed with air. Makes a very good lightweight aggregate, and is used for thermal insulation.
- Granulated: This is a high reactivity slag, and is usually quenched. The hardened matter is then ground to a fineness similar to cement. Thus, the name: Ground Granulated Blast Furnace Slag (GGBFS).

Effects on fresh and hardened concrete

- Apart from delaying the initial set, slag does not significantly alter the fresh concrete properties. The workability of slag concrete is similar to an equivalent PC concrete, primarily because slag possesses the same level of fineness as PC.
- The rate of strength gain is slowed down considerably when cement is replaced by slag. The delay increases with increasing replacement. 100% slag concrete is also possible, although the curing duration to produce the required strengths would need to be substantially increased
- The ultimate strengths with slag are generally improved; the durability is also improved with the replacement of cement by slag.
- Slag is the ideal admixture for marine concrete, as slag concrete shows excellent resistance to chemical attack and corrosion

5.8.2 Fly Ash

Fly ash is a by-product obtained during the combustion of coal in thermal power plants. Nearly 73% of India's electricity generation is through coal-burning thermal power stations. About 120 million tons of coal ash now being generated annually; could reach 200 million tons in 2010. Only about 10% of fly ash is being utilized in various industries; remaining amount gets dumped in landfills. According to World Bank estimates, by 2015, the disposal of coal ash would require 1000 square kilometers or one square meter of land per person. Thus, the utilization of fly ash is a matter of primary concern.

During combustion of coal, 75 – 80% of the ash flies out with the flue gas, and is thus called 'fly ash'. The ash that doesn't fly out is called 'bottom ash'.

Types of fly ash (ASTM classification)

- **Type C**: This is also called High Calcium fly ash, and possesses both cementitious and pozzolanic properties. 10 – 15% of the material has a particle size greater than 45 μm , and the fineness (Blaine) is 300 – 400 m^2/kg . The particles are primarily solid spheres with a smooth texture. The average particle size is less than 20 μm .
- **Type F**: This is also called Low Calcium fly ash, and is a normally pozzolanic material. 15 – 20% of the material is larger than 45 μm , and the fineness is 200 – 300 m^2/kg . Particles are solid spheres with a smooth texture, and the average particle size is 20 μm .

Effect on fresh concrete properties

- The setting time is increased when fly ash is used.
- Workability and flow of concrete are increased due to the spherical shape of the fly ash particles.
- Bleeding and segregation are usually reduced for well-proportioned fly ash concrete.

Effect on hardened concrete properties

- Strength gain of fly ash concrete is slower than normal concrete. The potential for thermal cracking is much reduced compared to ordinary PC concrete. Ultimate strengths are usually improved when fly ash is used.
- Pozzolanic activity is proportional to the amount of particles under 10 μm in diameter.
- Expansions during alkali aggregate reaction are reduced by the use of fly ash, because of the dilution of Portland cement.

5.8.3 Silica Fume

Silica fume is a very fine amorphous (non-crystalline) silica produced in electric arc furnaces as a by-product of the production of elemental silicon or alloys containing silicon. There are several types of silica fume including: condensed silica fume, micro-silica, silica flour, fume silica, silica gel, and precipitated silica.

Properties

- Specific gravity: 2.2
- Typical fineness: 20000 m^2/kg (average particle size $\sim 0.1 - 0.5 \mu\text{m}$)
- Colour: light grey to dark grey (lighter implies purer)
- Typically used at 5 – 15% replacement level.
- Benefits from silica fume are due to the pozzolanic reaction that produces additional C-S-H, as well as due to the particle packing (filler effect) of the fine silica fume particles

Effects on fresh concrete properties

- Because of its high fineness, the use of silica fume causes an increase in the water demand of concrete. Typically, it is always used in conjunction with a superplasticizer.

- Silica fume causes the mix to be sticky and cohesive. Because of its cohesiveness, a higher slump is needed to place silica fume concrete.
- Bleeding is reduced drastically. In fact, most silica fume mixes do not show any bleeding. In dry areas, if the evaporation rate exceeds the rate at which concrete sets, plastic shrinkage may occur.

Effects on hardened concrete properties

- Reduction in permeability occurs when silica fume is used. Due to a combined effect of silica fume as a highly reactive pozzolan and filler, the transition zone between aggregate and paste is strengthened.
- Compressive and flexural strengths are increased, while the chloride permeability and diffusion are reduced significantly compared to ordinary PC concrete.
- In most cases, silica fume concrete shows better resistance to chemical attack, owing to the decreased permeability, as well as due to reduced CH in the paste.
- Expansions due to ASR are reduced in silica fume concrete.
- Corrosion rate is reduced with the use of silica fume. This is because of two reasons: the low permeability of SFC causes a lower availability of moisture and oxygen at the cathodic sites, and the high resistivity of SFC makes the flow of electrons difficult.

5.8.4 Other mineral admixtures

Student Activity: find other mineral admixtures