MIXING WATER

Mixing water has two main functions in concrete mix:

- To ensure the hydration of the cement,
- To ensure the workability of concrete by wetting the surface of aggregate particles. That is, to ensure that the concrete can be easily mixed, placed, compacted and its surface smoothed without segregation and bleeding.

The amount of water required for the hydration of cement is approximately 25% of the cement weight. However, due to the workability function of water, 2-3 times the amount of water required for hydration is often added to the mixture.

The quality and quantity of the mixing water used in concrete production significantly affects the properties of the concrete. The mixing water should not contain organic substances, fine particles such as clay, silt, acid and alkalis, and sewage wastes. If there are unwanted amounts of foreign matter in the mixing water, the setting and hydration process of the cement may be adversely affected. Consequently, the strength and durability of hardened concrete are also negatively affected. Such substances can also cause stains on the concrete surface; it may even cause corrosion of the reinforcement. Therefore, the water used as mixing water or for curing must be suitable.

All natural waters that do not have a specific smell and that are potable (drinkable) can be used as mixing water. However, drinking water containing high concentrations of sodium and potassium may not be suitable for use as mixing water due to the risk of alkali-aggregate reaction. On the other hand, some waters that are not drinkable can be used as mixing water, such as running water. As a rule, every water with a pH (degree of acidity) value of 6-8, not bitter or salty, but dark in color or odor does not mean that it contains harmful substances and therefore can be used as mixing water. Slightly acidic natural waters are harmless, but waters containing humic or other organic acids can adversely affect the hardening of concrete. Therefore, such waters and waters with high alkalinity must be tested before use.

In some countries, it can be very difficult to find enough fresh water; only marsh water can be found. These types of water contain chlorides and sulfates. Waters with a chlorine ion content of 500 ppm or a SO_3 content of 1000 ppm are considered harmless. At the same time, alkali carbonates and bicarbonates should not exceed 1000 ppm in such waters.

Sea water can be used as mixing water, but wetness and efflorescence may occur as a result of the crystallization of salts on the concrete surface, as well as corrosion of the reinforcement in reinforced concrete members. Therefore, it should avoid using sea water in cases where appearance is important or in concretes using plaster and reinforced concrete and should never be used in prestressed concretes. On the other hand, sea water can be used in concrete produced for reinforced concrete structures completely immersed in sea water or fresh water. However, in practice, the use of sea water as mixing water is generally not recommended.

When the quality of the water is suspected, the water can be analyzed, or the properties of the concrete produced with this water are compared with the properties of the concrete produced using water of known quality. For example, the compressive strength of concretes produced with both waters can be evaluated. Accordingly, the compressive strength of the concrete produced with suspicious water should not be less than 90% of the compressive strength of the concrete produced with water of known quality.

CHEMICAL ADMIXTURES

Chemical admixtures are substances that dissolve completely in water and are added to concrete in small amounts before or during mixing. Chemical admixtures are substances that change the fresh and/or hardened properties of concrete for a specific purpose. There are a wide variety of chemical admixtures on the market. These consist of several components, most of which are obtained as by-products from various industries. Chemical admixtures can be used in concrete production for one or more of the following purposes:

- Reduce the cost of construction
- Providing certain properties to concrete more effectively than by other means
- Ensuring the quality of concrete during mixing, transportation, placing, compacting and curing in adverse weather conditions
- To overcome some emergency situations during concrete pouring

It should be borne in mind that no admixtures that can replace proper design, manufacture, placement, compaction and curing processes have yet to be produced. Chemical admixtures, which are added to the concrete mixture in very small amounts, affect the rheology of fresh concrete by changing the structure of the cement paste and the hydration process. For this reason, chemical admixtures are often known as "modifiers". Chemical admixtures are classified according to the effect they provide. This effect depends on the type and amount of cement as well as on the concrete composition, mixing time, temperature, aggregate shape and surface texture and granulometry. Depending on the effect they have on concrete properties, it is possible to classify chemical admixtures as follows:

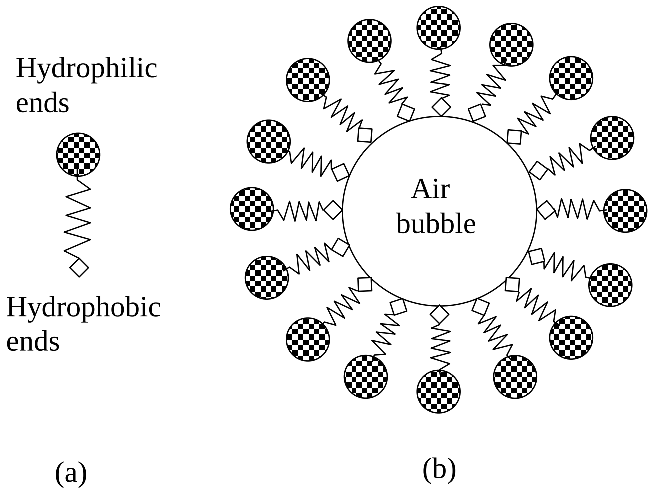
- Air entraining admixtures
- Water reducing admixtures (Plasticizers)
- Retarding admixtures
- Accelerating admixtures
- Water reducing and retarding admixtures
- Water reducing and accelerating admixtures
- High-range water reducing admixtures (Superplasticizers)

In addition to these chemical admixtures, various chemical admixtures are available in the market such as damp-proofing, permeability-reducing, expansion producing, corrosion inhibiting, gas forming, coloring and pumping admixtures.

<u>Air Entraining Admixtures</u>: These are admixtures that allow the formation of very small and stable air spaces that are not interconnected within the cement paste. Air entraining admixtures are used to increase the frost resistance of concrete. Thanks to the millions of tiny air voids formed within the cement paste, the consistency of fresh concrete becomes more fluid and the workability increases; segregation and bleeding are reduced. The entrained air also increases the resistance to surface scaling caused by deicers in concrete. As a result of the decrease in the compressive strength of concrete caused by air voids, their use in road and airport runway constructions requires attention.

Mechanism of Action of Air-Entraining Admixtures

Most air entraining agents are organic substances and are surfactants that cause foaming of water by affecting the air-water interface during mixing. Surfactants are generally molecular in nature and as shown schematically below, the hydrophobic end of the molecule enters the air bubble and settles at the air-water interface. One end of the molecule is normally hydrophilic (water-loving) and dissolves in water while the other end is hydrophobic (water repellent). Air bubbles form in fresh concrete and preserve their structure in the form of a thin spherical void within the hardened concrete. This structure is known as "air-space system" in concrete.



Schematic representation of air entrainment by surfactant molecules:
(a) Surfactant molecule; (b) Stabilized air bubble

<u>Water Reducing Admixtures</u>: These are admixtures that make the consistency of the concrete they are used more fluid. Water reducers are also known as "Plasticizers". Water reducers can be classified according to the amount of water they reduce and the effect they have on setting time as well as water reduction.

Normal water reducing admixtures usually reduce water by 5% to 11%. These are also known as "Plasticizers". High-range water reducers reduce water by at least 12%. These admixtures are also known as "Superplasticizers". In addition to water reducing properties, water reducers also have set retarding and set accelerator properties. The dosage of high-water reducers is higher compared to normal water reducers and they can reduce water by up to 30% as a result of the fluidity they provide.

Water reducing chemical admixtures are generally used for three main purposes:

- To increase the workability of concrete without changing the concrete composition; therefore, to facilitate the placement of concrete in hard-to-reach places.
- To reduce the water to cement ratio by reducing the amount of water added to the concrete without changing the consistency of the concrete and thus obtaining higher strength.
- To reduce the amount of water and cement by keeping the water to cement ratio of concrete constant; hence, to provide technical and economic benefits.

<u>Retarding Admixtures</u>: These are admixtures that have the property of extending the setting time of concrete in order to balance the rapid setting effect that hot weather conditions can create on concrete. Consequently, the workability time of concrete with longer setting time also increases. Gross concrete application is a common application area for these admixtures. These admixtures may have drawbacks such as increasing drying shrinkage and bleeding. Set retarding admixtures are generally used for the following purposes:

- Eliminating the accelerating effect of hot air on the setting of concrete.
- Delaying the initial setting in case of unusual conditions during concrete casting.
- Delaying setting for special aggregate-looking surface finishes.

<u>Accelerating Admixtures</u>: These are admixtures that enable the hardening process of the concrete in which they are used to take place faster compared to the hardening process of concrete without admixture. These admixtures accelerate the setting of concrete and have increasing effects on the strength gaining speed and hydration heat. These are mostly used in construction works where molds are required to be taken quickly, repairs where the building is required to be used in a short time and concrete casting in cold weather. These admixtures can also shorten the maintenance time required to eliminate the damage to concrete due to freeze-thaw in concrete casting in winter, as they partially accelerate hydration. These admixtures may have drawbacks such as reducing the strength, corroding the reinforcement and increasing the drying shrinkage.

<u>High-Range Water Reducers</u>: These are new and more effective water reducing chemical admixtures, also known as "Superplasticizers". Super plasticizers are used to produce "flowable" concrete that is very fluid but workable, can be placed with little vibration or

compaction, and still does not suffer excessive bleeding and segregation. Such concrete is known as “Self-Compacting Concrete”. This concrete is generally used for:

- in concrete casting to thin sectioned members,
- in concrete casting in densely reinforced members,
- in concrete casting with the tremi method (underwater concrete),
- in places where conventional consolidation methods are impractical or cannot be employed,
- in pumped concrete to reduce pump pressure, so to be able to pour concrete to higher and longer distances,
- for reducing handling cost.

Such admixtures are usually used in higher doses compared to normal water reducers, and a 20% to 30% reduction in mixing water can be achieved. While these admixtures provide full dispersion of cement grains for maximum fluidity, normal plasticizers can only partially achieve this. The use of superplasticizers increases the slump of the concrete but does not necessarily reduce the rate of sump loss. In order to prevent this, these admixtures should be added to the mixture just before the concrete is discharged from the mixer. Another solution, known as retempering procedure, is to add the admixture to the concrete mixture in two doses at regular intervals and mix the mixture again for a certain period. New generation admixtures allow the high slump to be maintained for up to 2 hours.

By reducing the amount of water and the water to binder ratio, the production of concretes with the following properties can be made possible.

- Concretes with an ultimate compressive strength exceeding 100 MPa,
- Increased early strength gain,
- Low chloride ion permeability as well as other beneficial properties associated with low water to binder ratio concrete.

MINERAL ADDITIVES

Mineral additives, when finely ground, are substances that show pozzolanic properties that are used both in cement production and concrete production. Mineral additives are used in powder form; their fineness must be at least cement fineness. Unlike chemical admixtures, mineral additives are used in concrete production at rather high rates. Mineral additives can be divided into three groups according to the sources from which they are obtained:

- Natural materials (volcanic ash, volcanic tuffs, trass, diatomaceous earth, stone dust)
- Materials obtained as by-products in an industry not directly related to concrete production (fly ash, granulated blast furnace slag, silica fume)
- Heat treated materials (baked clay, baked shale)

Mineral additives are directly incorporated into the concrete mix as a separate component, as well as aggregate, cement and water, and mixed. Usage rates are generally between 10% to 50% of the cement weight used in the mixture, and they are often used instead of cement by reducing the amount of cement. When necessary, chemical admixtures are also used in the mixture. The effect of mineral additives on the properties and performance of concrete depends not only on the type, physical and chemical properties of the mineral additives, but also on the amount of use. These substances can generally be used for one or more of the following purposes in concrete production:

- To increase the workability of fresh concrete.
- To improve certain properties of concrete. For example,
  - √ reducing segregation and bleeding,
  - √ reducing the hydration rate and the heat released,
  - √ reducing permeability,
  - √ increasing the freeze-thaw resistance,
  - √ reducing the expansion caused by the alkali-silica reaction,
  - √ increasing resistance to sulphate,
  - √ increasing the ultimate strength,
- To obtain more economical concrete by reducing the production cost of concrete.
- To save energy and provide ecological (environmental) benefits.

All mineral additives used in concrete production, except stone dust, are pozzolanic materials. Some of them have both pozzolanic and hydraulic properties.

POZZOLANIC MATERIALS

Pozzolanas are siliceous or siliceous and aluminous materials that do not have any or little binding properties on their own but show hydraulic binding property by reacting with $Ca(OH)_2$ in the aquatic environment when finely ground. In addition to high amounts of silica and alumina, small amounts of iron oxide, calcium oxide, alkalis and carbon can be found in their structure.

POZZOLANIC ACTIVITY

When finely ground pozzolanas are combined with $Ca(OH)_2$, one of the hydration products of cement, in an aqueous environment, a number of chemical reactions occur at normal temperature. These reactions, also known as "pozzolanic reaction", form a calcium-silica-hydrate (C-S-H) gel with hydraulic binding properties as in the hydration of cement. This reaction can be represented simply as follows:

$$\underset{C}{Ca(OH)_2} + \underset{S\ (silica)}{\text{Pozzolan}} + \underset{H}{\text{Water}} \longrightarrow \underset{C\text{-}S\text{-}H}{\text{Calcium-Silica-Hydrate}}$$

The (C-S-H) gel formed as a result of this reaction is formed in addition to the (C-S-H) gel formed by the hydration of the cement. Thanks to the binding property of this gel known as tobermorite, it directly contributes to the strength development of concrete.

The extent to which pozzolanic materials can react with $Ca(OH)_2$ and water and to what extent they can provide binding is known as *pozzolanic activity*. For pozzolanic materials to have enough activity, they must have an amorphous structure and have an enough content of silica + alumina + iron oxide, as well as being finely ground. Several methods are recommended for determining pozzolanic activity, although none are quite sufficient.

Pozzolanic activity is determined by calculating the value expressed as "Strength Activity Index, DAI" for natural pozzolanas and fly ash as given below:

Strength Activity Index, $\mathrm{SAI} = \frac{\mathrm{A}}{\mathrm{B}} \times 100$

Here, A is the average compressive strength of the mortar cube specimens containing pozzolan and B is the average compressive strength of the control mortar cube specimens.

The strength activity index calculated in this way should not be less than a certain value. The value stipulated by the relevant Turkish standards is at least 70%.

Similarly, "Slag Activity Index, SAI" value is calculated to determine the pozzolanic activity of granulated blast furnace slag.

Pozzolanas are generally divided into two classes, natural and artificial pozzolanas.

NATURAL POZZOLANAS

Natural pozzolanas are siliceous and aluminous materials that are found in nature, and when finely ground, react with $Ca(OH)_2$ in an aqueous environment and exhibit binding properties. There are volcanic ones as well as heat treated ones. While volcanic ashes, volcanic tuffs and volcanic glasses are examples of volcanic ones; baked clay, shale and diatomaceous earth are examples of heat-treated ones. When finely ground, these materials have different uses as binders, as follows:

- They are used directly with slaked lime and water.
- They are ground together with clinker and used in the production of Portland-pozzolan type cement.
- They are used as additives in concrete production.

Today, natural pozzolanas are generally used in the production of Portland-pozzolan type cement and to a limited extent in the production of pozzolan-added concrete.

ARTIFICIAL POZZOLANAS

These are industrial by-product materials such as fly ash, granulated blast furnace slag and silica fume. Today, artificial pozzolanas are used extensively as direct additives in concrete production.

Fly Ashes: It is the very fine waste ash that occurs as a result of the burning of pulverized coal used as fuel in thermal power plants generating electrical energy. Fly ashes contain high levels of SiO_2, Al_2O_3 and Fe_2O_3. Depending on the type, fly ash also contains very small amounts of CaO, MgO, C (very fine-grained unburned coal) and Na_2O. Fly ash grains are generally spherical shaped solid particles and are 60% to 90% amorphous. The remaining part contains crystals such as quartz, mullite, magnetite and hematite.

Fly ashes with a CaO content of less than 10% are known as "low-lime fly ashes", those with CaO content higher than 10% are known as "high-lime fly ashes". ASTM C 618 divides fly ashes into two classes, F and C, according to their chemical composition. Fly ashes obtained from anthracite or bituminous coals and having $SiO_2 + Al_2O_3 + Fe_2O_3 \geq 70\%$ composition are known as F class. Fly ashes obtained from lignite or low bituminous coals and having $SiO_2 + Al_2O_3 + Fe_2O_3 \geq 50\%$ composition are known as Class C. Class F fly ash shows only pozzolanic properties. In addition to the pozzolanic property of type C fly ash, it also shows hydraulic properties when the CaO content is more than 10%.

Blast Furnace Slag: While iron is being produced, molten iron precipitates to the bottom of the crucible as a result of the burning of iron ores, and impurities such as CaO, SiO_2, Al_2O_3, Fe_2O_3, MgO, MnO and S, which are molten and lighter, are thrown out. These substances thrown out are collectively known as *blast furnace slag*. The temperature of the molten slag thrown out is approximately 1500°C. When the molten slag is cooled in air at a slow speed, the slag obtained has a crystalline structure. If the molten slag is subjected to very rapid cooling by spraying a large amount of pressurized water, it becomes granular in the size of large and small sand grains and also gains an amorphous (glassy) structure to a large extent.

Granulated blast furnace slag with an amorphous structure and containing large amounts of SiO_2 and Al_2O_3 shows pozzolanic properties similar to natural pozzolanas and fly ash when finely ground. In addition, since they contain a large amount of CaO, the ground granulated blast furnace slag has a binding (hydraulic) property. Crystalline slag that is slowly cooled in air does not show pozzolanic properties.

In practice, ground granulated blast furnace slag finds use as finely ground natural pozzolanas or fly ashes.
Silica Fume: Silica fume is a material consisting of very fine solid particles obtained by rapidly cooling and condensing the gases released during the production of silicon metal or silicon metal alloys. This material, which contains at least 85% silica and has an amorphous structure, is also known as "microsilicate".

Due to its very fineness, nitrogen absorption method is used instead of Blaine apparatus in determining the fineness of silica fume. While the specific surface of silica fume used in concrete production is in the order of 200 000 cm^2/g, the specific surface of Portland cement is usually 3 000 cm^2/g. It is an excellent pozzolanic material since the specific surface of silica fume is very large and it is amorphous and contains high amount of SiO_2. Like other pozzolanic materials, it shows hydraulic properties when combined with $Ca(OH)_2$ in an aqueous environment.

Silica fume is an artificial pozzolana commonly used in concrete production. In the concrete mixture, it is generally replaced with cement by 10%. Due to its high pozzolanic property, it is possible to produce high strength concretes with silica fume both in early ages and in later ages. These concretes are also very useful in preventing reinforcement corrosion since their permeability is low.

Since silica fume consists of very fine particles, the consistency and workability of concretes where silica fume is used decreases and the water requirement increases. In this respect, when silica fume is used to produce high strength concrete, a high-range water reducing chemical admixture must also be used.

In addition to the positive effects of mineral additives on concrete properties, there are potentially some negative effects as well.

<u>Positive effects</u>:

- Workability increases.
- High strength is obtained.
- Bleeding and segregation are reduced.
- A reduction in hydration heat is achieved.
- A significant reduction is achieved in the permeability of hardened concrete.
- Sulphate resistance of concrete increases.
- Alkali-silica reaction is reduced.
- Economy is provided.

<u>Potential harmful effects</u>:

- The rate of gaining strength decreases at early ages.
- Concrete needs to be cured more carefully and for longer.
- There may be a delay in the set. Hence, problems may occur in cold weather.
- More air entraining is used to entrain a certain amount of air.
- More mixing water is required as they are finely ground.
- Plastic shrinkage cracks may increase; especially when using silica fume.