CHAPTER THREE

MINERAL AND CHEMICAL ADMIXTURES

3.1 Introduction

An admixture, defined as a material other than water, aggregate, hydraulic cement, and fiber reinforcement, is used as an ingredient of concrete or mortar, and added to the batch immediately before or during its mixing to modify its freshly mixed, setting, or hardened properties. These properties may be modified to increase compressive and flexural strength at all ages, decrease permeability and improve durability there are two types of admixture**:**

- Mineral Admixtures
- Chemical Admixtures

3.2 Mineral Admixtures

Mineral admixtures refer to the finely divided materials which are added to obtain specific engineering properties of cement mortar and concrete. The other, equally important, objectives for using mineral admixtures in cement concrete include economic benefits and environmentally safe recycling of industrial and other waste by-products. Unlike chemical admixtures, they are used in relatively large amounts as replacement of cement and or of fine aggregate in concrete. Mineral admixtures are mostly pozzolanic materials. Sometimes these admixtures may also possess self cementitious properties in addition to being pozzolanic. These admixtures are available in abundance at a much lower cost compared to chemical admixtures. In the past, natural pozzolans such as volcanic earths, tuffs, trass, clays, and shales, in raw or calcined form, have been successfully used in building various types of structures such as aqueducts, monuments and water retaining structures. Natural pozzolans are still used in some parts of the world. However, in recent years, many industrial waste by-products such as fly ash, slag, silica fume, red mud, and rice husk ashare rapidly becoming the main source of mineral admixtures for use in cement and concrete.

Mineral admixtures are incorporated in portland-cement mortar and concrete, either in the form of blended cements, such as Portland pozzolan or Portland blast furnace slag cements, or directly added as admixtures to the concrete at the time of mixing. In Asia and Europe, large quantities of blended Portland cements containing pozzolanic and cementitious additives are commercially produced for use by the concrete industry. However, in North America, industrial by-products particularly fly ash, blast furnace slag and condensed silica fume, are used directly as mineral admixtures in concrete rather than as constituents of blended cements. Industrially developed countries such as the USA, the former USSR (Commonwealth of Soviet Countries), France, Germany, Japan and U.K. are among the largest producers of fly ash, granulated blast furnace slag and condensed silica fume. In rice producing countries such as China and India, there is apromising potential of generating large quantities of rice husk or rice hullash. Another industrial by-product which can be used as mineral a hxtureis calcined red mud, a waste material obtained from the aluminum extraction Industry.

Vast quantities of industrial by-products, which have been found suitable for use as mineral admixtures in cement and concrete, are produced every year. These waste by-products must be effectively disposed toeliminate air, soil, and surface, as well as ground water, pollution at added cost to the industry and thus to the society. Their utilization as mineral admixtures in cement and concrete transforms a costly liability into an economical proposition. Furthermore, the costs and environmental problems associated with their disposal are minimized or eliminated. Land requirements for disposal sites are considerably reduced.

The mineral admixtures are generally used as partial replacement of cement, an expensive and energy intensive material. Therefore, utilization of mineral admixtures leads to considerable saving in cost and energy consumption. Utilization of increased volumes of industrial by-products as mineral admixtures in cement and concrete will lead to conservation of energy and natural resources. Bulk quantities of some industrial by-products, such as fly ash, bottom ash, and slag have been used as aggregates for concrete, and for road embankment as well as sub-base construction, but such bulk uses represent low value applications. On the other hand, their use as mineral admixtures in cement and concrete due to their pozzolanic and cementitious properties represents high value applications.

Addition of mineral admixtures, particularly finely divided pozzolanic and cementitious materials, can affect the properties of cement mortar/concrete both in fresh and hardened state. In fresh or plastic state, mix proportions, water requirement for specified consistency, setting characteristics, including cohesiveness and bleeding, and heat of hydration are some of the properties influenced by mineral admixtures. In the hardened state, the rate of strength development and ultimate strength, permeability, durability against frost attack, sulfate attack, alkali silica reaction, carbonation, and resistance to thermal cracking are significantly affected with the incorporation of mineral admixture in cement concrete. [9]

3.3 Chemical Admixtures

Chemical admixtures, a very important group of admixtures used in small amounts, are water soluble or emulsified systems. Chemical admixtures include accelerators, retarders, water reducers, superplasticizers, etc. In a broad sense, chemical admixtures should also include among others, air entraining admixtures, pumping aids, coloring admixtures, alkali-aggregate expansion-reducing admixtures and others. [10]

The use of admixtures to enhance the properties of mortar, renders and screeds has taken place for many centuries.

The ancient Chinese were known to have used black grain molasses; the Romans used animal fat, milk and blood in their mortars. It is probable that the early use commenced when workmen found that the addition of a particular substance to a mortar mix enhanced the fresh properties.

The use of admixtures by ancient civilisations was thus based on practical experience and not on an understanding of chemical theory.

Admixtures can be divided into three categories;

- Active materials are those which react chemically with a component within the cementitious material.
- Surface active admixtures (surfactants). These are generally split into two components (one positively charged and the other negatively charged) and react with the air - water -solid material interface within the mortar there by resulting in orientation and adsorption. (Orientation means that the particles all face or point in the same direction, adsorption means a concentration of molecules gathering or being deposited on the surface of a solid material.
- Passive or inert admixtures. These do not change their form but have a physical effect such as light absorption and reflection as in the case of pigments.

It should also be noted that some admixtures are multi-functional, this means that the addition of the admixture to a mix results in more than one property of the mix being affected (e.g. a water reducing air entrainer).

Admixture, Organic or inorganic material added in small quantities to modify the properties of the mortar in the fresh/hardened state.

Additive, A finely divided inorganic material that may be added to mortar in order to improve or achieve special properties. (Note: some confusion exists over the differences between an admixture and an additive, generally additives are materials added to cement to control some property e.g. set controlling gypsum stearate added during the grinding of cement; other parts of the construction industry classify liquid materials as admixtures and solid materials as additives).[11]

3.3.1 Water Reducing/Plasticizing Admixtures

This group of admixtures which are surface active (surfactants) posses the ability to disperse or deflocculate the cement particles within the mix, some water reducers/plasticizers are based on detergents.

When these are incorporated into a mortar mix the admixture particles are adsorbed onto the surface of the cement particles and the negatively charged tails protrude. These repel each other, as illustrated diagrammatically in Figure (3.1). The repulsion of the like charges results in a powerful deflocculating action and hence a more uniform distribution of the cement particles throughout the mix; this action also frees some of the water trapped by the flocculation of the cement particles as shown in Figure (3.2). This has a lubricating effect on the mix components and results in an increase in workability, (a plasticizing effect). Where this is not desired the quantity of added water can be reduced (a water reducing effect), leading to an increase in the compressive strength of the mix.

A third way that this type of admixture can be used is to reduce the water content but keep the strength constant by reducing the cement content (an environmental benefit, the less cement that is used the less raw materials and fuel for production that are consumed).

The actual water reduction achieved by the use of this type of admixture depends upon the individual mix composition; typical water reductions are in the range 7.5 - 12.5%.

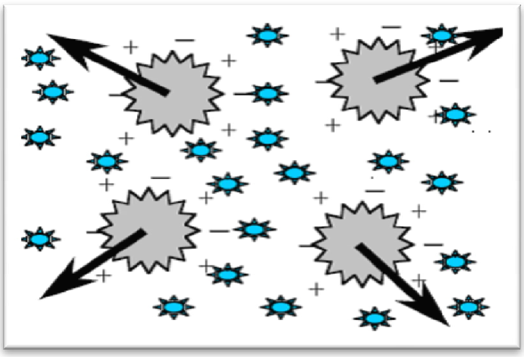

Figure (3.1): The effect of a water reducing the mix admixture on the dispersion of cement particles

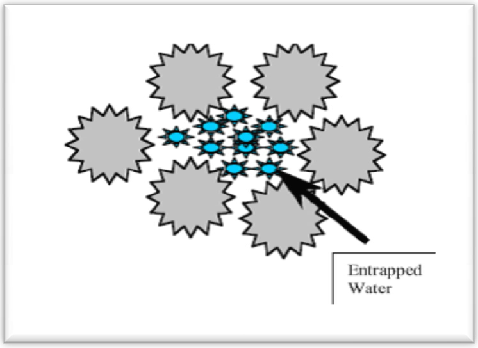

Figure (3.2): Flocculating cement particles trapping water

Water reducing admixtures are based on modified lignosulfonic acid derivatives, hydroxycarboxylic acids or hydroxylated polymers.

It is important to remember that the addition of an admixture can have secondary effects, which may be beneficial or detrimental. Water reducing/plasticizing admixtures normallyentrain small quantities of air, overdosing may lead to retardation of the hydration mechanism and or excessive entrainment of air. In addition to the single function water reducing/plasticizing admixture, multi-function admixtures such as water reducing/air entrainers, water reducing/retarders and water reducing/accelerators are available. [12]

3.3.2 Air Entraining Admixtures

Previously, it has been stated that the Romans used animal fat, milk and blood in their construction. No one can be absolutely sure of the reasons for this but, it was probably to improve the workability of the material in the fresh or plastic state.

Air entraining admixtures are surfactants, they act at the air-water interface in cement paste, resulting in the stabilisation of air entrapped during the mixing process in the form of very small separate bubbles. The addition of the admixture to the mix lowers the surface tension of the water thereby assisting in the formation of bubbles. It is important to distinguish between entrapped air and entrained air. Entrapped air normally exists in the form of relatively large air voids, which are not dispersed uniformly throughout the mix, entrained air exists in the form of minute disconnected bubbles (0.02 - 1.0mm in size) well distributed throughout the mix. To achieve an increase in durability the air-entrained bubbles have not only to be of the correct size, but also correctly spaced.

The resistance of hardened mortar to the destructive effects of frost damage (freezing and thawing) is significantly improved by the use of intentionally entrained air (improved durability). As the water in the hardened mortar paste freezes, it causes pressure that can rupture the material. The entrained air voids act as reservoirs for the excess water forced into them, thereby relieving pressure and preventing damage to the mortar or screed.

Air entraining admixtures are manufactured from a number of raw materials including:

- Natural wood resins and their sodium salts, for example vinsol resin.
- Animal and vegetable fats and oils.
- Alkali salts of sulfated and sulfonated organic compounds.
- Water soluble soaps.

The minute air bubbles present in the fresh mortar mix can be said to act almost like fine particles (the spherical particles behave like small ball bearings and increase workability) and result in a more cohesive mix with reduced bleeding characteristics being obtained. Air entraining agents also have a plasticizing effect and less water is required to achieve the desired workability. A very important requirement of air entraining agents is that the bubbles they entrain are stable. A practice which should never be encouraged, is the addition of detergents (washing up liquid) to mortar mixes. A more cohesive mix will be obtained in the short term, but the bubbles formed are not stable and confer no long-term advantage to the product.

In concretes, the optimum content of air entrainment is approximately 5.5% (this varies with the aggregate size). Mortar mixes are very different and the optimum air entrainment content is approximately20%. Admixtures designed for plasticizing /air entraining mortars should never be used for concrete production, unless they have been specially designed for this purpose.

The quantity of air that is entrained is influenced by a number of factors including: cement content and type, aggregate grading and fines content, temperature and efficiency of mixing.

Air entrainment does lead to some loss in compressive strength of the mix, because the same quantity of binder is being used to cement a larger volume of mortar.[13]

3.3.3 Water Reducers/Retarders Admixtures

Most water reducers as well as most retarders are organic, water soluble products and many formulations of these admixtures are based on the same raw materials, such as lignosulfonates, hydroxycarboxylic acids, carbohydrates, etc. A water reducer can be defined as an admixture that reduces the amount of mixing water for concrete for a given workability. It improves the properties of hardened concrete and, in particular, increases strength and durability. Usually, according to standards the reduction of mixing water by the use of these admixtures must be at least *5%*. However, commercial water reducers can reduce mixing water up to 10 to 15%.

There is another mode of use of these admixtures, involving reduction of both water and cement, so that workability and strength of concrete containing admixtures are similar to those of the control concrete. Admixtures could thus act as cement reducers. Besides allowing cement saving, these admixtures are capable of reducing the heat of hydration, a property that is useful for concreting in hot climates or massive structures.

If water reducers are added without modifying mix proportions, concrete workability improves; in this case they act as plasticizers. This is particularly useful for placing concrete in areas of high steel content that require a more workable concrete.

An admixture that lengthens setting time and workability time is known as set retarder or retarding admixture. This is particularly useful for concreting under high-temperature conditions. Ice, which can be added into the mixer to decrease the temperature, is more expensive than a retarding admixture and may not be readily available at the job site. [14]

3.3.4 Accelerating Admixtures

An accelerating admixture is a material that is added to concrete for reducing the time of setting and accelerating early strength development.

Accelerating admixtures are used in cold water concreting operations and also are components of antifreezing admixtures and shotcreting mixes. In cold weather concreting, there are other alternatives such as the use of type III cement, use of higher than normal amount of portland cement type I, orwarming of the concrete ingredients. Of the above, the most economical method is the use of type **I** cement in conjunction with an accelerator.

The advantages include: efficient start and finishing operations, reducing the period of curing and protection, earlier removal of forms so that the construction is ready for early service, plugging of leaks, and quick setting when used in shotcreting operations. Many substances are known to act as accelerators for concrete. The American Concrete Institute Committee 212 (Chemical Admixtures for Concrete, Report ACI-2 12, American Concrete Institute, Detroit, p. 3 1, 1990) has divided accelerators into four groups as

- soluble inorganic salts that include chlorides, bromides, fluorides, carbonates, thiocyanates, nitrites, nitrates, thiosulfates, silicates, aluminates and alkali hydroxides that accelerate the setting of Portland cement
- soluble organic compounds such as triethanolamine **(TEA),**calcium formate, calcium acetate, calcium propionate and calcium butyrate. The other two groups are used in combination with water reducers:
- quick setting admixtures used in shotcrete applications and which promote setting in a few minutes and may contain sodium silicate, sodium, aluminum chloride, sodium fluoride, strong alkalis and calciumchloride.
- miscellaneous solid admixtures such as calcium aluminate, seeds of finely divided portland cement, silicate minerals, finely divided magnesium carbonate and calcium carbonate. To these could be added multifunctional admixtures that improve the properties of concrete in more than one way.

Of these, calcium chloride is the most widely used because of its ready, low cost, predictable performance characteristics and successful application over several decades. [11]

3.3.5 Superplasticizers:

Superplasticizers belong to a class of water reducers chemically different from the normal water reducers and capable of reducing water contents by about 30%. The admixtures belonging to this class are variously known as superplasticizers, superfluidizers, superfluiddiers, super water reducers, or high range water reducers. They were first introduced in Japan in the late 60's and in Germany in early 70's. In North America they were used from 1974.

The advantages derived by the use of superplasticizers include production of concrete having high workability for easy placement, and production of high strength concrete with normal workability but with a lower water content. A mix having a combination of better than normal workability and lower than normal amount of water, or that with less cement but having the normal strength and workability are other possible application.

Reliable statistics on the extent of the use of superplasticizers are not available. The data provided by Malhotra in 1989 provides some indication. In industrialized countries, the percentage of ready mix concrete utilizing superplasticizers varied between 1 and 20%. In precast concrete however, the use varied between 20 and 100%.

The superplasticizers are broadly classified into four groups: sulfonatedmelamine-formaldehyde condensate (SMF); sulfonated naphthalene- formaldehyde condensate (SNF); modified lignosulfonates (MLS);and others including sulfonic acid esters, polyacrylates, polystyrene sulfonates,etc.

Applications:

Superplasticized concrete enables placement in congested reinforcement and in not easily accessible areas. The problem of cutting and adapting the formwork for vibration is thus eliminated. Easy and quick placement characteristics of flowing concrete and the need for only very nominal vibration makes it suitable for placement in bay areas, floors, foundation slabs, bridges, pavements, roof decks, etc. Pumping of concrete is very much facilitated by incorporation of superplasticizers.

Superplasticizers have also found successful application for placing concrete by tremie pipe, particularly in underwater locations. They have also been used for spray applications and for tunnel linings, and where special shapes are desired as in architectural work. Superplasticizers are used by the precast industry because strengths of the order of 40 MPa are achieved in 8 to 18 hrs. And the fuel costs and amount of cement used are reduced.

They have also been used to produce concrete of strength of more than 100MPa in combination with silica fume. Other important advantages include production of concrete with reduced permeability, improved surface finish, reduced shrinkage, and overall cost savings.

In addition to producing high strengths and flowable concretes, superplasticizers offer other possible benefits. There is a great need to use marginal quality cements and aggregates for the production of concrete. In such instances, the use of superplasticizers permits production of concrete at low w/c ratios and with good durability characteristics. Superplasticizers can be used advantageously in the production of fly ash concrete, blastfurnace slag cement concrete, composites with various types of fibers and lightweight concrete.[15]

3.4 Handling and Storage of Admixtures

Admixtures are complex chemicals and one type may not be compatible with another, therefore admixtures should not be premixed without seeking advice from the manufacturer.

Generally liquid admixtures should be introduced into the mixer by means of automatic dispensing equipment at the same time as the water and aggregates. Liquid admixtures should never be added to dry material. The quantity of admixture to obtain the desired performance may be quite small and overdosing may result in undesirable effects.

Admixture manufacturer's data sheets list approximate dosage figures for individual admixtures based on trials they undertake. Field trials should always be undertaken to determine the optimum dosage for the particular mix constituents and proportions.

Admixtures may deteriorate if stored for prolonged periods. Where admixtures have been stored in drums or tanks for periods in excess of twelve months, advice on their use should be sought from the manufacturer. Generally, admixtures should be stored above 0C° and protected from frost, however some admixtures have depressed freezing points in the range -5 to -10 C°. Manufacturers data sheets give further information on the storage facilities/conditions necessary to maintain the properties of the admixture. In periods of hot weather drums should be stored in shaded conditions.