

UNIT-II
CHEMICAL AND MINERAL ADMIXTURES

1. What are admixtures?
Admixtures are ingredients other than cement, fine aggregate and coarse aggregate to improve the quality of concrete. The addition of an admixture may improve the concrete with respect to its strength, hardness, workability, water resisting power etc.
2. Define chemical admixtures
Chemicals mixed with concrete ingredients and spread throughout the body of concrete to favorably modify the molding and setting properties of concrete mix known as chemical admixtures.
3. Define Mineral admixtures
It is a siliceous materials used to strengthen the durability properties that is classified as pozzolanic or cementitious materials. It acts as by-product agent. E.g.: fly ash
4. What is accelerators
Accelerators reduce the setting time and produce early removal of forms and speed up hardening. The common accelerators are CaCl_2 , Al_2Cl_3 , NaCl , Na_2SO_4 .
5. What is the purpose of retarders?
Retarders increases the setting time of concrete mix and reduce the water cement ratio. Up to 10% water reduction is achieved.
6. Define plasticizers
Plasticizers are defined as chemical admixtures added to wet concrete mix to impart adequate workability properties.
7. Mention the types of plasticizers
 - a. Finely divided minerals
 - b. Air entraining agents
 - c. Synthetic derivatives
8. Define superplasticizers
Superplasticizers produce extreme workability and achieve reduction of water content without loss of water cement ratio i.e workability.
9. Mention few mineral admixtures.
 - a. Fly ash
 - b. Silica fume
 - c. Rice husk ash
 - d. Metakaoline
 - e. GGBFS

10. What are the various admixtures used other than chemical and mineral admixtures/
- Gas forming and expansive chemicals
 - Pigments
 - Antifungal admixtures
 - Curing compounds
 - Sealants
 - Flooring
 - Guniting aids.
11. Name the admixtures available in India?
- Plasticizers
 - Conplast P211- Water reducing plasticizers
 - Conplast P509- Water reducing plasticizers/High performance plasticizers
 - Super Plasticizers
 - Conplast SP337- High workability aid
 - Conplast SP430- High range water reducer

1. Write short notes on Plasticizers and super plasticizers and their effects on properties of concrete.

Plasticizers (water reducers)

Requirement of right workability is the essence of good Concrete. Concrete in different situations require different degree of workability. A high degree of workability is required in situations like deep beams, thin walls of water retaining structures with a high percentage of steel reinforcement, column and beam junctions, pumping of Concrete, hot weather Concreting. Today, we have plasticizers which can help in difficult conditions for obtaining higher workability without using excess of water. The organic substances or the combinations of organic and inorganic substances, which allow a high reduction in water content for the given workability or give a higher workability at the same water content, are termed as Plasticizing Admixtures. The basic products constituting plasticizers are: 1. Anionic surfactants such as lignosulphonates and their modifications and derivatives, salts of sulphonates hydrocarbons. 2. Nonionic surfactants such as polyglycol esters, acid of hydroxylated carboxyl acids and their modifications and derivatives. 3. Other products, such as carbohydrates etc. Among these, calcium, sodium and ammonium lignosulphonates are the most used. Plasticizers are used in the amount of 0.1% to 0.4% by weight of cement. At these doses, at constant workability the reduction in mixing water is expected to be of the order of 5% to 15%. This naturally increases the strength. The increase in workability that can be expected, at the same w/c ratio, may be anything from 30 mm to 150 mm slump, depending on the dosage, initial slump of concrete, cement content and type.

ACTION OF PLASTICIZERS

The action of plasticizers is mainly to fluidify the mix and improve the workability of concrete, mortar or grout. The mechanisms that are involved could be explained in the following way:

Dispersion:

Portland cement, being in fine state of division, will have a tendency of flocculate in wet concrete. These flocculation entraps certain amount of water used in the mix and thereby all the water is not freely available to fluidify the mix. When plasticizers are used, they get adsorbed on the cement particles. The adsorption of charged polymer on the particles of cement creates particle-to-particle repulsive forces which overcome the attractive forces. This repulsive force is called Zeta Potential, which depends on the base, solid content, quantity of plasticizer used. The overall result is that the cement particles are deflocculated and dispersed. When cement particles are deflocculated, the water trapped inside the flocs gets released and now available to fluidify the mix. When cement particles get flocculated there will be interparticles friction between particle to particle and floc to floc. But in the dispersed condition there is water in between the cement particle and hence the interparticle friction is reduced. Retarding Effect: The plasticizer will get adsorbed on the surface of cement particles and form a thin sheath. This thin sheath inhibits the surface hydration reaction between water and cement as long as sufficient plasticizer molecules are available at the particle/solution interface. The quantity of available plasticizers will progressively decrease as the polymers become entrapped in hydration products.

SUPERPLASTICIZERS (HIGH RANGE WATER REDUCERS)

Superplasticers constitute a relatively new category and improved version of plasticizer, the use of which was developed in Japan and Germany during 1960 and 1970 respectively. They are chemically different from normal plasticizers. Use of superplasticizer permits the reduction of water to the extent upto 30 per cent without reducing workability in contrast to the possible reduction up to 15 per cent in case of plasticizers. The use of superplasticizer is practiced for production of flowing, self leveling, and self compacting and for the production of high strength and high performance concrete. The mechanism of action of super plasticizers is more or less same in case of ordinary plasticizer. Only thing is that the super plasticizers are more powerful as dispersing agents and they are high range water reducers. They are called High Range Water Reducers in American literature. It is the use of superplasticizer which has made it possible to use w/c as low as 0.25 or even lower and yet to make flowing concrete to obtain strength of the order 120 Mpa or more. It is the use of superplasticizer which has made it possible to use fly ash, slag and particularly silica fume to make high performance concrete. The use of superplasticizer in concrete is an important milestone in the advancement of concrete technology. Since their introduction in the early 1960 in Japan and in the early 1970 in Germany, it is widely used all over the world. India is catching up with the use of superplasticizer in the construction of high rise buildings, long span bridges and the recently become popular Ready Mixed Concrete industry. Common builders and Government departments are yet to take up the use of this useful material. Super plasticizers can produce:

- At the same w/c ratio much more workable concrete than the plain ones,
- For the same workability, it permits the use of lower w/c ratio,
- As a consequence of increased strength with lower w/c ratio, it also permits a reduction of cement content.

The super plasticizers also produce a homogeneous, cohesive concrete generally without any tendency for segregation and bleeding. Classification of Superplasticizer: Following are a few polymers which are commonly used as base for super plasticizers.

- Sulphonated melamine-formaldehyde condensates (SMF)
- Sulphonated naphthalene-formaldehyde condensates (SNF)
- Modified lignosulphonates (MLS)

EFFECTS OF SUPERPLASTICIZERS ON FRESH CONCRETE

It is to be noted that dramatic improvement in workability is not showing up when plasticizers or super plasticizers are added to very stiff or what is called zero slump concrete at nominal dosages. A mix with an initial slump of about 2 to 3 cm can only be fluidized by plasticizers or super plasticizers at nominal dosages. A high dosage is required to fluidify no slump concrete. An improvement in slump value can be obtained to the extent of 25 cm or more depending upon the initial slump of the mix, the dosage and cement content. It is often noticed that slump increases with increase in dosage. But there is no appreciable increase in slump beyond certain limit of dosage. As a matter of fact, the over dosage may sometime harm the concrete.

2. Write short notes on retarders and accelerators and their effects on properties of concrete.

RETARDERS

A retarder is an admixture that slows down the chemical process of hydration so that concrete remains plastic and workable for a longer time than concrete without the retarder. Retarders are used to overcome the accelerating effect of high temperature on setting properties of concrete on hot weather concreting. The retarders are used in casting and consolidating large number of pours without the formation of cold joints. They are also used in grouting oil wells. Oil wells are sometimes taken up to a depth of about 6000 meter deep where the temperature may be about 200°C. The annular spacing between the steel tube and the wall of the well will have to be sealed with cement grout. Sometimes at that depth stratified or porous rock strata may also require to be grouted to prevent the entry of gas or oil into some other strata... for all these works cement grout is required to be in mobile condition for about 3 to 4 hours, even at that high temperature without getting set. Use of retarding agent is often used for such requirements. Sometimes concrete may have to be placed in difficult conditions and delay may occur in transporting and placing. In ready mixed concrete practices, concrete is manufactured in central batching plant and transported over a long distance to the job sites which may take considerable time. In the above cases the setting of concrete will have to be retarded, so that concrete when finally placed and compacted is in perfect plastic state. Retarding admixtures are sometimes used to obtain exposed aggregate look in concrete. The retarder sprayed to the surface of the formwork, prevents the hardening of matrix at the interface of concrete and formwork, whereas the rest of the concrete gets hardened. On removing the formwork after one day or so, the unhardened matrix can be just washed off by a jet of water which will expose the aggregates. The above are some of the instances where a retarding agent is used. Perhaps the most common known retarder is calcium sulphate. It is interground to retard the setting of cement. The appropriate amount of gypsum to be used must be determined carefully for the given job. Use of gypsum for the purpose of retarding setting time is only recommended when adequate inspection and control is available, otherwise, addition of excess amount may cause undesirable expansion and indefinite delay in the setting of concrete. In addition to gypsum there are number of other materials found to be suitable for this purpose. They are: starches, cellulose products, sugars, acids or salts of acids. These chemicals may have variable action on different types of cement when used in different quantities. Unless experience has been had with a retarder, its use as an admixture should not be attempted without technical advice. Any mistake made in this respect may have disastrous consequences. Common sugar is one of the most effective retarding agents used as an admixture

for delaying the setting time of concrete without detrimental effect on the ultimate strength. Addition of excessive amounts will cause indefinite delay in setting. At normal temperatures addition of sugar 0.05 to 0.10 percent have little effect on the rate of hydration, but if the quantity is increased to 0.2 percent, hydration can be retarded to such an extent that final set may not take place for 72 hours or more. Skimmed milk powder (casein) has a retarding effect mainly due to sugar content. Other admixtures which have been successfully used as retarding agents are Ligno sulphonic acids and their salts, hydroxylated carboxylic acids and their salts which in addition to the retarding effect also reduce the quantity of water requirement for a given workability. This also increases 28 days compressive strength by 10 to 20 percent. Materials like mucic acid, calcium acetate and commercial products by name “Ray lig binder” are used for set retarding purposes. These days” admixtures are manufactured to combine set retarding and water reducing properties. They are usually mixtures of conventional water reducing agents plus sugars or hydroxylated carboxylic acids or their salts. Both the setting time and the rate of strength build up are effected by these materials.

ACCELERATORS

Accelerating admixtures are added to concrete to increase the rate of early strength development in concrete to

- permit earlier removal of formwork;
- reduce the required period of curing;
- advance the time that a structure can be placed in service;
- partially compensate for the retarding effect of low temperature during cold weather concreting;
- in the emergency repair work. In the past one of the commonly used materials as an accelerator was calcium chloride. But, now a days it is not used. Instead, some of the soluble carbonates, silicates fluosilicates and some of the organic compounds such as triethenolamine are used. Accelerators such as fluosilicates and triethenolamine are comparatively expensive. The recent studies have shown that calcium chloride is harmful for reinforced concrete and prestressed concrete. It may be used or plain cement concrete in comparatively high dose. Some of the accelerators produced these days are so powerful that it is possible to make the cement set into stone hard in a matter of five minutes or less. With the availability of such powerful accelerator, the under water concreting has become easy. Similarly, the repair work that would be carried out to the waterfront structures in the region of tidal variations has become easy. The use of such powerful accelerators have facilitated, the basement waterproofing operations. In the field of prefabrication also it has become an invaluable material. As these materials could be used up to - 100C, they find an unquestionable use in cold weather concreting. Some of the modern commercial accelerating materials are Mc-Schnell OC, McSchnell SDS, Mc-Torkrethilfe BE, manufactured by Mc-Bauchemic (Ind) Pvt. Ltd. MC-Torkrethilfe BE is a material specially formulated to meet the demand for efficient and multifold properties desired for sprayed concrete and shotcreting operations. A field trial is essential to determine the dose for a given job and temperature conditions when the above materials are used.

3. Write short notes on fly ash and also their effect on properties of concrete.

FLY ASH:

Fly ash is finely divided residue resulting from the combustion of powdered coal and transported by the flue gases and collected by electrostatic precipitator. In U.K. it is referred as pulverized fuel ash (PFA). Fly ash is the most widely used pozzolanic material all over the world. Fly ash was first used in large scale in the construction of Hungry Horse dam in America in the approximate amount of 30 per cent by weight of cement. Later on it was used in Canyon and Ferry dams etc. In India, Fly ash was used in Rihand dam construction replacing cement upto about 15 per cent. In the recent time, the importance and use of fly ash in concrete has grown so much that it has almost become a common ingredient in concrete, particularly for making high strength and high performance concrete. Extensive research has been done all over the world on the benefits that could be accrued in the utilization of fly ash as a supplementary cementitious material. High volume fly ash concrete is a subject of current interest all over the world. The use of fly ash as concrete admixture not only extends technical advantages to the properties of concrete but also contributes to the environmental pollution control. In India alone, we produce about 75 million tons of fly ash per year, the disposal of which has become a serious environmental problem. The effective utilization of fly ash in concrete making is, therefore, attracting serious considerations of concrete technologies and government departments. There are two ways that the fly ash can be used: one way is to intergrind certain percentage of fly ash with cement clinker at the factory to produce Portland pozzolana cement (PPC) and the second way is to use the fly ash as an admixture at the time of making concrete at the site of work. The latter method gives freedom and flexibility to the user regarding the percentage addition of fly ash. ASTM broadly classifies fly ash into two classes. Class F: Fly ash normally produced by burning anthracite or bituminous coal, usually has less than 5% CaO. Class F fly ash has pozzolanic properties only. Class C: Fly ash normally produced by burning lignite or sub-bituminous coal. Some class C fly ash may have CaO content in excess of 10%. In addition to pozzolanic properties, class C fly ash also possesses cementitious properties. Fly ash, when tested in accordance with the methods of test specified in IS: 1727- 1967.

EFFECT OF FLY ASH ON FRESH CONCRETE

Good fly ash with high fineness, low carbon content, highly reactive forms only a small fraction of total fly ash collected. The ESP fly ash collected in chambers I and II are generally very coarse, non spherical particles showing large ignition loss. They can be called coal ash rather than fly ash. Such fly ash (coal ash) is not suitable for use as pozzolan and they do not reduce the water demand. Use of right quality fly ash, results in reduction of water demand for desired slump. With the reduction of unit water content, bleeding and drying shrinkage will also be reduced. Since fly ash is not highly reactive, the heat of hydration can be reduced through replacement of part of the cement with fly ash.

EFFECTS OF FLY ASH ON HARDENED CONCRETE

Fly ash, when used in concrete, contributes to the strength of concrete due to its pozzolanic reactivity. However, since the pozzolanic reaction proceeds slowly, the initial strength of fly ash concrete tends to be lower than that of concrete without fly ash. Due to continued pozzolanic reactivity concrete develops greater strength at later age, which may exceed that of the concrete without fly ash. The pozzolanic reaction also contributes to making the texture of concrete dense, resulting in decrease of water permeability and gas permeability. It should be noted that since pozzolanic reaction can only proceed in the presence of water enough moisture should be available for long time. Therefore, fly ash concrete should be cured for longer period. In this

sense, fly ash concrete used in under water structures such as dams will derive full benefits of attaining improved long term strength and watertightness.

4. Write short notes on silica fume and also their effect on properties of concrete.

SILICA FUME

Silica fume, also referred to as micro silica or condensed silica fume, is another material that is used as an artificial pozzolanic admixture. It is a product resulting from reduction of high purity quartz with coal in an electric arc furnace in the manufacture of silicon or ferrosilicon alloy. Silica fume rises as an oxidized vapor. It cools, condenses and is collected on cloth bags. It is further processed to remove impurities and to control particle size. Condensed silica fume is essentially silicon dioxide in noncrystalline form. Since it is an airborne material like fly ash, it has spherical shape. It is extremely fine with particle size less than 1 micron and with an average diameter of about 0.1 micron, about 100 times smaller than average cement particles. Silica fume has specific surface area of about 20000 m²/kg, as against 230 to 300 m²/kg that of cement. Since silica fume or micro silica is an important new material, let us see this material in some detail.

- Micro silica is initially produced as an ultra fine undensified powder
- At least 85% SiO₂ content
- Mean particle size between 0.1 and 0.2 micron
- Minimum specific surface area is 15000 m²/kg
- Spherical particle shape. Available forms
- Undensified forms with bulk density of 200-300 kg/cum
- Densified forms with bulk density of 500-600 kg/cum
- Micro-palletized forms with bulk density of 600-800 kg/cum
- Slurry forms with density 1400 kg/cum
- Slurry is produced by mixing undensified micro silica powder and water in equal proportions by weight. Slurry is the easiest and most practical way to introduce micro silica into the concrete mix
- Surface area 15-20 m²/g • Standard grade slurry pH value 4.7

INFLUENCE ON FRESH CONCRETE

Water demand increases in proportion to the amount of microsilica added. The increase in water demand of concrete containing microsilica will be about 1% for every 1% of cement substituted.

INFLUENCE ON HARDENED CONCRETE

Concrete containing micro silica showed outstanding characteristics in the development of strength.

5. Write short notes on GGBS and also their effect on properties of concrete.

GROUND GRANULATED BLAST FURNACE SLAG (GGBS)

Ground granulated blast-furnace slag is a non metallic product consisting essentially of silicates and aluminates of calcium and other bases. The molten slag is rapidly chilled by quenching in water to form a glassy sand like granulated material. The granulated material when further ground to less than 45 micron will have specific surface of about 400-600 m²/kg. Chemical composition Calcium oxide 30-45% Silicon dioxide 30-38% Aluminium oxide 15-25% Ferrous

oxide 0.5-2.0 Specific gravity 2.9 In India, we produce about 7.8 million tons of blast furnace slag. All the blast furnace slags are granulated by quenching the molten slag by high power water jet, making 100% glassy slag granules of 0.4 mm size. The blast furnace slag is mainly used in India for manufacturing slag cement. There are two methods for making blast furnace slag cement. In the first method blast furnace slag is interground with cement clinker along with gypsum. In the second method blast furnace slag is separately ground and then mixed with the cement. Clinker is hydraulically more active than slag. It follows then that slag should be ground finer than clinker, in order to fully develop its hydraulic potential. However, since slag is much harder and difficult to grind compared to clinker, it is ground relatively coarser during the process of inter grinding. This leads to waste of hydraulic potential of slag. Not only that the inter-grinding seriously restricts the flexibility to optimize slag level for different uses. Just as fly ash is used as an admixture in making concrete ground granulated blast furnace slag popularly called GGBS is used as an admixture in making concrete. In other countries it's as an admixture is more common than its use as slag cement. Recently for marine outfall work at Bandra, Mumbai, GGBS has been used as an admixture to replace cement to the tune of 70%. Presently in India, with the growing popularity of RMC, the scope for using GGBS for customer's tailor made requirements should also become popular.

PERFORMANCE OF GGBS IN CONCRETE FRESH CONCRETE:

The replacement of cement with GGBS will reduce the unit water content necessary to obtain the same slump. This reduction of unit water content will be more pronounced with increase in slag content and also on the fineness of slag. This is because of the surface configuration and particle shape of being different than cement particle. In addition, water used for mixing is not immediately lost, as the surface hydration slag is slightly slower than that of cement. Reduction of bleeding is not significant with slag of 4000 sqcm/g fineness. But significant beneficial effect is observed with slag fineness of 6000 sqcm/g and above.

HARDENED CONCRETE:

Exclusive research works have shown that the use of slag leads to the enhancement of intrinsic properties of concrete in both fresh and hardened conditions. The major advantages recognized are • Reduced heat of hydration • Refinement of pore structures • Reduced permeability to the external agencies • increased resistance to chemical attack