

Fly Ash in Cement Concrete

Ordinary Portland Cement (OPC) is a product of four principal mineralogical phases. These phases are Tricalcium Silicate- C_3S (3Cao.SiO₂), Dicalcium Silicate- C_2S (2Cao.SiO₂), Tricalcium Aluminate- C_3A (3CaO.Al₂O₃) and Tetracalcium alumino-ferrite – $C_4AF(4CaO.Al_2O_3Fe_2O_3)$. The setting and hardening of the OPC takes place as a result of reaction between these principal compounds and water. The reaction between these compounds and water are shown as under.

2C ₃ S	+6H →	$C_3S_2H_3$	+3CH
tricalcium silicate	water	C-S-H gel	Calcium Hydroxide
2C ₂ \$	+4H →	C ₃ S ₂ H ₃	+CH
dicalcium silicate	+water	C-S-H gel	Calcium Hydroxide

The hydration products from C_3S and C_2S are similar but quantity of calcium hydroxide (lime) released is higher in C_3S as compared to C_2S .

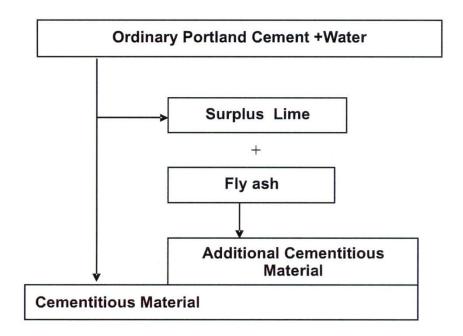
The reaction of C_3A with water takes placed in presence of sulphate ions supplied by dissolution of gypsum present in OPC. This reaction is very fast and is shown as under:

C₃A +3(CSH₂) +26H
$$\longrightarrow$$
 C₃A (CS)₃ H₃₂
tricalcium alluminate +gypsum +water ettringite
C₃A + CSH₂ +10H \longrightarrow C₃ACSH₁₂
monosulphoaluminate hydrate

Tetracalcium alumino-ferrite forms hydration product similar to those of C₃A, with iron substituting partially for alumina in the crystal structures of ettringite and monosulpho-aluminate hydrate.

Above reactions indicate that during the hydration process of cement, lime is released out and remains as surplus in the hydrated cement. This leached out surplus lime renders deleterious effect to concrete such as make the concrete porous, give chance to the development of micro- cracks, weakening the bond with aggregates and thus affect the durability of concrete.

If fly ash is available in the mix, this surplus lime becomes the source for pozzolanic reaction with fly ash and forms additional C-S-H gel having similar binding properties in the concrete as those produced by hydration of cement paste. The reaction of fly ash with surplus lime continues as long as lime is present in the pores of liquid cement paste. The process can also be understood as follows:



Advantages of Fly Ash in Concrete

a. Reduced Heat of Hydration

In concrete mix, when water and cement come in contact, a chemical reaction initiates that produces binding material and consolidates the concrete mass.

The process is exothermic and heat is released which increases the temperature of the mass. When fly ash is present in the concrete mass, it plays dual role for the strength development. Fly ash reacts with released lime and produces binder as explained above and render additional strength to the concrete mass. The unreactive portion of fly ash act as micro aggregates and fills up the matrix to render packing effect and results in increased strength.

The large temperature rise of concrete mass exerts temperature stresses and can lead micro crackes. When fly ash is used as part of cementitious material, quantum of heat liberated is low and staggers through pozzolanic reactions and thus reduces micro-cracking and improves soundness of concrete mass.

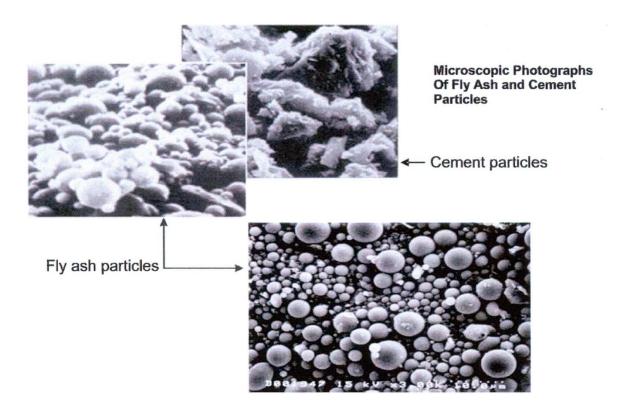
b. Workability of Concrete

Fly ash particles are generally spherical in shape and reduces the water requirement for a given slump. The spherical shape helps to reduce friction between aggregates and between concrete and pump line and thus increases workability and improve pumpability of concrete. Fly ash use in concrete increases fines volume and decreases water content and thus reduces bleeding of concrete.

c. Permeability and Corrosion Protection

Water is essential constituent of concrete preparation. When concrete is hardened, part of the entrapped water in the concrete mass is consumed by cement mineralogy for hydration. Some part of entrapped water evaporates, thus leaving porous channel to the extent of volume occupied by the water. Some part of this porous volume is filled by the hydrated products of the cement paste. The remaining part of the voids consists capillary voids and give way for ingress of water. Similarly, the liberated lime by hydration of cement is water-soluble and is leached out from hardened concrete mass, leaving capillary voids for the ingress of water. Higher the water cement ratio, higher will be the porosity and thus higher will be the permeability. The permeability makes the ingress of moisture and air easy and is the cause for corrosion of reinforcement. Higher permeability facilitate ingress of chloride ions into concrete and is the main cause for initiation of chloride induced corrosion.

Additional cementitious material results from reaction between liberated surplus lime and fly ash, blocks these capillary voids and also reduces the risk of leaching of surplus free lime and thereby reduces permeability of concrete.



d. Effect of Fly Ash on Carbonation of Concrete

Carbonation phenomenon in concrete occurs when calcium hydroxides (lime) of the hydrated Portland Cement react with carbon dioxide from atmospheres in the presence of moisture and form calcium carbonate. To a small extent, calcium carbonate is also formed when calcium silicate and aluminates of the hydrated Portland cement react with carbon dioxide from atmosphere. Carbonation process in concrete results in two deleterious effects (i) shrinkage may occur (ii) concrete immediately adjacent to steel reinforcement may reduce its resistance to corrosion. The rate of carbonation depends on permeability of concrete, quantity of surplus lime and environmental conditions such as moisture and temperature. When fly ash is available in concrete; it reduces availability of surplus lime by way of pozzolanic reaction, reduces permeability and as a result improves resistance of concrete against carbonation phenomenon.

e. Sulphate Attack

Sulphate attacks in concrete occur due to reaction between sulphate from external origins or from atmosphere with surplus lime leads to formation of etrringite, which

causes expansion and results in volume destabilization of the concrete. Increase in sulphate resistance of fly ash concrete is due to continuous reaction between fly ash and leached out lime, which continue to form additional C-S-H gel. This C-S-H gel fills in capillary pores in the cement paste, reducing permeability and ingress of sulphate ions.

f. Corrosion of Steel

Corrosion of steel takes place mainly because of two types of attack. One is due to carbonation attack and other is due to chloride attack. In the carbonation attack, due to carbonation of free lime, alkaline environment in the concrete comes down which disturbs the passive iron oxide film on the reinforcement. When the concrete is permeable, the ingress of moisture and oxygen infuse to the surface of steel initiates the electrochemical process and as a result-rust is formed. The transformation of steel to rust increases its volume thus resulting in the concrete expansion, cracking and distress to the structure.

In the chloride attack, Chloride ion becomes available in the concrete either through the dissociation of chlorides-associated mineralogical hydration or infusion of chloride ion. The sulphate attack in the concrete decomposes the chloride mineralogy thereby releasing chloride ion. In the presence of large amount of chloride, the concrete exhibits the tendency to hold moisture. In the presence of moisture and oxygen, the resistivity of the concrete weakens and becomes more permeable thereby inducing further distress. The use of fly ash reduces availability of free limes and permeability thus result in corrosion prevention.

g. Reduced alkali-aggregate reaction

Certain types of aggregates react with available alkalis and cause expansion and damage to concrete. These aggregates are termed as reactive aggregates. It has been established that use of adequate quantity of fly ash in concrete reduces the amount of alkali aggregate reaction and reduces/ eliminates harmful expansion of concrete. The reaction between the siliceous glass in fly ash and the alkali hydroxide of Portland cement paste consumes alkalis thereby reduces their availability for expansive reaction with reactive silica aggregates.

In a nutshell, it can be summarized that permeability and surplus lime liberated during the hydration of Portland cement are the root causes for deleterious effect on the concrete. Impermeability is the foremost defensive

mechanism for making concrete more durable and is best achieved by using fly ash as above.

Salient advantage of using fly ash in cement concrete

- Reduction in heat of hydration and thus reduction of thermal cracks and improves soundness of concrete mass.
- Improved workability / pumpability of concrete
- Converting released lime from hydration of OPC into additional binding material – contributing additional strength to concrete mass.
- Pore refinement and grain refinement due to reaction between fly ash and liberated lime improves impermeability.
- Improved impermeability of concrete mass increases resistance against ingress of moisture and harmful gases result in increased durability.
- Reduced requirement of cement for same strength thus reduced cost of concrete.

h. Environmental Benefits of Fly Ash in Concrete

Use of fly ash in concrete imparts several environmental benefits and thus it is ecofriendly. It saves the cement requirement for the same strength thus saving of raw materials such as limestone, coal etc required for manufacture of cement.

Manufacture of cement is high-energy intensive industry. In the manufacturing of one tonne of cement, about 1 tonne of CO₂ is emitted and goes to atmosphere. Less

requirement of cement means less emission of CO₂ result in reduction in green house gas emission.

Due to low calorific value and high ash content in Indian Coal, thermal power plants in India, are producing huge quantity of fly ash. This huge quantity is being stored / disposed off in ash pond areas. The ash ponds acquire large



View of tunnel of Delhi Metro Rail Corporation where fly ash has been used

areas of agricultural land. Use of fly ash reduces area requirement for pond, thus

saving of good agricultural land.

Chemistry of Fly Ash

Fly ash is complex material having wide range of chemical, physical and mineralogical composition. The chemistry of fly ash depends on the type of coal burnt in boiler furnace, temperature of furnace, degree of pulverization of coal, efficiency of ESP etc.



Fly ash from NTPC Dadri has been used in building constructed at Gurgaon, Haryana

a. Chemical Composition

The major constituents of most of the fly ashes are Silica (SiO_2), alumina ((Al_2O_3), ferric oxide (Fe_2O_3) and calcium oxide (CaO). The other minor constituent of the fly ash are MgO, Na₂O, K₂O, SO₃, MnO, TiO₂ and unburnt carbon. There is wide range of variation in the principal constituents - Silica (25-60%), Alumina (10-30%) and ferric oxide (5-25%). When the sum of these three principal constituents is 70% or more and reactive calcium oxide is less than 10% - technically the fly ash is considered as **siliceous fly ash** or class F fly ash. Such type of fly ash is produced by burning of anthracite or bituminous coal and possess pozzolanic properties. If the sum of these three constituent is equal or more than 50% and reactive calcium oxide is not less than 10%, fly ash will be considered as **Calcareous fly ash** also called as class C fly ash. This type of fly ash is commonly produced by burning of lignite or sub-bituminous coal and possess both pozzolanic and hydraulic properties.

Siliceous fly ash characteristically contains a large part of silicate glass of high silica content and crystalline phases of low reactivity mullite, magnetite and quartz. The active constituents of class F fly ash is siliceous or alumino-silicate glass. In calcareous or class C fly ash, the active constituents are calcium alumino-silicate glass, free lime (CaO), anhydrate (CaSO₄), tricalcium aluminate and rarely, calcium silicate. The glassy materials of fly ash are reactive with the calcium and alkali hydroxides released from cement fly ash system and forms cementitious gel, which provide additional strength.

b. Physical Properties:

The fly ash particles are generally glassy, solid or hollow and spherical in shape. The hollow spherical particles are called as cenospheres. The fineness of individual fly ash particle rage from 1 micron to 1 mm size. The fineness of fly ash particles has a significant influence on its performance in cement concrete. The fineness of particles is measured by measuring specific surface area of fly ash by Blaine's specific area technique. Greater the surface area more will be the fineness of fly ash. The other method used for measuring fineness of fly ash is dry and wet sieving.

The specific gravity of fly ash varies over a wide range of 1.9 to 2.55.

c. Pozzolanic Properties of Fly Ash

Fly Ash is a pozzolanic material which is defined as siliceous or siliceous and aluminous material which in itself possesses little or no cementitious value, chemically react with Calcium Hydroxide (lime) in presence of water at ordinary temperature and form soluble compound comprises cementitious property similar to cement.

The pozzolana term came from Roman. About 2,000 years ago, Roman used volcanic ash along with lime and sand to produce mortars, which possesses superior strength characteristics & resistances to corrosive water. The best variety of this volcanic ash was obtained from the locality of pozzoli and thus the volcanic ash had acquired the name of Pozzolana.

d. Pozzolanic Activity

Pozzolanic activity of fly ash is an indication of the lime fly ash reaction. It is mostly related to the reaction between reactive silica of the fly ash and calcium hydroxide which produce calcium silicate hydrate (C-S-H) gel which has binding properties. The alumina in the pozzolana may also react in the fly ash lime or fly ash cement system and produce calcium aluminate hydrate, ettringite, gehlenite and calcium monosulpho-aluminate hydrate. Thus the sum of reactive silica and alumina in the fly ash indicate the pozzolanic activity of the fly ash.

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