The Chemico-Mineralogical Characteristics of Fly ash and its impact of Properties of PPC & resultant Concrete

SUMMARY

The country in last decade has gradually seen a growing acceptance for fly ash blended cements. The improved understanding of the beneficial properties imparted by fly ash for both the plastic and hardened stages of blended cement concrete has led to the use of fly ash based cements for some of the major projects in the country. The enhanced durability of blended cement concretes has made it the preferred cement thereby replacing the earlier scepticism regarding its performance.

It is now beyond doubt that in the Tropical climatic condition of the country, Blended cement concrete either with the blending component as a part in cement or alternatively as site blended at the Ready – Mix locations, is the preferred option for a durable civil structures. The choice being governed by the judiciousness of quality control of the properties of the individual components at the manufacturing stage of the blended cement or at the Ready-Mix locations.

The fly ash characteristics such as the combustible content, particle shape & size distribution of the fly ash and its Chemico-mineralogical characteristics i.e its oxide composition, nature & contents of the crystallites and the amorphous glassy phase have been observed to substantially influence the properties of the blended cement and concrete. These properties are dependent on coal characteristics and on the operating conditions of the coal fired thermal plants as also on the collection points of the fly ashes.

The paper discusses the effect of the compositional characteristics of the amorphous glassy phase & the nature of crystalline contents of the fly ash on its enhanced pozzolanic reactivity, the early and later age strength developments of the blended cement and the influence on the properties related to durability of the concrete such as resistance to reinforcement corrosion, resistance to sulphate attack and resistance to expansion due to ASR reaction.

A proper understanding of these interrelations of the fly ash & OPC characteristics is of immense importance for engineering the properties of the blended cements for durable Concrete.

1.0 INTRODUCTION

In the Tropical climatic condition of the country, fly ash based Blended concrete is being presently equivocally accepted as an option for durable concrete structure. The blended concrete being produced either with use of blended cements or through site blending of fly ash in Ready Mix plants. The performance characteristics of the blended concrete would be function of the characteristics of the fly ash used as well as homogenous blending of this lighter and finer component in the blended cement / blended concrete.

At the Research & Consultancy Directorate of The Associated Cement Cos. Ltd., considerable studies have been carried out on the fly ashes of different coal fired thermal plants and of differing compositions and mineralogy to understand the influence of fly ash characteristics on the properties of resultant cements and concrete. The studies indicate that the fly ash characteristics play a significant role in determining the performance of the cements and concrete. An understanding on this interrelationship thus would help in engineering the fly ash properties of the available fly ash so as to produce blended cement / concrete with improved performance.

It is well known fact that the characteristics of fly ash produced in the coal fired thermal plant is a function of nature of the coal, coal comminution system, boiler type & efficiency, fly ash collection ESP fields, loading at which the thermal plant operates etc.. As a result the fly ash characteristics could vary substantially from the same source.
In India the chemico-mineralogical characteristics of dry fly ash produced, has been observed to vary considerably. The mineralogy of fly ash available in the country shows 15 - 30% Mullite, 15 - 45 % Quartz, 1 - 5% Magnetite, 1 - 5% Hematite and around 25 - 35% of amorphous glassy aluminosilicate phase \(^{(1)}\), the fineness of the fly ash from the different thermal plants in the country ranges from 12 % to 50 % residue on 45 microns. The scenario thus necessitates that the available fly ash to be engineered so as to produce consistent Blended Cement.

The paper discusses the effect of the chemico-mineralogical characteristics of the fly ash on its enhanced pozzolanic reactivity, the early and later age strength developments of the blended cement and its influence on the concrete properties related to durability of the concrete such as resistance to reinforcement corrosion, resistance to sulphate attack and resistance to expansion due to ASR reaction.

Use of Fly ash imparts a number of technical benefits to concrete both in the plastic and hardened states. These benefits are derived from both the physical and chemical properties of fly ash such as combustible content, mineralogy the extent of crystallites and amorphous glassy phase and in particular, the finer fraction of fly ash, i.e. those particles that are less than 45µ. These particles act as a solid particulate plasticiser. The sphericity of the particles and fine size of the fly ash, act like ball bearings and as plasticiser, within the concrete, reducing the water requirement for a given workability. A reduction in the water content lowers the permeability and increases strength and durability. In addition the concrete is more cohesive, has a lower rate of bleeding and is less prone to segregation.

Based on the experimentally observed results with Fly ash based Composite Cement & the reported data on the effect of use low lime Class-F fly ash based cement / concrete on the properties of the concrete, the authors make an attempt at evolving an understanding of the influence of the properties and reaction mechanics of the fly ash component in determining the limiting / favoring conditions for improved properties related to the durability of the concrete.

2.0 FLYASH CHARACTERISTICS -INFLUENCES ON PROPERTIES OF CEMENT/CONCRETE

2.1 Combustibles in fly ash:
The carbon or combustible contents of fly ash can be determined by loss-on-ignition (LOI, a measure of carbon mass). It is the carbon’s porous surface area, which determines the capacity of the carbon to adsorb air entrainment admixtures or other chemical admixtures \(^{(2,3)}\). This adsorption is undesirable, as it degrades the freeze-thaw resistance of the concrete because air bubble content is lowered. Most fly ash carbon samples have surface areas much larger than would be expected from the external geometric area of the particles. This is because the carbon particles have a large amount of porosity contributed from the micropores (<20Å), mesopores (20Å-500Å) and macropores (>500Å). Three microscopically distinct carbon types have been reported to be present in high carbon fly ashes i)inertinite, which appears to have been entrained in the particles, prior to melting or combustion ii) isotropic and iii) anisotropic carbon which appear to have passed through the melting stage. It has been observed that the capacity of the carbon in fly ash to adsorb the chemical admixtures is a function of the type of carbon present in the fly ash \(^{(4)}\) and thus it is not always related to the LOI or carbon content of the fly ash.

The porosity in carbons contained in Class-C fly ashes differs from that in Class-F Fly ash \(^{(5)}\) in two important characteristics. First, the carbons in Class-C fly ashes generally contain significantly more microporosity, as revealed by standard nitrogen isotherm data, and the BET surface areas derived therefrom. It is typical for class C carbons to have a surface area in the range of 300 to 400 m\(^2\)/g, whereas the carbons from Class-F fly ashes have surface areas which are typically in the range from about 30 to 70 m\(^2\)/g. Some unusually poor Class-F ashes have carbon surface areas, which approach those in Class-C fly ashes. A second difference in the porosities observed in the carbons from Class-C and Class-F fly ashes has to do with the total amount of porosity per mass of carbon. The carbons from Class-F fly ashes tend to be somewhat less porous than the carbons from Class-C fly ashes.

Presence of high carbon in fly ash thus could result in increased requirement of chemical admixtures, the high-carbon fly ash tend to use more water \(^{(5)}\) thus affect the compressive strength characteristics of the resultant blended cements of fly ash based blended concrete. The presence of carbon content would also darken the cement and concrete as well. It is not recommended to use a high-carbon (> 5 percent) content fly ash, but if used, the dosages of air-entraining agent and other chemical admixtures need to be optimised with the use high carbon fly ash. The Fig.1 depicts the physical properties (Indian standards) of the PPC (Portland Pozzolana Cement) produced with 20% of high carbon (12.5%) and low Carbon (2.5%) fly ash.
2.2 Chemico–Mineralogical properties of fly ash:

In India the chemico - mineralogical characteristics of dry fly ash produced, has been observed to vary. The mineralogy of fly ash has 15 -30% Mullite, 15-45 % Quartz, 1-5% Magnetite, 1-5% Hematite and around 25 - 35% of amorphous glassy alumino - silicate phase.

The ternary phase diagram of SiO$_2$-Al$_2$O$_3$-CaO indicates the relative positions of cementitious materials. As the lime in the fly ashes increases i.e. as the fly ash composition changes from low lime Class-F fly ash to the lime containing Class - C fly ashes , their relative position moves towards the center of the ternary diagram.

In the high lime Class - C fly ashes besides the presence of crystalline hydraulic Calcium aluminates (C$_3$A), the amorphous glassy phase is calcium rich and more reactive than the alumino silicates amorphous glassy phase of Low Lime Class - F fly ashes, which is comparatively latently hydraulic.$^{(6,7,8)}$

The amorphous phase in fly ash is thus the reactive part in fly ash responsible for the secondary hydration and the consumption of free calcium hydroxide during the pozzolanic reactions. The crystalline phases of fly ashes such as Mullite, $\alpha$-quartz, hematite, magnetite are non hydraulic while crystalline calcium aluminate phases present in some of the Class - C fly ashes are cementitious in nature. Thus the chemico-mineralogical composition of the fly ash would determine the reactivity of the fly ashes, it also has a bearing on the concrete properties determining the durability of the concrete structures such as Sulphate resistance, corrosion resistance, resistance to the ASR expansion etc.

2.2.1 Effect of Mineralogical composition of the fly ash:

It would be immensely important to understand that the characteristics of fly ashes are assemblages of particles produced by combustion and melting of individual small particles of ground coal. Each particle is heated and undergoes changes independently of other particles, while passing through the burning zone of the power plant boiler. Its composition reflects that of the inorganic portion of the particular coal fragment, with whatever changes have occurred due to selective vaporization of components and perhaps subsequent surface deposition. In any of these events, the composition of each particle is necessarily different from its neighboring particles and overall chemical analysis is only an average description of the assemblage. Another feature of fly ash is that individual fly ash particle vary in content of crystalline component like quartz, Mullite, Iron oxide, calcium bearing compounds (in Class - C fly ashes) and amorphous or glassy phases.

As discussed above a considerable distinction exists between low lime Class - F fly ash from bituminous coal and high lime Class - C fly ash produced from lignitic or sub-bituminous coal. Depending on composition of the clay mineral constituents, the boiler temperatures, coal fineness used in the boiler, type of the boiler, as well as the efficiency of the heat recuperation systems, the fly ashes produced would show a difference in the glassy amorphous phase contents and the nature and extent of minerals present. This would determine the pozzolanic potential of the fly ash and its resultant effect on the performance characteristics of the cements /concrete.

Fig 3 depicts comparative pozzolanic reactivity of two compositionally similar low lime Class – F fly ashes differing in Mineralogy and amorphous contents. The method used has been evolved at the authors
laboratory for comparing the reactivity of fly ashes \(^{(9)}\). The XRD showing the difference in mineralogy is shown in Fig.4.

2.2.2 Effect of amorphous phase composition of the fly ash:

It has been observed that as the composition of the amorphous phase changes that is as the alumino-silicate amorphous glassy phase becomes calcium rich or as the Si/Al ratio of the amorphous phase changes there is distinct shift observed in the peak maxima of the amorphous hump observed in XRD, i.e there is a shift in the maxima of the amorphous hump towards that of the hump maxima of the granulated blast furnace slag. This could be related to the changes in the composition of the amorphous glassy phase, however some more evaluations need to be done to confirm and quantify this observation.

Fig 5 depicts the amorphous hump maxima of Class C and Class F fly ashes, the figure also shows the nature of the amorphous hump of slag for comparison.

As already indicated that the lime rich amorphous alumino silicate has higher pozzolanic reactivity. Fig 6 depicts the compressive strength characteristics of PPC with 20% Fly ash AP (low lime) and fly ash CAP (high lime amorphous phase composition).

2.3 Particle size Distribution of fly ash:

Fly ash contributes to the performance of the resultant cement and concrete as a pozzolanic additive, as an inert/reactive filler and as an inorganic particulate plasticiser because of the sphericity of and smaller size of its particles.

As discussed earlier the fineness of the fly ash available from a given source varies considerably depending on the ESP field from which it is collected as well as other operational parameters of the thermal plant. On an average the fineness of fly ash in terms of residues on 45 microns ranges from 12 to 50%.
Fig 7 illustrates \(^{(11)}\) the mortar properties with 30 % fly ash of different size fractions, it indicates that the each size fraction of the fly ash tends to behave differently and have different influence on the pozzolanic properties

Studies carried out at the authors laboratory \(^{(12)}\) have helped evolve an understanding of the influence of the particle characteristics and reaction mechanics of the fly ash component and it could be stated with a high degree of confidence that by optimization of the comminution system, an engineered particle size distribution of fly ash can be achieved in the size fractions of the resultant cement(Fig.7) which enhances the pozzolanic activity fly ash and helps improve the performance of the resultant blended cement. Fig.8 &9 illustrates mortar and concrete properties of the Normal PPC and Engineered PPC.

3.0 INFLUENCE OF FLY ASH CHARACTERISTICS ON PROPERTIES OF CONCRETE

The fly ash characteristics discussed earlier results in hardened fly ash based blended concrete.

- **Improved workability and pumpability, Reduced**
- **Lower drying shrinkage** due to the lower water demand of the fly ash.
- **Improved surface finish** : Due to increased fineness and higher cohesiveness of the fly ash based Cements
- **Lower heat of hydration** due to the slower initial rate of reaction of the fly ash, which reduces the peak temperature and the risk of thermally induced cracking.
- **Similar setting time as OPC**: The fly ash blended cements with engineered particle size distribution have similar setting time to OPC, at times the clinker phase composition needs to be marginally modified.
• **Increased long-term strengths** due to the continuing pozzolanic reaction between the fly ash and the lime produced during the hydration of the Portland cement.

• **Reduced porosity and permeability** due to the pore-filling characteristics of the fine fly ash particles and their reaction products. This also leads to denser concrete, which reduces shrinkage, creep and gives greater resistance to chloride ingress and sulfate attack.

• **Increased resistance to sulfate attack and chloride penetration**

• **Increased resistance to alkali aggregate reaction** with fly ash at or above 20% of the total cementitious content.

### 3.1 Effect on workability, water requirement with use of Fly ash based cements

The small size, relative sphericity of the fly ash particles in these cements influence the rheological properties of the cement pastes causing a reduction in the water required or an increase in workability compared with that of an equivalent paste of OPC. This improved workability thus allows a reduction in the amount of water used in the concrete with use of the Pozzolanic Cement (Fly ash based cements) (Fig. 10). As compared to the OPC concrete the reduction of water requirement is 7.5–9.4%. Thus at the lower water content the Pozzolanic cement/concrete would show higher compressive strength.

The Pozzolanic Cement generally shows reduced segregation and bleeding and is more satisfactory than OPC concrete in its pumpability characteristics. At site this aspect needs to be understood and its difference from the general OPC needs to be kept in mind to derive the benefit from this behavior of the Pozzolanic Cement.

#### 3.1.1 Leaching:

As compared to OPC, the hydrated pastes of the fly ash based cement show decreased leachability. The main reasons behind the resistance to leaching are:

- The hydrated cement paste matrix of the Pozzolanic cements show comparatively lower levels free calcium hydroxide than OPC, at same age of hydration, as a part of the liberated free calcium hydroxide liberated from the hydration of the OPC component, reacts with the reactive silica/alumino-silicate of the Fly ash thus reducing the available free calcium hydroxide, Fig.11 illustrates the free calcium hydroxide present in hydrated OPC and PPC at different ages of hydration.

- The hydrated products formed from the secondary hydration reactions fill in the pores in the hydrated matrix thus reducing the permeability and interconnected porosity of the PPC concrete which prevents the percolation of water and thereby decreases the transport of the calcium ions in the hydrated concrete mass, thereby reducing the extent of leaching.

![Fig.10: Water requirement of PPC and OPC for equal workability in concrete](image1)

![Fig.11: Comparative Free calcium hydroxide content of cement pastes at different ages of hydration](image2)

### 3.2 Heat of Hydration:

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The Heat of hydration of an high strength OPC typically is in the range of 60 – 75 cal /g at 3-days and 70 – 85 cal / g at 28 – days the values being dependent on the phase composition of the clinker and the fineness of the OPC. The higher heat of hydration results in increased temperature of the concrete.

Incorporation of fly ash reduces the temperature rise in concrete almost in direct proportion to the amount of Portland cement replaced, partially by delaying heat evolution (due to slower rate of reaction and partially by reducing the total heat evolved. The Fly ash absorption levels in Pozzolanic cement however need to be optimized to balance the compressive strengths and Heat of Hydration thus abating cracking and are thus more suitable for mass concreting. Typically the PPC has a heat of hydration of 50 – 55 cal /g at 3 - days and 65 – 68 cal / g at 28 – days (Fig. 12) . This low heat of hydration of these cements can be used to good advantage during hot-weather concreting.

Fig. 13 gives a comparative temperature of the OPC concrete with that of PPC concrete. The high strength OPC concrete is thus more prone to shrinkage / thermal cracks which would permit moisture and acidic ions like SO₂, CO₂ penetrate into concrete and react with the high levels of free hydrated lime available causing structural instability thus making the OPC concrete more prone to chemical attack.

3.3 Permeability:

Fly ash based blended cements have higher fineness with the fly ash particles distributed in the finer fractions of the cement, the slow pozzolanic reaction produces a more denser impermeable cement paste matrix. Thus in the fly ash based cement concrete, the Maximum Continuous Diameter and Average Pore diameter is lower than that in OPC concrete. The slower hydration of the pozzolanic component continues in the capillary pores resulting into mass precipitation of the gel products into these pores consequently decreasing the permeability of the concrete.

This decreased permeability of the PPC concrete results in a better flexural/compressive strength ratio and reduced tendency towards cracking. It also accounts for the reduced gas diffusion, lower depths of carbonation and there by maintaining alkalinity of the pore solution and reducing the susceptibility of reinforcement to corrosion. The lowered permeability of blended cement concrete also results in decreased tendency of leaching out of lime in these concrete.

The water retention property and lower heat of hydration of the fly ash based Cements help keep the micro climate of the concrete at suitable temperatures of around 30°C and maintain the humidity around 80% in the initial stages of hydration thus facilitating the concrete hardening process. The reduced micro-cracking at the interface in these concrete improves the interface bond as observed in the micro structure.

3.3.1 Comparison of Microstructure of OPC & Blended Cement Concrete

On comparison of both the concretes, the notable feature observed is a dense orientation of Portlandite (calcium hydroxide crystals) at 90° to the aggregate surface. Such type of preferential orientation is almost missing in the M20 fly ash based cement concrete. A dark channel (Fig.14a) is observed at the interface between aggregate and the bulk hydrated cement paste, this is the weak link in the OPC concrete, however, in the blended cement concrete of the same age, the channel width is much reduced and there is development of C-S-H gel over the aggregate surface. The bulk hydrated cement paste is also relatively denser as
compared to OPC concrete and the compaction increases with age of hydration. The comparative microstructure is illustrated in Fig.14a & Fig.14b.

3.4 Corrosion Resistance:

The concrete cover over the reinforcement should be sufficiently thick and impermeable to provide adequate resistance to corrosion. The protective effect of concrete is both physical and chemical and functions in three ways

- It provides alkalinity in the vicinity of the steel.
- It provides physical & chemical barrier to ingress of moisture, oxygen carbon dioxide, chlorides and other aggressive chemicals.
- Provides electrical resistivity around the steel.

The corrosion process of the reinforced steel can be described in a simplified way (12) by an equivalent electrical circuit and the corrosion current \( I_{\text{corr}} \) can be expressed as:

\[
I_{\text{corr}} = \frac{U_c - U_a}{R_a + R_c + R_L}
\]

\( I_{\text{corr}} \) = Corrosion current, \( U_c \) = Open circuit potential at cathode, \( U_a \) = Open circuit potential at anode, \( R_a \) = anodic polarization resistance, \( R_c \) = cathodic polarization resistance, \( R_L \) = electrolyte resistance of concrete.

### Table 1: Corrosion Causing Reactions in concrete

<table>
<thead>
<tr>
<th>Agents</th>
<th>Reactions</th>
<th>Resultant effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>Anode: ( 2\text{Fe}(s) \rightarrow 2\text{Fe}^{++} + 4\text{OH}^- )</td>
<td>Corrosion of steel. Formation of protective passive film of nano-meter thickness of iron hydroxide/oxides.</td>
</tr>
<tr>
<td></td>
<td>Cathode: ( 2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^- \rightarrow 4\text{OH}^- )</td>
<td></td>
</tr>
<tr>
<td>Chloride</td>
<td>A) Without oxygen at anode ( \text{Fe}(s) + 2\text{Cl}^- \rightarrow (2\text{Fe}^{++} + 2\text{Cl}^-) + 2\text{e}^- )</td>
<td>Chloride ions break the passivating film formed on steel.</td>
</tr>
<tr>
<td></td>
<td>B) In presence of oxygen at anode ( 6(\text{Fe}^{++}+2\text{Cl}^-) + \text{O}_2 + 6\text{H}_2\text{O} \rightarrow 2\text{Fe}_3\text{O}_4 + 2\text{H}^+ + 2\text{Cl}^- )</td>
<td>External penetration causes differential concentration and sets up micro-cell. Presence of micro-cells increases electrical conductivity.</td>
</tr>
<tr>
<td>C) Attack on hydrated pastes</td>
<td>( \text{Ca(OH)}_2 + \text{MgCl}_2 \rightarrow \text{CaCl}_2 + \text{Mg(OH)}_2 )</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \text{CaO,Al}_{2}\text{O}_3 + \text{CaCl}_2 + \text{H}_2\text{O} \rightarrow \text{Friedel salt} )</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \text{CaO,Al}_{2}\text{O}_3,\text{CaCl}_2,10\text{H}_2\text{O} )</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Friedel salt( \rightarrow \text{Ettringite (in presence of CaSO}_4) ) C-S-H + Mg</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C-M-S-H</td>
<td></td>
</tr>
<tr>
<td>CO(_2)</td>
<td>( \text{Ca(OH)}_2 + \text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} )</td>
<td>Reduces alkalinity, Releases more water, increases risk of corrosion.</td>
</tr>
<tr>
<td>Sulphates</td>
<td>Discussed under resistance to sulphate attack</td>
<td></td>
</tr>
</tbody>
</table>

### Table 2: Resistivity of concrete v/s Corrosion probability

<table>
<thead>
<tr>
<th>Resistivity (ohm-cm)</th>
<th>Corrosion probability</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt; 20000</td>
<td>Negligible</td>
</tr>
<tr>
<td>10000 to 20000</td>
<td>Low</td>
</tr>
<tr>
<td>5000 to 10000</td>
<td>High</td>
</tr>
</tbody>
</table>

### Table 3: State of corrosion as per ASTM C - 876 - 91

<table>
<thead>
<tr>
<th>Potential (mV SCE)</th>
<th>State of Corrosion</th>
</tr>
</thead>
<tbody>
<tr>
<td>More negative than -270</td>
<td>Active</td>
</tr>
<tr>
<td>More positive than -220</td>
<td>Passive</td>
</tr>
<tr>
<td>-220 to -270</td>
<td>Active or passive</td>
</tr>
</tbody>
</table>
The Icorr, i.e., the rate of corrosion (µm/year) would show an increase if either or both R_a & R_L decrease. The R_a (anodic resistance) is due to the passive film of Fe – hydroxide / oxides during the process of corrosion, the R_a decreases if this passive film is broken. Presence of chlorides decreases the R_a as it depassivates the steel (Table-1) and forms metallic hydroxides / oxides depending on the pH and availability of oxygen and water. These products increase the PBR ratio and results in expansive pressure. The Pilling & Bedworth ratio is the ratio of metal oxide volume to metal volume and used to predict whether or not the scale that forms will protect a metal from further oxidation. A PBR ratio > 1.4 is sufficient to cause cracking & spalling.

The electrolytic resistance of concrete (R_L) (concrete resistivity) is directly relates to the corrosion current (Hope & Alan (13)). Table 2 gives general guidelines on resistivity values and probable corrosion risk in concrete structures.

Studies carried out (14,15) indicates that onset of corrosion takes place when molar ratio [Cl⁻]/[OH⁻] crosses 0.6. In order to obtain a qualitative information on state of corrosion ASTM C – 876 – 91 gives the half cell potentials for Std Calomel Electrode (SCE) under standard conditions (Table 3) the values are however only a guideline, the potentials can vary in a wide range depending on the moisture of the concrete.

The parameters of concrete which directly or indirectly determine the rate of reinforcement corrosion are:

- Pore structure & permeability
- Chloride /oxygen diffusion coefficients
- Chloride binding capacity
- Electrical resistance parameters such as density and resistivity of concrete.

Tests carried out (15) on low lime Class-F fly ash based Blended cements with ~ 30 % fly ash, indicate that although the total porosity is more in the 90-day hydrated blended cement as compared to the OPC, the pores in the former are finer than the OPC. The average pore radius of the Fly ash based cement was observed to be 166 °A as against 240 °A in the OPC. A comparison of coefficient of permeability of water and chloride diffusivity in OPC and blended cements is shown in Table-4;

<table>
<thead>
<tr>
<th>Cement type</th>
<th>Coefficient of Permeability (10⁻¹¹ cm/sec) (Age : 180 days)</th>
<th>Av. pore Radius (°A) (Age : 90 days)</th>
<th>Chloride diffusivity (10⁻⁹ cm/sec) (Age:90 days)</th>
<th>Electrical resistivity (k ohm-cm) (Age:120 days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPC</td>
<td>8.70</td>
<td>240</td>
<td>24.5</td>
<td>13.14</td>
</tr>
<tr>
<td>Fly ash based Blended Cement</td>
<td>1.77</td>
<td>166</td>
<td>4.1</td>
<td>29.08</td>
</tr>
</tbody>
</table>

The difference in the characteristics of the OPC and Fly ash based cements / concrete is attributable to the compacted, dense microstructure of the cement paste matrix of the fly ash blended cements. The lesser permeability of the fly ash based cement / concrete prevents leaching of lime there by maintaining the concrete less porous and less permeable to oxygen and penetration of chlorides. The fly ash based cement/ concrete exhibit lower coefficients of chloride diffusion compared to Portland Cements. The imperviousness of the blended concrete prevents carbonation to the depths of the steel reinforcements there by maintaining the alkalinity in the vicinity of the steel rendering it passive from corrosion.

The presence of fly ash also reduces the free chlorides in the pore solution, as the fly ash hydrated products tend to bind the free chlorides (Friedel salt formation). The binding of the free chlorides is however a function of the C_3A content of the cement clinker used for the blended cement. The presence of higher levels of Friedel salt can be identified by DTA analysis.
Table- 5 illustrates the unbound chlorides in pore solution in plain and fly ash blended cements when treated with different levels of chlorides. It has been observed that use of 30% fly ash reduces the free OH⁻ ions in the pore solution from an average value of 260 mM/L (pH=13.41) to an average value of 205 mM/L (pH=13.31) for the low C₃A cement while for the high C₃A cement solution, from an average value of 520 mM/L (pH=13.72) to an average value of 315 mM/L (pH=13.50) at all the chloride levels, resultantly the Cl⁻/OH⁻ ratio is also reduced. The effect of pore refinement, reduced chloride/oxygen diffusivity, reduced chloride mobility, is evident in the electrical resistance and the corrosion observed in the concrete. As expected the electrolytic resistance of concrete increases with time and fly ash incorporation levels. This is finally reflected in the corrosion initiation & Corrosion rate observed in the blended cement concrete. (Fig.15 & 16).

<table>
<thead>
<tr>
<th>% C₃A in Cement clinker</th>
<th>Cement Type</th>
<th>% Total chlorides addition</th>
<th>% Cl⁻ in Pore solution</th>
<th>Unbound chlorides (as %of Total Cl⁻)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>OPC</td>
<td>0.6</td>
<td>74.4</td>
<td>50.7</td>
</tr>
<tr>
<td></td>
<td>FA-cement</td>
<td>0.6</td>
<td>44.1</td>
<td>33.9</td>
</tr>
<tr>
<td>2.43</td>
<td>OPC</td>
<td>1.2</td>
<td>94.1</td>
<td>61.8</td>
</tr>
<tr>
<td></td>
<td>FA-cement</td>
<td>1.2</td>
<td>64.4</td>
<td>49.3</td>
</tr>
<tr>
<td></td>
<td>OPC</td>
<td>0.6</td>
<td>18.1</td>
<td>11.6</td>
</tr>
<tr>
<td></td>
<td>FA-cement</td>
<td>0.6</td>
<td>11.7</td>
<td>8.3</td>
</tr>
<tr>
<td></td>
<td>OPC</td>
<td>1.2</td>
<td>38.4</td>
<td>24.4</td>
</tr>
<tr>
<td></td>
<td>FA-cement</td>
<td>1.2</td>
<td>33.5</td>
<td>23.3</td>
</tr>
</tbody>
</table>

The improvement in the corrosion resistance property with ground (Mechanically activated) fly ash has been reported by Saraswathy et al (16) (CECRI Karaiudi). Indicating the role of particle characteristics of fly ash in increasing the corrosion resistance of the steel reinforced concrete. In inter-ground fly ash based blended cements such a mechanical activation of the fly ash is achieved during the intergrinding process. As compared to OPC concrete, the fly ash based cement concrete, have higher elastic Modulus, higher Modulus of rupture and split tensile strengths (Fig.17 & 18). These properties would help over come the stresses caused and effectively increase the crack initiation time by corrosion.
3.5 Resistance to sulphate attack:

The hydration of tri-calcium aluminate (C₃A) in Portland cement in presence of solubilised sulphate ions (from gypsum) results in formation of ettringite which is harmless as the concrete is still in semi-plastic state.

\[
\text{C}_3\text{A} + 3\text{CSH}_2 + 26\text{H} \rightarrow \text{C}_6\text{AS}_3\text{H}_32
\]

Calcium aluminate Gypsum Water Ettringite

Sulphate attack is observed when structures are exposed to sulphatic environments such as sulphate bearing soils or ground waters causing an increase in volume of cement paste in concrete or mortar due to chemical reaction between hydration products of cement and solution containing sulphate ions.

The reactions take place in either or both of the following ways

\[
\text{Ca(OH)}_2 + \text{Na}_2\text{SO}_4.10\text{H}_2\text{O} \rightarrow \text{CaSO}_4.2\text{H}_2\text{O} + 2\text{NaOH} + 8\text{H}_2\text{O}
\]

Calcium Sulphates Gypsum

\[
4\text{CaO.Al}_2\text{O}_3.19\text{H}_2\text{O} + 3(\text{CaSO}_4.2\text{H}_2\text{O}) \rightarrow 3\text{CaO.Al}_2\text{O}_3.3\text{CaSO}_4.32\text{H}_2\text{O} + \text{Ca(OH)}_2
\]

Ca-aluminate Hydrates Gypsum Ettringite

The formation of gypsum and/or ettringite causes expansion and cracking or softening of the concrete.

The sulphate attack can be from calcium, sodium, potassium or magnesium sulphates. The Magnesium sulphate has a more damaging effect because it leads to decomposition of the C-S-H as well as calcium hydroxide and hydrated calcium aluminate hydrates eventually forming hydrated magnesium silicates, which has no cementing properties.

The sulphate attack involves the calcium hydroxides and C₃A and also depends on the effective permeability of the concrete to sulphate ions. Experimental data indicates that fly ash based cement concrete, especially those made with low calcium, Class-F fly ash are more resistant to sulphate attack than the PPC concrete made with high calcium Class - C fly ash and that the sulphate resistance is also a function of the fly ash incorporation levels. A relation evolved between the CaO/\text{SiO}_2 ratio of fly ash and sulphate resistance of the concrete is shown in Fig.19 \(^{(17)}\). In 1980 Dunstans \(^{(18&19)}\) summarized the results of studies on sulphate attack of fly ash concrete and proposed the use of resistance factor ( \( R \)).

\[
R = \frac{(C-5)}{F}
\]

where C is the CaO and F is the Fe₂O₃ contents of the fly ash.

The selection of fly ashes (25 % absorption levels ) in terms of ‘R’ limits for sulphate resistant concretes are as follows:

<table>
<thead>
<tr>
<th>‘R’ Limits (Fly ash)</th>
<th>Sulphate resistance *</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 0.75</td>
<td>Greatly improved</td>
</tr>
<tr>
<td>0.75 – 1.5</td>
<td>Moderately improved</td>
</tr>
<tr>
<td>1.5 – 3.0</td>
<td>No significant Change</td>
</tr>
<tr>
<td>&gt; 3.0</td>
<td>Reduced</td>
</tr>
</tbody>
</table>

* Relative to ASTM Type II cement at W/C ratio of 0.45
Fig. 20 Illustrates the sulphate resistance of the concrete with fly ash of different ‘R’ values.

These results indicate that the Low Lime class – F fly ashes available in country are chemico-minerologically better suited for improved sulphate resistance of the resultant concrete.

3.6 Resistance to Alkali Silica Reaction (ASR):

Alkalis in hardened concrete react with the reactive aggregates forming high volume gel products. Although the actual reactions are still to be understood completely the common accepted formations are summarised below:

Reactive silica + alkalis $\rightarrow$ alkali silicates

For Dolomitic Aggregates:

Reactive Carbonate + Alkalis $\rightarrow$ Dedolomatisation $\rightarrow$ Alkali Carbonates + Magnesium Hydroxide + Calcium Carbonate

The volume expansion linked with the formation of alkali silicate hydrate gels or the de-dolomatisation induces expansion and severe deterioration of concrete.

The aggregates and their mineralogical constituents known to react with alkali include the following:

- Silica materials – Opal/ Chalcedony, Tridymite and Crystobalite
- Zeolites especially Heulandite
- Glassy to cryptocrystalline rhyolites, dacites andesites and their tuffs
- Certain Phyllites

The factors that effectively minimize the ASR reactions in blended cement concrete can be summarised as follows:

- Use of fly ash in concrete show reduced expansion compared to control OPC concrete (Fig. 21).
- Low C/S ratio in the C-S-H fixes the alkalis through adsorption or solid solutions there by decreasing the alkali ion concentrations in the pore solution. Fig.22 illustrates the relation between the C/S ratio of C-S-H and % alkali retained in the C-S-H.
- C-S-H formed in the secondary reaction of fly ash & Ca(OH)$_2$ fills up the pores in the hardened cement paste matrix suppresses the movement of in pore solution.
- Use of fly ash changes the zeta potential making the surface of the pores in hardened paste positively charged there by suppressing the movement of the alkali ions in the pore solution.
- Composition of fly ash i.e CaO content of fly ash (Fig.23).

Generally fly ashes with higher alkali or CaO contents are less effective in controlling the expansion due to ASR and consequently have to be used at higher replacement levels (Fig 24 illustrates the relation between the minimum safe replacement level and CaO+2Na$_2$O/SiO$_2$ ratio of fly ash).

Use of Low lime Class – F fly ash available in the country is compositionally more suited for resistance of concrete to ASR reaction. It may be noted here that minimum safe levels of fly ash thus would vary
depending on the nature & reactivity of aggregates, available alkalis in concrete (from Cement), exposure conditions of the concrete and finally on the composition of Fly ash used.

CONCLUSIONS:
The aspects discussed in the paper illustrates that the low Lime Class-F fly ash available in the country are compositionally most suited for use in Blended cement/blended concrete for improving the resistance of the concrete to deterioration due to corrosion of steel reinforcements, Sulphate attack and expansion due to ASR reaction.
A proper understanding of the influences of the fly ash characteristics and adoption of appropriate methods for reducing variability, improving particle characteristics, would help to engineer the properties of the resultant blended cement for Durable Civil structure.

REFERENCES:


14. Compton F.R and Macnis C. Field trials of fly ash based concrete Ontario Research News (Jan- March ) 18 - 21


