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# DURABILITY OF CONCRETE: HOLISTIC ROLE OF FLY ASH

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## PREAMBLE

The definitions for performance and durability got redefined with advancements in concrete technology. At one point of time strength of concrete used to be considered as criterion for durability. To meet this criterion high grade Ordinary Portland Cement (OPC) is preferred and, in the process, very little attention is paid to pronounce specifications under durability criteria, without exception to Indian codes. In reality, high grade OPC proved as detrimental for durability in comparison to that of blended cements.

According to ACI committee 201, durability of Portland cement concrete is defined as its ability to resist weathering action, chemical attack, abrasion, or any other process of deterioration. A durable concrete is the one that is dimensionally stable and retains quality and serviceability over ageing through varied environmental conditions.

Ever since durability has drawn the attention of concrete technologists globally, fly ash has become a value added admixture and, became almost an indispensable input for concrete in many world-class constructions. To elaborate this fact, one needs to retrospect to the material science of the past. The age-old low grade cement in coarse particle size was associated with two sound performing features:

1) Heat Bank and 2) Lime Bank

Both heat and lime used to be available for concrete on sustainable basis for formation of hydrated mineralogy and microstructure refinement progressively with ageing. When the construction world shifted from low grade cements to high grade cements, problems have cropped up in concrete quality triggered off by profuse heat of hydration and rapid release of lime, both at very early ages. After investigations on many admixtures, Fly ash was found to be the unique cost effective admixture not only to counteract the problems of concrete deterioration but also to improve the durability and enhance the service life.

Despite impressive developments globally, upholding fly ash as the performance improver, these virtues and sound engineering techniques in tapping the fly ash have not sufficiently percolated in India. This needs extensive enlightenment campaign and dispersion of knowledge.

## FLY ASH-THE POZZOLAN

The potential of pozzolans was tapped only through the addition of lime (or calcareous binder) to achieve a set product of water impermeable characteristics. Here it is a point of observation that while lime can harden and set independently, pozzolan does not possess such property independently and is solely dependant on lime to attain cementitious characteristics. Nevertheless, lime-pozzolanic combinations yield superior hydrated mineralogy when compared to that of plain lime. With this supremacy, lime-pozzolan binders had become popular towards versatile applications in constructions.

Lime-pozzolan mortars were used as building mortars in many parts of Europe and enjoyed a great credibility. It is very much obvious through the claim of Vitruvius in his *'Treatise on Architecture'* where he mentioned the use of lime-pozzolan mortars in all kinds of structures, with particular reference to maritime constructions. This aspect gets strengthened further when experience on 2000-year-old structures uphold durability aspects of lime-pozzolan mortars.

Fly ash is qualified and cost effective pozzolan. When pulverised coal is burnt, each coal particle undergoes reactions independently; variation in specified combustion conditions to which each coal particle is exposed to and the efficiency of combustion that is subjected to makes fly ash heterogeneous material. Hence, chemical composition of fly ash depends on the source of coal and also on operating parameters of the boilers, thus varying from source to source and within the same source also. Loss on Ignition (LOI), majorly the measure of unburnt carbon, is one of the important criteria. With use of pulverised coal and efficiency in combustion systems of thermal plants, LOI is very much controlled in most of the fly ashes. Fly ash with unburnt carbon at $\leq 5\%$ is not detrimental in principle but when the same is used in concrete, water cement ratio goes up and demand increases for air entraining agents and plasticisers.

Fly ash has a chemical composition akin to burnt clays those have high alumina and iron oxides. Nevertheless, fly ash is highly a material of complex compounds where no two fly ashes resemble each other. The general constituents of fly ash are glass and crystalline components. Silica and alumina are chiefly contained in glass, formulated into solid or hollow spherical particles, with some iron oxide, lime, alkalies and magnesia. In coals of high sulphur, $SO_3$ is present either as anhydrite or as gypsum or even associated with glass.

The solidification in the path of traveling results in condensation of powderous mass into particles, which are then, separated from flue gases through different collection techniques. Fly ash particles attain spherical or near spherical shape when condensed from molten clay compounds from high temperature zone. The particle sizes vary from 1 μ to 150 μ for ASTM Class F fly ashes and 1 μ to 15 μ for ASTM Class C fly ashes. The formation of plerospheres and cenospheres due to the collision between particles at high temperature is not very uncommon. While cenospheres are completely hollow, plerospheres are filled with smaller cenospheres. When collected after segregation, fly ash has fineness in wide range of 2000 to 9000 $cm^2/gm$.

As far as constitution of fly ashes throughout the globe, the principal constituents are $SiO_2$ and $R_2O_3$. Their combined quantity varies from 50% to 85%. These constituents render the pozzolancity to the fly ash based on their reactive portion. Thus the chemical analysis of a fly ash does not reflect its pozzolanic characteristics. Fly ash serves dual purpose that is complementary to each other while supplementing cement; one by converting the surplus hydrated lime of cement into productive mineralogy; second by contributing for microstructure refinement towards durability improvement. There are certain fly ashes, which do contain lime characteristically. It is to identify them; ASTM C618 has accorded classification to fly ash as Class C and Class F. While the fly ash containing equal to or more than 10% lime is classified as Class C, the one containing less than 10% lime is classified as Class F. Class C fly ash is generally produced from lignite or sub-bituminous coals and Class F fly ash from bituminous and anthracite coals.

## LT & HT Fly ash

In India, almost all the boilers generate Class F fly ash, except in a couple of pockets in South India and extreme West where Class C fly ash is generated. But with reference to Indian operations, the authors have observed two more distinct behaviours of fly ash based on boiler operating parameters that has prompted them to accord further classification as LT (low temperature) fly ash and HT (high temperature) fly ash. The fly ash generated out of boilers operating at combustion temperatures of 750-850 $^{o}$C is classified as LT whereas the same generated at combustion temperatures of 900-1400 $^{o}$C in high capacity boilers is classified as HT.

It is observed that, despite parallel constituent level, both LT and HT fly ashes behave distinctly different. The reactive $SiO_2$ and $Al_2O_3$ are available as metakaolnite phases in LT fly ash to render rapid hydration in the presence of lime, with particular reference to $Al_2O_3$. The same constituents attain molten state and form as cenospheres in HT fly ash with relatively slow reactivity. The unburnt carbon at 4-6% is high in LT as against 1-2 % in HT. There is a concept that higher the lime absorption, higher the reactivity strength, which is not always true. Studies show that the strengths attained in fly ash + lime mixes using the same quantity of lime as reflected in LAF has no linear relation with the latter. This is evident from a study on typical LT and HT fly ashes as shown vide Table below:

LAF Vs COMPRESSIVE STRENGTHS ON SOME TYPICAL FLY ASHES (MPa)

| | Fineness $cm^2/gm$ | LAF | 7-day | 28-day |
|---|---|---|---|---|
| HT1 | 5470 | 0.34 | 2.2 | 6.3 |
| HT2 | 4100 | 0.33 | 3.3 | 4.9 |
| LT1 | 3100 | 0.22 | 9.0 | 17.0 |
| LT2 | 3700 | 0.26 | 11.0 | 15.8 |

Fly ash is generally judged of its quality in terms of strength. Fly ash is studied for its pozzolanic characteristics in two approaches; Lime Reactivity Strength (LRS) and PAI. IS:3812-1981, Specifications for fly ash for use as pozzolan and admixture, accords two grades to fly ash based on LRS. Grade I is identified with minimum 4 MPa whereas fly ash with lower strength is categorised as Grade II. The same code has also specified PAI as another yardstick. The LRS given for these grades generally does not correlate with pozzolanic activity index of 0.8. It is observed that certain fly ashes registering low LRS prove better for PAI and certain other fly ashes recording good LRS.

LRS Vs PAI FOR CERTAIN FLY ASHES (MPa)

| | LRS (MPa) | PAI (%) |
|---|---|---|
| LT (a) | 7.9 | 95 |
| LT (b) | 4.1 | 77 |
| HT (a) | 5.8 | 104 |
| HT (b) | 5.6 | 74 |

The investigations have revealed very interesting issues. The LRS reflects the strength of lime-pozzolanic reactions that are purely manifested out of calcium silicate hydrates. Though calcium aluminate hydrates form in lime-pozzolanic reactions, they do not contribute for strength. Whereas, the same mineralogy gets converted to calcium sulpho aluminate hydrates, drawing gypsum from cement in the study of PAI, to contribute for its part of additional strength. This aspect further explains that a fly ash with high reactive $Al_2O_3$ may exhibit poor LRS but good PAI. Thereby the authors uphold that the study on LRS has more relevance where fly ash is used in association with lime. In case of blending fly ash with cement, PAI may be taken as the ultimate yardstick. Most of the developed countries rely on PAI ignoring the lime reactivity strength.

## THE CEMENT CHEMISTRY

As explained by many, the rapid setting and strength gain characteristics of OPC pushed the pozzolanic binders into oblivion. The need for construction speed, more so after World War II, lead to the development of high grade cements to render high early strengths, basically by increasing $C_3S$, as indicated by the Table below:

ASTM TYPES OF CEMENT Vs MINERALOGY

| Type | ASTM Designation | Silicate phase (%) | | Surplus lime (%) *based on* | | Total surplus lime |
|---|---|---|---|---|---|---|
| | | $C_3S$ | $C_2S$ | $C_3S$ | $C_2S$ | |
| I | General purpose | 50 | 24 | 19.5 | 4.32 | 23.82 |
| II | Moderate sulphate resistant- Moderate heat of hydration | 42 | 33 | 16.38 | 5.94 | 22.32 |
| III | High early strength | 60 | 13 | 23.40 | 2.34 | 25.74 |
| IV | Low heat | 26 | 50 | 10.14 | 9.00 | 19.14 |
| V | Sulphate resisting | 40 | 40 | 15.60 | 7.20 | 22.80 |

With increase in $C_3S$, surplus lime also increases. This is what happens with reference to 43 and 53 grades of OPC where $C_3S$ increases with grade. Hence, from $C_3S$ point of view, higher the grade of cement, higher the vulnerability of concrete for surplus $Ca(OH)_2$ at early ages, leading to distress. In addition to this change, the fineness was also increased, during the same period, as another tool to derive high grade strengths. But, all these changes have resulted in ‘high early strength cements’ rather than high strength cements. This is because, the major quantum of net potential of chemical reactions and strength in a cement are tapped at early ages leaving little room for late age chemistry and strength gain, thus inviting problems of distress rather than soundness. If a choice is given, it is preferable to aim the high grade through enriching $C_3S$ mineralogy rather than increasing the fineness.

The structures, built using high grade cements during 40s to 60s, have yielded to premature distress within 10 to 20 years, proving the purpose and synthesis of high grade cements undependable for durability. The introspection that took place in the melee lead to the comparison of OPC with age old pozzolanic chemistry that, in turn, lead to the conclusion that strength and durability are independent issues. A concrete of high strength alone may not offer durability to the concrete. The durability of age-old structures with low strength grade of concrete out of lime-pozzolanic binders lent credence to delink durability from strength.

Much earlier to the crisis of early distress of concrete, the initiatives to use fly ash and blast furnace slag in structural concrete have helped the renaissance in concrete technology.

Before getting into the reactions of fly ash with cement, it is essential to go through the chemistry and hydration of OPC, which is a product of four principal mineralogical phases viz.

$3\,CaO.\,SiO_2$ - $C_3S$ … Tricalcium Silicate
$2\,CaO.\,SiO_2$ - $C_2S$ … Dicalcium Silicate
$3\,CaO.\,Al_2O_3$ - $C_3A$ … Tricalcium Aluminate
$4\,CaO.\,Al_2O_3.\,Fe_2O_3$ - $C_4AF$ … Tetracalcium Aluminoferrite

Upon adding water, the anhydrous mineralogy gets dissociated as CaO, $SiO_2$, $Al_2O_3$ and $Fe_2O_3$ for associating into hydrated mineralogy. Setting is the interface for this transformation.

## Setting and hardening of cement

In the first phase, as a result of the hydrolysis of the calcium silicates, a super saturated solution of calcium hydroxide is formed when water is added to the cement. Sulphate and alkali ions, as well as small amounts of silica, alumina and ferric oxide are also present in the solution. Calcium hydroxide and ettringite precipitate out and a dense C-S-H gel coating is formed on the cement grains. This coating and ettringite coating on $C_3A$ grains retard further hydration and explain the existence of a dormant period, i.e., the period of relative inactivity lasting for one to two hours. During this dormant period the paste remains ***plastic and workable***. The end of the dormant period can be identified as ***initial set***. This is attributable to the break up of C-S-H coating and the resultant continuation of hydration process. Due to the osmotic pressure the gel coating gets ruptured, exposing the cement grain, wherein hydration is resumed and setting takes place. Consequently, as the hydration proceeds, the hydration products gradually fill in the spaces of the cement grains.

Points of contact are formed causing stiffening of the paste. At some later stage, the concentration of hydration products and the resulting concentrations of points of contact restrict the mobility of the cement grains to such an extent that the paste becomes rigid, reaching the state of ***final set*.** The volume of the hydration products, through the process of crystallisation and matrix formation, is more than twice that of the anhydrous cement. The dissociation and association of mineralogy continues as long as the moisture is available and release of lime continues in the matrix. This activity was sustainable for longer ages in low grade cements, accredited for their durability, and in contrast to accelerated reactions in high grade cements for relatively shorter periods.

## METABOLISM OF CEMENT

There is close parallel of nucleotides of DNA in genetic code, consisting of four bases, adenine (A), thymine (T), Guanine (G) and cytosine (C), with that of four principal mineralogical phases of cement.

The cell division and further formation is the genetic activity to cater the needs of life, which may be compared to the dissociation of anhydrous phases, in the presence of moisture, for formation of hydrated mineralogy in cement through associations and progressive crystal growth.

The cell of life system and the particle of cement are the power points for growth. A cell is intensely active for growth as much as the cement particle for growing into hydrated phases. For reproduction, the cell derives its energy within itself (from mitochondria, which avails the food a person eats and burns it to produce energy and provide it to the cell whenever it is needed). For mineralogical growth, the cement particle draws its energy from the endothermic heat bank, formed during clinkerisation. Here comes a note of observation. When the product was synthesised, OPC was specified relatively with coarser particle size that used to hydrate slowly, making available the heat of hydration (from the endothermic heat bank) for a longer period, whenever there was availability of moisture. Thus the growth of hydrated mineralogy was destined to be a long term phenomenon with low grade OPC. But in the process of high early strengths, the fine particles of cement trigger off higher rate of hydration and heat liberation, spending the heat bank lavishly much before the need, inviting premature deterioration.

## Lime in OPC: The Natural Embodiment

Nature has bountifully blessed the mankind with specified material science towards safe and sustainable practice. But the nature’s course is disturbed in the anxiety of varietal needs, bringing, in its melee, numerous vows to the mankind. Lime has a much specified role for the application of cement in a secured way. However, as much as the ‘nature’ is punctured environmentally to satiate the needs of mankind, cement system is also abused to meet the need i.e., the ‘high early strength’. In the process, the mineralogy and fineness are manoeuvred and the ‘protective action of lime’ is ignored.

Though remedial steps are identified in blended cement route, many a time arguments raised about exhaustion of lime and threat to passivity film through reduction of pH on account of formation of secondary mineralogical hydrates. If the cement chemistry is not realised in holistic perspective one may tend to come to such conclusions. In this context, it is quite interesting to learn the intricate role of lime in cement at the pre-hydration and post-hydration stages:

- Lime exists in cement but it is not in free-state unless the cement is subjected for hydration.
- When cement hydration takes place progressively, lime is released gradually out of which major portion gets into hydrated mineralogy and some portion remains as hydrated lime to maintain pH, which also triggers off the formation of further hydrated mineralogy. The surplus hydrated lime also maintains the stability of hydrated calcium silicates, aluminates and ferrites in the system.
- Because of progressive release, the hydrated cement system is assured of lime till late ages, required to maintain pH in RCC.
- By 'fine grinding' the cement, in the target of early strength, rapid hydrations are induced, affecting the nature's locus for progressive hydration and sustained availability of lime till late ages. This is one of the many reasons for the shorter life of concretes made of so called high (early) strength cements in contrast to the long lived concretes made of coarser cements of yester decades.

## Lime for Passivity film

The role of lime to render passivity film to reinforcement needs to be realised in right perception. Otherwise, one may misunderstand the lime-exhaustion scenario in pozzolanic cement chemistry and raise debates, as have been witnessed already.

Many a time arguments are promoted that the passivity film gets affected if the total surplus lime is engaged by CCM. However, it is to be realised that a surplus lime of about 75 kg is available in a typical concrete containing OPC at 300 kg/$m^3$, whereas a nominal quantity of 24 gm is sufficient enough to maintain a pH at not less than 11.5 in the same cubic meter of concrete with 12% porosity; which means surplus lime is almost 3125 times more than what is required.

The huge quantities of surplus lime from OPC system, released at early ages, leach out to make the concrete porous. It is proved that a porous concrete is vulnerable for distress despite having lime to protect passivity film, rather than blended cement concrete with sound microstructure (optimum pore refinement and grain refinement) wherein the surplus lime is engaged into secondary mineralogy. Hence the contribution of fly ash to tap the lime in order to develop dense microstructure and, in turn, impermeability for the concrete, mitigates the chances for ingress of moisture to the reinforcement, thus holding the steel in safe environment. In other words, wherever impermeability becomes the first defensive mechanism in the concrete, the role of lime for passivity film may be considered as secondary and even redundant.

The studies on minimising surplus lime have lead to the development of concrete with binary and ternary blends of cement. In the process, pozzolanic chemistry has been availed for its best part of performance.

## Analogy of surplus lime with surplus sugar

There is close analogy between the sugar-reserve (glycogen) of human system to lime-reserve of concrete system. Both of them are imminent to make the systems strong and workable. But these basic and essential inputs, if exist in surplus levels, cause durability problems to their respective systems. Various parallels have been drawn between these two indispensable material needs of the respective systems.

In a human system, strength is drawn from carbohydrates whereby the reaction of insulin for glucose utilisation results in liberation of energy and cell growth. Insulin is an activator that helps to convert an energy media into strength, through regulating the glucose levels, thereby vetoing the occurrence of deleterious reactions to the human system.

This means, if the intake of carbohydrates (sugar) is more beyond the availability of insulin in the body, such excess quantity does not render any strength and, on the other hand, leads to various complex problems to the health.

Hence there is a dire need of threshold levels of compatibility to the sugar intake and availability of insulin in the body, which is balanced by intake of additional sugar or insulin, as the need be. Without such harmony the human body malfunctions, leading ultimately to collapse.

In a concrete system, strength is drawn from cement by the reaction of its constituents, including that of lime, resulting in the formation of strength rendering hydrated mineralogy. In this case, all the reactants come from cement, which are in the form of anhydrous mineralogy, wherein certain quantity of lime is essential at the manufacturing stage but out of the same lime certain portion proves to be excess upon hydration.

The transition zone between cement paste and coarse aggregate has parallel to the muscles in human system. The lime around aggregate or the glucose to the muscle occurs as a natural phenomenon of the ‘system performance’. In the muscles insulin increases the activity of the enzyme, glycogen synthase, which increases the glycogen deposition through dehydrolysis of glucose. Most of the glucose disappears in this way, liberating energy. So much so the lime at the transition zone is converted into strength through secondary mineralogy formation when the CCM are added.

This is where the parallel of fly ash to insulin makes a sense whereby, the fly ash converts the surplus lime to form secondary mineralogy, as much as the insulin helps to convert glucose into energy.

Fly ash has dual role to play for the strength development. While the reactive phases do react with lime to formulate strength rendering mineralogy, the unreactive portion of fly ash fills up the matrix to render packing effect and resultant strength. The unreactive portion may also be considered as the micro aggregate to contribute for the strength. As far as the strength is concerned, the role played by reactive portion of fly ash is decisive and dominant in comparison to the strength derived out of unreactive portion through packing effect.

The surplus lime released from OPC hydration becomes the source for pozzolanic reactions those contribute for additional mineralogy that is identified as ‘Secondary Hydrated Mineralogy’, as shown below:

$$\text{OPC} + \text{H} \xrightarrow{\text{Fast}} \text{Primary hydrated mineralogy} + \text{CH}$$

$$\text{Pozzolan} + \text{CH} + \text{H} \xrightarrow{\text{Slow}} \text{Secondary hydrated Mineralogy}$$

As per various studies, the ultimate hydration of OPC yields approximately 75% strength rendering mineralogical phases. The balance $Ca(OH)_2$, whose contribution for strength is insignificant, renders deleterious effect to concrete as discussed later. However, the same $Ca(OH)_2$ attains significance in the chemistry with CCM towards formation of secondary mineralogical phases, majorly contributing for additional strength. The above reactions attain technical importance from three main features.

| | | |
|---|---|---|
| The quantum of heat liberated is low and staggers through pozzolanic reactions. | : | This reduces micro-cracking and improves soundness. |
| The reaction is lime consuming | : | This mitigates chance for chemical attacks and, in turn, deterioration of concrete. . |
| The reaction results in the formation | : | This contributes for the mechanism of hydrated secondary mineralogical phases of pore refinement and grain refinement, resulting in enhanced strength, impermeability and strong transition zone. |

## DURABILITY

### Latrogenecism of Concrete

Latrogenecism is a phenomenon in human system on account of induced diseases through the use of drugs or medicinal poisoning which is common with modern pharmacology.

A survey has computed that consumer spending on alternative traditional medicine surges to 69% since 1989, which is currently estimated at US$ 62 billions or Rs 2,670 billions, to abate and overcome the phenomenon of latrogenecism. Thus the whole pharmaceutical industry is retrospecting the traditional medicinal practices for possible redressal in the formulations. This is the potential of renaissance of traditional system, which is gaining utmost importance in every walk of life.

All of us are worried about human system. But, *what about latrogenecism in concrete system that has a lot of role to serve the human race by generations to come!* In either of the systems, the shift from the sound principles of traditional practices, and crave for early results lead to the distress phenomenon.

Concrete is an indispensable construction material for housing, industrial and infrastructure development. Hence, it plays a crucial role in the economy of any nation. But, unfortunately, this is one of the neglected subjects, more so in India, leading to rapid deterioration of concrete structures. The cost of such negligence in India alone comes to about Rs 500 billions annually on account of distress. More than the monetary loss, the wastage of materials of concrete is unforgivable in present day's concern for rapid depletion of resources of earth.

Lime mortars have proved their durability with centuries of life. When cement was developed with higher strength during 19th century, durability was taken for granted. It was assumed that cement concrete structures render longer service life. Things were proved; the sound and linear relation between strength and durability of concrete developed with low grade Portland cements infused confidence on the latter as the unique construction material of modern world with long-lasting service life.

While the Portland Cement Concrete (PCC) has a history of about 185 years, the subject on durability of concrete has drawn the attention of cement and construction industry only after 130 years. To emphasise more, the durability of concrete was not a subject for deliberations at various international fora held on cements and concretes till 1940s. It was in 1952, during the 3rd International Symposium on the Chemistry of Cement, that interestingly 82 papers have been referred on various issues of durability. Though there was ongoing research inter-relating durability of concrete with various aspects of cement, the need was felt only during 1950s to correlate the relation in the field level. The reason for this need is quite obvious – it was the time when high strength cements have been produced and profusely used to meet the construction boom during post-war period of World War II. The sound and balanced relation between concrete/cement strength and its durability was the major reason why Portland Cement has been so popular and confidently used for all the structures till such time.

After the World War II, there has been a lot of pressure on cement and construction industry for massive deployment of concrete. This was the time in 1940s when high strength cements had been developed by bringing in change in the proportions of mineralogical constituents of cement with special reference to increasing the ratio of $C_3S$ to $C_2S$. During the same period, the fineness was also increased, targeting high strengths. These changes have resulted in 'high early strength cements' rather than high strength cements. Concrete mix designs and construction practices were also changed simultaneous to cement composition. But, the same changes have been associated with problems that impaired the sound and linear relation between strength and durability of concrete, questioning the wisdom of depending on strength as the yardstick for durability. As per Mehta :

> *"Extensive drying shrinkage, excessive heat of hydration, and increased vulnerability to various types of physical and chemical attacks; the problems considered to be minor at one time have come to the forefront disturbing the soundness of concrete and resulting in the reduced durability."*

Fly ash contributes for durability enhancement of a concrete in multiple ways:

- Reduction in heat of hydration and minimisation of thermal cracks.
- Absorption of surplus lime released out of OPC to form into secondary hydrated mineralogy.
- Pore refinement and grain refinement due to the secondary hydrated mineralogy, thus, contributing for impermeability.
- The improved impermeability of the concrete, results in increased resistance against the ingress of moisture and gases.
- The failure of moisture and gases to go through the concrete, results in the durability enhancement.

But interestingly, none of the codes in the world have set specifications nor pronounced parameters for durability in categorical terms. This has happened because, till the premature failure of structures built with high grade cements, no attention was focused on durability issues. ASTM has included C1202, the method for rapid chloride ion permeability, as one of its specifications to rate the performance of concrete in qualitative terms but appears to have not given any quantified linkage for coulomb value to projected service life.

On the home front in India, leave aside models for service life projections, the knowledge on blended cements for durability is at nascent state. However, awareness is percolating slowly for the last few years. This has prompted the codes to cite the use of blended cements on durability criteria in the revision of IS:456-2000. But even at this juncture, the code was silent on specifications and parameters to rate the durability or service life of a structure. While the market for blended cements has picked up on durability count, the claims are not substantiated with parameters in quantitative terms, leaving the marketing departments of cement in the lurch.

It is difficult to set a service life for a structure, just based on certain qualitative studies, because the service life is a holistic outcome of concrete performance on various durability factors. In this context the holistic model conceived by Mehta deals with the issues for their integrated behaviour. The tangible explanations available on structures projected with service life need to be supported with codal specifications. There are scientific approaches to assess the health of concrete in quantitative terms on each count independently. But, the research has to find an approach to assimilate the data to project the service life holistically in the lines of Life-365.

The following have been identified as the main issues to affect the durability of concrete:

- Micro-cracks
- Permeability
- Carbonation
- Chemical attack
- Corrosion

## Micro Cracks

Heat of hydration for a cementitious material is a positive phenomenon that helps for the rapid hydration of the mineralogy. The early hardness and strength gain of OPC over age-old lime mortars may be attributed to this aspect. Rapid hardening of Plaster of Paris (POP) is another striking example for the conducive role of heat of hydration for the formation of hydrated mineralogy and crystal growth.

But, the development of high early strength cements by increasing the $C_3S$ content and fineness has violated the locus of heat of hydration that was conducive in (age old) earlier OPC of 25-33 grade for progressive hydration to prolonged ages. It is ruled that the temperature difference should not cross 25 $^{o}$C between the core temperature of the concrete and the ambience.

## Permeability

Water is the invariable constituent in concrete preparation. Once the concrete is set, the entrapped water in the matrix is availed by cement mineralogy for hydration and some water is evaporated, thus leaving pores to the extent of volume occupied by the water. Part of this volume is filled up by the hydrated products of the cement paste. It is observed:

> *"The space not taken up by the cement or the hydrated products consists of capillary voids, the volume and size of the capillary voids being determined by the original distance between the anhydrous cement particles in the freshly mixed cement paste (i.e., water/cement) and the degree of cement hydration".*

The higher the w/c higher is the porosity resulting in permeability. Permeability facilitates the ingress of air and moisture. In case of aggressive environment, the sub-soil chemicals permeate into the foundation and, depending on the level of permeation, the moisture travels to the body of the structure through capillary phenomenon.

One of the important adverse effects of permeability is chloride ion ingress into the concrete that becomes cause of initiation for chloride induced corrosion. Hence in the context of assessment of performance of concrete and service life of structures, studies on chloride ingress play a vital role.

Capillary absorption, hydrostatic pressure and diffusion are the means by which chloride ions can penetrate concrete. The most familiar method is diffusion, the movement of chloride ions under a concentration gradient. For this to occur the concrete must have a continuous liquid face and there must be a chloride ion concentration gradient.

A second mechanism for chloride ingress is permeation, given by pressure gradients. If there is an applied hydraulic head on one phase of the concrete and chlorides are present, they may permeate into the concrete.

A more common transport method is absorption. As a concrete surface is exposed to the environment, it will undergo wetting and drying cycles. When water encounters a dry surface, it will be drawn into the whole structure through capillary suction. Absorption is driven by moisture gradient. ASTM 1202 has codified Rapid Chloride Permeability Test (RCPT) that is being popularly practiced in recent studies.

In this test method, a water saturated 100 mm dia concrete specimen with a thickness of 50 mm is subjected to 60 V, applied DC voltage for 6 hours; in one side of the specimen cell contains 3% sodium chloride (NaCl) solution and in the cell of the other side 0.3 M sodium hydroxide (NaOH) solution. The total charge passed is determined and used to rate the concrete according to the criteria as below where the third column, durability criteria, is added by the authors to give an understanding about the coulomb rating:

| Charge passed Coulombs | Chloride ion penetrability rating | Durability Criteria |
|---|---|---|
| > 4000 | High | Very poor |
| 2000 – 4000 | Moderate | Poor |
| 1000 to 2000 | Low | Good |
| 100 – 1000 | Very low | Very good |
| < 100 | Negligible | Excellent |

The chemical reactions of reactive constituents of fly ash with lime contribute for secondary hydrated mineralogy, resulting in pore size and grain size refinement. The ultrafine particulate matter of fly ash, which is inert and could not participate in chemistry, renders packing effect. Permeability studies were conducted on different market samples of OPC and PPC to understand the phenomena. Table below shows the improvement in impermeability for PPC concrete over that of OPC at the same w/c. PPC2 has also developed reduction in impermeability despite having higher slump at 100 mm. Coulomb rating below 1000 at 90-day in certain concretes shows the health of matrix because of sound chemistry offered by pozzolans in respective concretes.

CHLORIDE PERMEABILITY ON M-20 CONCRETE AT 0.6 W/C ON OPC AND PPC

| | | Coulombs | | |
|---|---|---|---|---|
| Sample | Slump mm | 28-day | 60-day | 90-day |
| OPC A | 65 | 3924 | 3352 | 3245 |
| OPC B | 63 | 2971 | 2640 | 2297 |
| OPC C | 60 | 3575 | 3106 | -- |
| PPC 1 | 56 | 2046 | 1451 | 853 |
| PPC 2 | 100 | 2305 | 1359 | 886 |
| PPC 3 | 60 | 2492 | 1823 | 1415 |
| PPC 4 | 60 | 2101 | 1150 | 937 |
| PPC 5 | 55 | 2470 | 1973 | 1633 |

## Chemical attacks

For many occurrences of chemical attacks on cement concrete, availability of surplus free lime may be taken as one of the prime causes. It is desirable to have harmony for the release of lime from anhydrous cement, with that of formation of hydrated mineralogy. This was largely assimilated in the hydration of coarse particles of low grade cements with progressive release of lime over ages. At early ages, when the concrete is porous and vulnerable for external chemical attacks, the lime from the coarse particles of cement counteracts and gives protection. At late ages, the attacks have hardly any impact due to the microstructure densification resulted out of progressive and sustained chemistry of low grade cements. In present days' high grade OPC with finer particles, release of lime is lavish, that too at early ages, failing to resist chemical attacks at late ages.

Mehta *et al.* observe that the rate of chemical attack on concrete is a function of the pH of the aggressive fluid and the permeability of concrete. When the pH of the aggressive water is above 6, the rate of chemical attack is considered too slow to be taken seriously. Free $CO_2$ in soft water, acidic ions such as $SO_4^{2-}$ and $Cl^-$ are frequently responsible for lowering the pH below 6, which is considered detrimental to Portland cement concrete. This situation reaches to an alarming state when the lime bank in cement concrete is bankrupt through leaching out prematurely at early ages.

When concrete is permeable through which the chemicals find their way in to the matrix, the availability of free lime triggers off a chain of chemical reactions.

Since permeability is the route cause for all the attacks, manufacturing an impermeable concrete is of vital importance that can be largely served by fly ash when added as supplement to cement in the concrete. Rolling back the cement fineness to yester years may also offer plausible solution to resist chemical attacks but only in association with supplementary cement materials.

**Carbonation**

Carbonation phenomenon occurs in concrete over ageing. The cement in concrete releases hydrated lime that is left as surplus and, in turn, is attacked by the atmospheric $CO_2$ leading to carbonation.

$$Ca(OH)_2 + H_2CO_3 \longrightarrow CaCO_3 + 2H_2O$$

$$Ca(OH)_2 + 2CO_2 \longrightarrow Ca(HCO_3)_2$$

(Dissolves in water and leaches out
thereby exhausting lime successively)

The rate of carbonation mainly depends on:

- Permeability of concrete to allow ingress of $CO_2$
- Quantity of hydrated lime that remains as surplus
- Environmental conditions such as humidity, temperature etc.

In a concrete blended with fly ash, the remedy is provided both ways; one by minimising the chances of surplus lime due to pozzolanic reactions; the other by minimising the permeability due to secondary mineralogy.

## Corrosion

When the reinforced concrete is subjected to service loads various physical phenomena occur within the concrete system. In addition, the reactions of constituents in concrete cause chemical changes. These physical and chemical changes reflect on the dimensional and structural stability, by which the service life of the concrete becomes an intrinsic issue. Quite often corrosion of reinforcement is the penultimate phenomenon before the structure gets deteriorated.

Though corrosion of rebars is not a common phenomenon it is also not an uncommon feature, because for it to occur various factors contribute right from the synthesis of cement chemistry till the placement and curing of concrete. Not minding any other issues, the impermeability is the first and foremost defensive mechanism to make a concrete durable. Once a concrete is made to extend better performance, it offers an inherent security to the reinforcement. Considering durability and strength of concrete as two independent parameters, a relatively low strength concrete can be made durable through densifying the matrix. This is where fly ash is identified to play an effective role in mitigating the chances for corrosion of rebars as identified by Gerwick.

The discussions of Bamforth are of great significance in projecting the service life of blended cement concrete vis-à-vis OPC concrete, which takes into account the surface chloride level, the chloride corrosion threshold concentration, the effective diffusion coefficient and the cover to reinforcement. According to him 24/30 grade concrete, containing 40% fly ash is comparable to 50/60 grade concrete of OPC to offer 75-year service life. In other words, he projected that fly ash blended concrete at lesser grade of 32/40 is sufficient with a cover thickness of 50 mm as against 50/60 grade of OPC concrete with 100 mm cover thickness to meet the service life criteria of 75-year. This study once again establishes the redundancy of high strengths for service life, more so when complementary cement materials are blended with OPC in the concrete. The data of Bamforth on different grades of fly ash blended concrete vis-a-vis cover thickness are given in Table below.

SERVICE LIFE PROJECTION BY BAMFORTH ON DIFFERENT GRADES OF CONCRETE

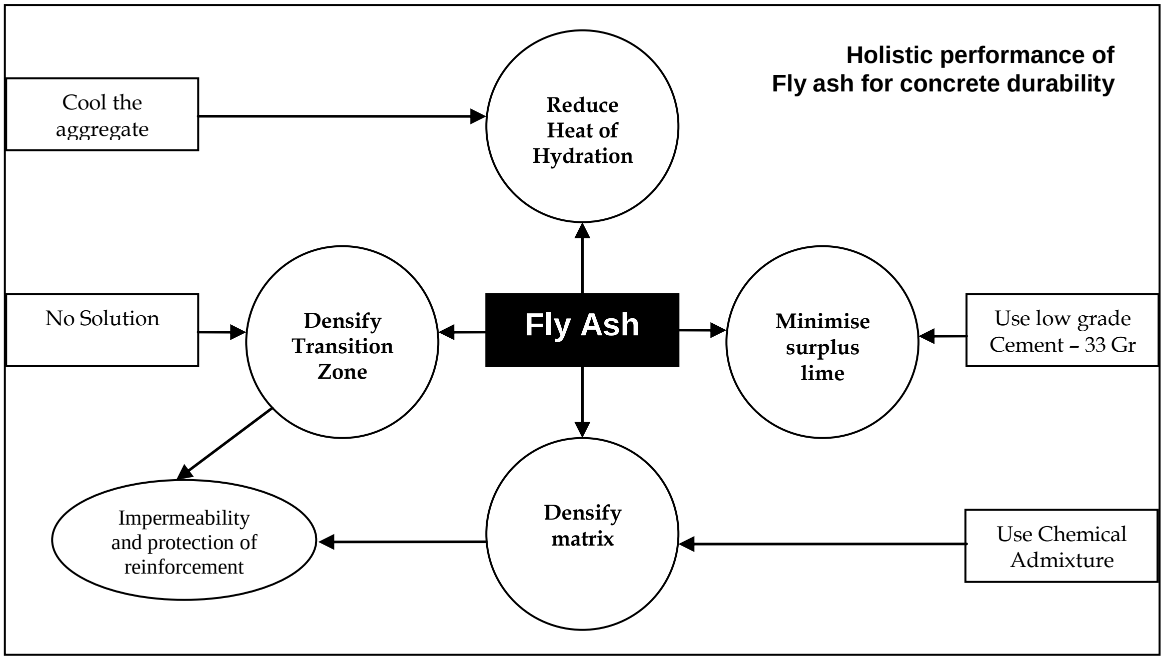
| Mix type | Recommended mix class for cover of | | |
|---|---|---|---|
| | 50 mm | 75 mm | 100 mm |
| OPC | N.A | N.A | C50/60 |
| OPC with: | | | |
| 20 % fly ash | C50/60 | C40/50 | C32/40 |
| 30 % fly ash | C40/50 | C32/40 | C24/30 |
| 40 % fly ash | C32/40 | C24/30 | C24/30 |

Advanced concrete technology blends the sound principles of material science with the needs of rapid construction practices. The role of complementary cementing inputs ultimately enlarged the scope to *'sustainable high performance concrete'*, resulting in enhanced service life of structures. The following are certain target parameters to achieve the same:

- Control water-cement ratio for high impermeability;
- Control heat of hydration for reduced micro-cracks;
- Achieve high early strength, but through safe measures;
- Densification of microstructure progressively;
- Strengthening of transition zone.

## THE HOLISTC PERFORMANCE OF FLY ASH

Various issues have to be addressed on multiple fronts to accomplish durability. Durability enhancement through fly ash is a holistic performance in a single go as shown in the chart below, at no extra cost.



## CONCLUSIONS

Strength is an intrinsic property of cement/concrete, whereas durability is a manifestation of physico-chemical assimilation of various factors in the preparation and placement of concrete. OPC concrete failed to meet the criteria unless blended with complementary cement materials. Fly ash is one of the best cost effective solutions in this direction.

Maintaining pH is a curative mechanism derived through cement to protect the concrete at early ages during which the latter is still permeable due to incomplete matrix formation.

What should be targeted is the ultimate preventive mechanism i.e., impermeability. Once the latter is achieved, the former becomes secondary in the context of protecting the reinforcement. There is no better cost-effective solution than tapping the potential of fly ash for its holistic performance towards concrete durability.

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