CHAPTER 2

REVIEW OF LITERATURE
2.1 Sustainability:

The term “sustainable Development”\textsuperscript{(73)} has been defined by many people in many ways. As recorded at the Massachusetts Institute of Technology, Cambridge, USA, the term “sustainable development” has as many as 57 competing definitions \textsuperscript{(65)} However, most accepted definition by Dr. Gro Harlem Brundtland \textsuperscript{(65)}, Director General of the World Health Organization (WHO) is “The ability of humanity to ensure that it meets the needs of the present without compromising the ability of future generations to meet their own needs”.

The primary greenhouse gas emission affecting the sustainable development is the Carbon dioxide (CO\textsubscript{2}). The other greenhouse gases of concern include nitrous oxide (NO\textsubscript{2}) and methane (CH\textsubscript{4}) but their amount emitted is relatively small compared to that of CO\textsubscript{2}.

Apart from USA and Australia almost all other developed countries are placing mandatory quotas on the emission of these gases and these involve stabilizing these emissions to 6\% below the 1990 level by the year 2010-2012. As the manufacturing of Portland cement contributes significantly to the CO\textsubscript{2} emissions, the increased use of large volumes of fly ash, other supplementary cementing materials & super plasticizers in the construction industry is to reduce these emissions.

<table>
<thead>
<tr>
<th>Country</th>
<th>CO\textsubscript{2} Emissions in Tonnes per Capita per year*</th>
</tr>
</thead>
<tbody>
<tr>
<td>U.S.A</td>
<td>20</td>
</tr>
<tr>
<td>Canada</td>
<td>20</td>
</tr>
<tr>
<td>EU</td>
<td>9</td>
</tr>
<tr>
<td>China</td>
<td>&gt;3</td>
</tr>
<tr>
<td>Latin America</td>
<td>3</td>
</tr>
<tr>
<td>India</td>
<td>&gt;1</td>
</tr>
</tbody>
</table>

* The numbers are approximations only, and have been collected from published information
Ordinary Portland cement is a major construction material worldwide and will remain so for the foreseeable future (Table 2.2). The net cement production is expected to rise from about 1.7 billion tonnes in 2000 to about 2 billion tonnes in 2010. In view of the huge tonnage involved, it is imperative that the manufacturing of cement should be made as environmentally friendly as possible.

**Table 2.2 Regional and World Cement Production up to Year 2010 In Million Tons**

<table>
<thead>
<tr>
<th>Region</th>
<th>1995</th>
<th>2000</th>
<th>2005</th>
<th>2010</th>
<th>%age of Total 1995</th>
<th>%age of Total 2010</th>
</tr>
</thead>
<tbody>
<tr>
<td>European Union</td>
<td>168.1</td>
<td>187.9</td>
<td>194.1</td>
<td>189.3</td>
<td>12.1</td>
<td>9.4</td>
</tr>
<tr>
<td>Other Europe</td>
<td>65.8</td>
<td>80.0</td>
<td>90.2</td>
<td>94.7</td>
<td>4.7</td>
<td>4.9</td>
</tr>
<tr>
<td>Former Soviet Union</td>
<td>58.1</td>
<td>80.3</td>
<td>110.1</td>
<td>128.2</td>
<td>4.2</td>
<td>6.6</td>
</tr>
<tr>
<td>North America</td>
<td>92.9</td>
<td>94.9</td>
<td>94.8</td>
<td>94.7</td>
<td>6.6</td>
<td>4.9</td>
</tr>
<tr>
<td>C/S America</td>
<td>89.4</td>
<td>106.6</td>
<td>127.4</td>
<td>145.0</td>
<td>6.4</td>
<td>7.5</td>
</tr>
<tr>
<td>Africa</td>
<td>64.8</td>
<td>74.3</td>
<td>80.7</td>
<td>85.5</td>
<td>4.6</td>
<td>4.4</td>
</tr>
<tr>
<td>Middle East</td>
<td>63.5</td>
<td>75.6</td>
<td>76.9</td>
<td>73.4</td>
<td>4.6</td>
<td>3.8</td>
</tr>
<tr>
<td>East Asia</td>
<td>623.4</td>
<td>732.7</td>
<td>798.8</td>
<td>844.3</td>
<td>44.6</td>
<td>43.4</td>
</tr>
<tr>
<td>S/SE Asia</td>
<td>161.2</td>
<td>219.1</td>
<td>255.0</td>
<td>179.2</td>
<td>11.6</td>
<td>14.4</td>
</tr>
<tr>
<td>Oceania</td>
<td>8.0</td>
<td>10.6</td>
<td>11.1</td>
<td>11.8</td>
<td>0.6</td>
<td>0.6</td>
</tr>
<tr>
<td>World Totals</td>
<td>1396.1</td>
<td>1662.1</td>
<td>1839.1</td>
<td>1946.1</td>
<td>100.0</td>
<td>100.0</td>
</tr>
</tbody>
</table>

Note: Recent published data indicate that the North American production has already exceeded 120 million tons in the year 2002, and will reach 130 million tons in the year 2010.

The cement industry’s sustainable program developed by the World Business Council for Sustainable Development (WBCSD) resulted in 2002 “Agenda for Action”. This industrial protocol was undersigned by the C.E.O’s of the world’s ten leading cement manufactures. The “Agenda for
Action” covers a five year period & is directed at improving among other things like:

- Climate protection
- Fuels & raw materials
- Emission reductions
- Environmental impact

The Swiss Global cement producer HOLCIM Ltd., a member of WBCSD has taken a leading role in the cement industry in this response to sustainable development and has pledged to reduce by 2010 specific net CO$_2$ emissions by 20% globally against reference year 1990 \(^{(5)}\)

**Green House Gas Emissions from the Manufacturing of Portland Cement Worldwide.**

Not only is the manufacturing of Portland cement is highly energy intensive, and it also is a significant contributor of the green house gases. The production of one tonne of cement contributes about 1 tonne of CO$_2$ to the atmosphere, together with minor amount of NO$_2$ & CH$_4$. The total CO$_2$ emissions per tonne of cement can range from about 1.1 tonnes of CO$_2$ from the wet processing plants to about 0.8 tonnes from a plant with precalcinators. About half of the CO$_2$ emissions are due to the calcinations of lime stone and the other half are due to the combustion of fossil fuels.

According to Cahn et al, \(^{(14)}\) emissions from the calcinations of lime stone are fairly constant at about 0.54 tonnes of CO$_2$ per tonne of cement; the emissions from the combustion depend on the carbon content of the fuels being used and the fuel efficiency. Thus, the worldwide cement production accounts for almost 7 percent of the total world CO$_2$ emissions.
From the projections made by the cement companies, this proportion is expected to remain steady in the next decade. Notwithstanding the “Agenda for Action” of WBCSD. This implies that the cement companies are not expecting the emergence of major environmentally friendly cement manufacturing technologies in the foreseeable future. It is anticipated that by the year 2010, India will double the capacity of the electric power generation from what is being generated today, resulting in an increase in fly ash availability to about 160 million tonnes annually. In that year, the Portland cement production is expected to reach more than 130 million tonnes.

Unfortunately, the much needed industrial developments in China & India are affecting adversely the environment in two ways. The installation of new cement plants is increasing substantially the CO\textsubscript{2} emissions and the construction of very large capacity thermal power stations is resulting in huge amounts of fly ash and bottom ash becoming available that are not being recycled in any meaningful manner. **Most of the fly ash is being dumped in lagoons, landfill sites and abandoned quarries.** Thus, potentially valuable cementing resources are being wasted in precisely the countries that need it most to reduce the green house gas emissions and to make economical and durable concrete structures.

One of the major developments in the area of fly ash utilization has been the technology of high volume fly ash (HVFA) concrete by Malhotra
\textsuperscript{(47)} and his associates at CANMET, Ottawa, Canada. It is believed that in years to come, this development will affect profoundly the use of cement. In addition to fly ash, the other supplementary cementing materials that are available in large quantities and can be used to replace Portland cement in concrete include granulated blast furnace slag, natural pozzolona and rice husk ash.
The combined use of super plasticizers and supplementary cementing materials can lead to economical high performance concrete with enhanced durability.

2.1.1 Sustainable Development and the Concrete industry by Jain A.K (34)
Status Report from India

A sustainable development only can last over a long period of time. In this regard we can learn from nature. There is no wastage in nature. All output or byproducts of one natural system are inputs or nutrients to another system. But we run an economic system that truly produces “waste” visible and invisible byproducts of our industrial process that can go nowhere they just pile up.

Green House Gases, industrial and agriculture byproducts such as fly ash, rice husk ash, blast furnace slag, silica fume, mine rejects, phosphogypsum, red mud and host of similar products can be easily cited in this regard. Construction industry is one such industry which requires very large quantity of materials derived from the upper crust of the earth. The removal and transportation of these raw materials adversely affect the ecological balance on one hand and generate large amount of industrial waste during processing on the other. The system at some point of time will become self defeating and degenerating if appropriate corrective measures are not taken in time. Construction industry has capacity to use waste generated from other human activities provided adequate awareness is created and proper steps are taken. The waste generated by construction activity can be minimized by using proper technology and construction techniques.
There has been appreciable awareness and progress in utilization of these byproducts in construction during the last 10 years. It is possible due to the untiring efforts of organizations like CANMET, INSWAREB & Fly Ash Mission, and TIFAC. The Indian codal provisions of Portland pozzolona cement (IS 1489 Part-I) and Portland slag cement (IS 455) have also been amended to utilize larger percentage of fly ash and Granulated Glass Blast furnace Slag (GGBS). The cement and construction industry have accepted the challenge and come forward to progressively increase the utilization of these byproducts year after year.

The results of these efforts have definitely brought a change in mind-set and now more & more construction materials and products incorporating such waste materials are being accepted. The major construction materials and products which use these byproducts in India at present can be broadly put in different categories:

**Cementitious and binding materials:** In this category we can put PPC, PSC, fly ash, GGBS, silica fumes, metakaolin, rice husk ash etc. as supplementary cementitious materials directly used in concrete making.

Applications of byproducts and waste materials are utilized as under:
(a) Building Blocks, Partitions and Roofing System: This category comprises fly ash bricks, blocks, paving blocks, partition boards (gypsum / phosphogypsum), roofing sheets, soil stabilized blocks, etc.
(b) Filling under embankments / low lying areas: Land reclamation, embankment filling, mine filling and similar applications.
(c) Partition boards, compressed panels, particle and block boards etc.
2.1.2 Future trends regarding waste materials and byproducts

Awareness about clean environment, reduction in greenhouse gases and optimization of cost through gainful utilization of industrial and agricultural by-products is increasing with every passing day in all sections of the society. Clean Development Mechanisms (CDM) is such incentive, which will accelerate space of development of appropriate technologies to reduce Green House Gases (GHG). In fact cement and construction industry can act as scavenger to use large quantity of waste generated by various human activities through proper incentives and awareness.

The major thrust areas are likely to emerge:
(a) Utilization of Municipal waste
(b) Fly ash bricks.
(c) High Volume Fly ash Concrete (HVFAC) and Roller Compacted Concrete (RCC)
(d) Waste Derived Fuels (WDF)
(e) Agricultural & plants waste utilization

It is hoped that the concrete industry would show leadership and resolve and make contributions to the sustainable development of the industry in the 21st century by adopting new technologies to reduce the emission of the greenhouse gases and thus contribute towards meeting the goals and objectives of the 1997 Kyoto Protocol (44).

Praveen Kumar et.al (60) suggested that the High strength concrete generally involves high cement contents of the order of 400 kg/m$^3$ to 500 kg/m$^3$ in their mix proportioning. Such high cement contents result in the presence of substantial amount of Calcium Hydroxide Ca (OH)$_2$ in the
hardened concrete. This Ca(OH)$_2$ is soluble in water, thus making concrete vulnerable to deterioration, in case water seeps into such concretes.

According to Mehta P K (49) to enhance durability, Efforts should be directed towards reduction of Ca(OH)$_2$ content in the concrete on one hand and reduction of permeability on the other to enhance durability. This objective can be accomplished by use of mineral admixtures such as fly ash, silica fume or Metakaoline. **Fly ash addition proves most economical among these choices. However, when high early strength is desired, use of Metakaoline or silica fume is more useful according to Basu Prabir** (9)

In India good quality silica fume is mostly imported only, thus it is about 9 to 10 times costlier than cement. On the other hand Metakaoline can be produced in large quantities in the country, as it is a processed product of the kaolin mineral, which has wide spread proven reserves available in the country according to Deshpande, Basu, Tiwari (22,68). Presently, the market price of Metakaoline in the country is about 3 to 4 times that of cement. Hence the use of Metakaoline proves to be economical over that of silica fume. However there is need for the test data regarding the performance of commercially available Metakaoline and Indian Cements in case of high strength concrete in the country (9, 68, 57).

2.2 Supplementary Cementitious Materials (SCM)

The contribution of the MK & fly ash (FA) in a ternary cement system results in a no. of synergistic effects some of which may include:

- MK compensates for low early strength of concrete with FA (binary blend of FA and cement)
- FA increases long term strength development of MK Concrete
FA with its round particle size & slower reactivity, offsets the increased water demand of MK
FA compensates for higher heat release from MK
The relative low cost of FA offset the increase cost of MK.

2.2.1 Metakaolin and Flyash

Jiping Bai et al\textsuperscript{36} found that when MK is combined in equal amount with FA, the effect of FA & MK on the temperature rise at early age (during the first 72 hours) tends to compensate for one another (i.e. temp. rise for a 10% MK, 10% FA mortar is the same as that of plain cement concrete). Compressive strength of 8% addition of MK ternary blend produced at w/cm of 0.30 matched the strength of ordinary concrete by 3 days of age and exceeds the strength of ordinary concrete at 7 days & 28 days. In addition at a w/cm of 0.4, the 5% & 8% ternary blend generally match or exceed 28 days strength of ordinary concrete for the highest 0.5 w/cm. Only the 8% MK ternary blended matched the 28 days strength.

2.2.2. Ultrafine Flyash

Influence of ultrafine fly ash on the early age property development, shrinkage and shrinkage cracking potential of concrete is investigated. In addition, the performance of ultrafine fly ash as cement replacement is compared with that of silica fume. The mechanisms responsible for an increase of the early age stress due to restrained shrinkage were assessed; free shrinkage and elastic modulus were measured from an early age. In addition, the materials resistance to tensile fracture and increase in strength were also determined as a function of age.
Cement replacement with ultrafine fly ash results in a comparable development of elastic modulus and fracture parameter with age when compared with the control mixture. There is, however, a significant decrease in the autogeneous shrinkage and a decrease in the age of cracking. The autogeneous shrinkage in concrete obtained by cement replacement with ultrafine fly ash is significantly smaller in magnitude than the drying shrinkage. There is an increase in the autogeneous shrinkage, while the drying shrinkage is relatively unaltered on increasing the volume of ultrafine fly ash in the mix of decreasing the w/cm ratio. Increasingly the volume of ultrafine fly ash and decreasing w/cm ratio resulted in an increase in the compressive strength, rate of strength gain and further improvement in age when the concrete cracks in restrained shrinkage tests.

The effects of replacing 10%, 40% or 60% of the cement content by low calcium fly ash, the compressive strength and durability of the concrete were investigated by G Baert, A.M.Poppe & N De Belie (29) an appropriate amount of super plasticizer was added to the mix to obtain good workability. Concrete with fly ash performed better in lactic / acetic and sulphuric acid during accelerated experiments. The chloride diffusion coefficients resulting from accelerated chloride migration tests were sufficiently lower for concrete with fly ash than for the control concrete except for the mixture with 60% replacement of the cement content. The resistance to frost /thaw cycles was similar for all concrete mixtures. Compressive strength at young age significantly decreased with increasing replacement of cement by fly ash. After 28 days, the compressive strength increased relatively more for high volume fly ash concrete than for the control concrete.

Fly ash has a positive effect on chemical aggression concrete
with high volume fly ash performed better in lactic/acetic and sulphuric acid during accelerated experiments. The chloride migration coefficients during CTH (resistance of concrete against chloride ingress) tests were significantly lower for concrete with cement replacement by fly ash than for the control concrete except for the mixture with 60% replacement of the cement. The resistance to frost-thaw cycles was similar for fly ash reference concrete (all without the use of air entrainment agents). The carbonation depth after 9 weeks in a 10% CO\textsubscript{2} environment increased with fly ash content. High volumes of fly ash also decreased significantly the resistance against the combined action of frost and de-icing salts (3% NaCl solution).

According to A.K. Tiwari, D.N. Jha & D Venkateswaran\textsuperscript{3} high volume fly ash (HVFA) concrete is a new composite system with unique mechanical and durability characteristics that allows the use of large volumes of fly ash for conventional concrete applications. In the HVFA concrete system, the classification of the cement paste matrix and the strength continues to improve at all ages due to the synergistic effect of chemical and physical factors. The test results show that the initial setting time of 5.5 hr is comparable to those of the control concrete made with the same water content and water cementious material ratio, where as the final time of set was retarded by 3 hr compared with that of control mixture. Bleeding tests performed on HVFA concrete have shown that this concrete does not bleed; this is because of the very low water content in this type of concrete. Additional curing in hot weather is needed to prevent plastic shrinkage cracks. The density of HVFA concrete is of the order of 2400 kg/m\textsuperscript{3}.

Some attempts have been made by A.K. Tiwari, D.N. Jha & D Venkateswaran\textsuperscript{3} to study the use of HVFA concrete for structural
applications and it has been found that fly ash dosage above 30% decreases the one day concrete strength so much that the forms cannot be removed according to the stripping schedule and hence it is not acceptable to the construction industry.

J.K. Dattatreya M, Neelamegam & M.P. Raja mane\(^{(33)}\) have studied mineral admixtures such as fly ash (FA) and silica fume (SF) are being extensively used in concrete for reasons of strength, durability and economy. While SF is a very fine material with submicron particles, FA can be processed to obtain the desired level of fineness to improve its performance. The performance of ultra fine fraction of FA & SF was compared in investigation on High Performance Concrete (HPC) mixtures.

The test results indicate that Ultra Fine Fly Ash (UFFA) had only a marginal effect on comp. strength when compared to that with concrete containing SF. SF was found to be more beneficial in improving the strength properties at all ages. The actual quantity of increase in strength beyond 7 days was not substantial. A similar trend was observed in case of controlled concrete mixtures. Each unit of Portland cement in Silica Fume Concretes (SFCs) contributed more efficiently towards the development of strength and reducing chloride permeability than in Flyash Concretes (FACs) and Cement Concretes (CCs). Both SF & UFFA caused drastic reduction in chloride permeability at all ages and for the entire w/b ratio; however SF was comparatively more efficient. In spite of the processing of UFFA to produce ultra fine particles, the magnitude of beneficial action of fly ash in concrete was observed to be less than that of SF with regard to both strength and durability characteristics, even though, the UFFA itself considerably improved the performance of concretes. In view of the large availability of
fly ash in India, it may be worthwhile to investigate the behaviour of indigenous UFFA and also evaluate its cost effectiveness as a cement replacement material for HPC.

2.2.3 Experimental Investigations

Several investigations at CAMMET indicate that HVFA concrete has very high resistance to the penetration of chloride ions measured RCPT and water penetration test. HVFA concrete is very effective in controlling alkaline aggregate reactivity. Abrasion resistance of these concretes is comparable to that of normal Portland cement concrete at 28 days and improves with age making it better than normal concrete. As the strength development after 28 days is significant, the design age for these concretes may also be changed to 60 days or 90 days depending upon the actual structural loading.

With respect to durability, HVFA concretes show water permeability similar to normal concretes at initial stage, but it is lower after 28 days. However, resistance to chloride permeability of these concretes is much better than conventional concretes at all ages. The abrasion resistance of these concretes is similar to the normal concrete and hence sited for pavement and industrial floor application.

Sentilkumar V & Mary Santhanam (66) brings out the details of an experimental investigation carried out to produce high performance concrete (HPC) at optimum cement content. Software LISA, based on particle packing model (Anderson’s approach) was used for adjusting the granulometry of the constituent materials. Cement Replacement Materials
(CRMs) such as quartz powder, lime stone powder, fly ash and micro silica were considered in the investigation. Mixtures were proportioned with low water content (144 L/m$^3$ - 120L/m$^3$). Sufficient workability was obtained by using a super plasticizer, influence on mechanical properties was ascertained by determination of compressive and flexural strengths. Durability was determined indirectly by rapid chloride permeability test (RCPT) & by water penetration test.

It was concluded that a part of cement content could be replaced by mineral fillers. By adopting the “optimal particle packing” mixture design approach along with the proper selection of CRM and super plasticizer, it was possible in this investigation to design sufficiently workable concrete mixtures with (270 kg/m$^3$ cement + 30 kg/m$^3$ flyash) cement content less than 300 kg/m$^3$ to achieve a 28 days cube compressive strength of 70 MPa -80 MPa along with very high durability (total charge passed in RCPT less than 500 coulombs).

### 2.2.4 Non Destructive and other Tests

Effect of partly replacing cement by equal weight of fly ash has been investigated for concrete of equal slump by K.K.Jain, B.D. Mautriyal and Dr. O.P.Jain. Compressive strength, elasticity and dynamic properties of plain and fly ash concretes at various ages under controlled ambient conditions are described. The effect of air curing on comp. strength is also reported. Fly ash concretes of equal slump proportioned on the basis of cement replacement by equal weight of fly ash develop significantly lower comp. strengths at 28 days. From strength development considerations, 15% cement replacement by fly ash is found to be the optimum. Air curing of fly ash concretes results in appreciably reduced comp. strength compared with
normal concretes. For 25% cement replacement, the loss of strength is also about 25%. Based on equal strength; the modulus of elasticity of fly ash concretes is slightly higher than that for corresponding plain concrete mixtures. Comp. strength correlates poorly with dynamic modulus and logarithmic decrement.

Investigations on 1:3 (cement and sand) mortar were carried out for comp. strength and water requirement of the mortar by using different percentages of fly ash both as cement replacement and as an additional ingredient of mortar by P.S. Gehlot and Dr. R.P. Lohtra\textsuperscript{(56)} It was found that by considering fly ash as an additional ingredient, comp. strength and workability of the mortar get improved along with an economy in cost of production. By replacing cement by equal wt. of fly ash in mortars, the strength goes down but the workability improves upto about 20% replacements. By considering fly ash to be an additional ingredient of mortar, it can be used upto 60%-80% by weight of cement in 1:3(cement: sand) mortar without affecting the properties of mortar. The cost of production of fly ash cement mortar with 80% additional fly ash is about 16.6% less as compared to that of plain cement mortar.

“Without regard to the actual quality of mixing water, the following rule is safe and one has to follow: use the smallest quantity of mixing water that will produce a plastic or workable concrete. The importance of any method of mixing, handling, placing and finishing concrete which will enable the builder to reduce the water content of the concrete to a minimum is at once apparent” - Duff A Abrams, 1918.
2.2.5 Objective of using fly ash

In most applications according to V.M. Malhotra & A.A. Ramezianpur (72) the objective of using fly ash in concrete is to achieve one or more of the following benefits:

1. Reducing the cement content to reduce costs
2. Obtaining reduced heat of hydration
3. Improving workability
4. Attaining required levels of strength in concrete at ages > 90 days
5. Improving durability

The mixture proportioning method can minimize the effects that the inclusion of different fly ash has on concrete performance.

(i) partial replacement of cement – the simple replacement method
(ii) addition of fly ash as FA – the addition method
(iii) partial replacement of cement, FA & water
• The modified replacement method
• The rational proportioning approach

“A concrete mixture may be so designed that when it is discharged from the mixture it is bulky and non-plastic and remains so during handling when so designed, it can be moulded only by pressure, tamping or vibration and in the process it does not become plastic. Compacting and moulding, such a mixture involves overcoming internal resistance to movement of one part of the material with respect to another part, and thus it involves internal strain and stress”. Traval C Powers, 1968(69).
Chi Sun Poon, Lik Lam & Yuk Lung Wang \(^{(17)}\) presented experimental results on porosity and pore size distribution of fly ash and silica fume, modified cement pastes and mortars using mercury intrusion porosimetry. It is found that replacement of cement by fly ash increases the porosity but reduces the average pore diameter of cement pastes at the age of 28 days and 56 days. The additional replacement of cement by up to 5% silica fume did not significantly change the pore size distribution and porosity of either the plain cement pastes or the fly ash cement pastes. Interfacial porosity, however, was significantly influenced by incorporating fly ash and silica fume in the mortars. At the ages of 28 days and 56 days, it was found that the mortars with 15% - 45% fly ash had smaller interfacial porosity compared with the plain cement mortars. The interfacial improvement effect was more significant when a small amount (5%) of silica fume was applied together with fly ash.

Jiping Bai, Albinas Gaillius \(^{(36)}\) has studied statistical models for predicting the consistency of concrete incorporating PC, FA & MK from the experimental results of standard consistency. They reflected the effect of variations of pozzolonic replacement materials including FA & MK at graduated replacement levels of up to 40% and 15% respectively. The predictions produced are compared with the experimental results of consistency of concrete blend. Models show that they can be used to predict the consistency parameters including slump, compacting factor and Vee-bee time with a good degree of accuracy in a wide range of FA – MK blends. Design guidelines for evaluating consistency parameters are tentatively recommended along with their confidence intervals of prediction limits at 5% significance levels.
Among the many factors that govern the durability and performance of concrete in service, type of cement receives greater attention. It describes the characteristics of cementitious systems required to meet the diverse requirements of strength concrete and highlights the advantages of part replacement of OPC by fly ash, granulated blast furnace slag and silica fume—either singly or in combination in ternary blends. In the absence of ideal OPC, ideal cement systems can be obtained by use of fly ash, granulated blast furnace slag or silica fume in requisite amounts as part replacement of OPC. Both blended cements like PPC or Portland Slag Cement (PSC) or cement substitution in the concrete mixer at site can be adopted.

Ternary blends of OPC with silica fume and fly ash or granulated slag are particularly useful to render greater durability to concrete according to A.K.Mullick (2) IS specifications on cements and concrete codes like IRC 21, IS 456 or IS 455 are however not very explicit about using ternary mixtures for cement systems. The use of ternary blends should be encouraged for ensuring greater durability in constructions.

N.P.Rajamane & D Sabtha (5) suggested that the steel reinforcement in any reinforced concrete structures is protected by alkaline environment created by the hydrated Portland cement since pozzolona such as fly ash (FA) and silica fume (SF), react with the calcium hydroxide \( \text{Ca(OH)}_2 \), that is generated during cement hydration and is the main contributor for the alkalinity of the cementitious material; it is necessary to understand the effect of adding pozzolonic material as cement replacement material (CRM) on pH of the hydrated matrix. The test results indicate that pozzolona affect the pH of cement mortars only marginally and the actual pH level remains high enough for continuation of protective environment for the...
embedded steel. Addition of SF as cement replacement material (CRM), comp. strength at all curing periods, and addition of FA as CRM reduces the strength of mortar and the difference between strengths of cement mortar and Fly Ash Mortar (FAM) reduces with increased curing period and decreases with cement replacement level (CRL). Despite lower values of comp. strength observed for FAMs, the strength developed per unit weight of actual Portland cement content in FAMs is higher than that in Cement Mortar (CM). Thus FAMs can be considered to utilize Portland cement more efficiently than CM.

pH values of aqueous solutions of the hydrated mortars containing FA & SF are in the range of 12.1 & 12.82 depending upon the CRL, curing period and type of pozzolona. This high value of pH indicates that the steel embedded in cement composites containing FA & SF can remain protected from corrosion since the passing of the oxide films on the steel is protected in such an alkaline environmental. There is no need for apprehension on marginal reduction in pH that may occur due to the presence of SF and FA. These additives should be used as CRMs, as suggested in IS 456-2000, since they improve the degree of impermeability of hydrated cement resulting in higher durability of cement composites.

Virendra Raghav Savalia, Praveen Kumar and Surendra Kumar Kaushik (75) carried out an experimental study aimed at investigating the performance of fly ash based blended cement for comp. strength; chloride permeability & electrical resistivity of concrete are presented. Three concrete mix proportions were made with w/c ratios in the range 0.42 to 0.27, each with three different brands of commercially available PPCs and one OPC. Significant amount of decrease in the chloride permeability of concrete is observed with the use of fly ash based PPC as compared to OPC. Significant
reduction in chloride increase and an increase in concrete resistivity were observed in concretes made with PPC as compared to those in concrete mixes made with OPC. Concrete exhibiting higher compressive strength may not necessarily have better durability characteristics when compared with a concrete with lower strength. A reduction in the w/c ratio from 0.35 to 0.26 shows only marginal increase in comp. strength to 60 days age, but a substantial improvement in the durability attributes is noted.

2.2.6 Potential of Metakaolin

According to K. Ganeshbabu and P Dinkar\textsuperscript{(40)} Metakaoline in general is a purely crystalline white powder and has a specific surface area of $12000 \, \text{m}^2/\text{kg}$ with average particle size varying from 1.5 $\mu$m to 2.5 $\mu$m. Thus particle size of MK lies between FA and silica fume. It comprises nearly 95\% ($\text{SiO}_2 + \text{Fe}_2\text{O}_3$) as elongated particles and exhibits a diffused band (in the $2\theta$ range 20$^\circ$ to 30$^\circ$) in X ray diffraction studies. High Reactive Metakaoline (HRM) has extremely high reactivity and than that of the strength and performance of 10\% MK was similar or better than 10\% silica fume.

At one day where the contribution owing to pozzolonic activity is expected to be small, the relative strength increases with an increase of MK up to amount of 1.18\%, at 10\% replacement and than falls linearly to 0.76\% at 30\% replacement. The increase in one day strength was interpreted as being principally a result of the increased acceleration of OPC hydration combined with the contribution from the filler effect. The fall in relative strength in high MK contents must clearly be a result of the dilution effect. At 90 days all the cementitious reactors are close to completion and short term strength enhancement owing to the acceleration of OPC has been lost.
Therefore 90 days figure represent the long term effect that the pozzolonic activity and filler effect have an enhancing concrete strength.

According to K Ganesh Babu & P Dinakar\textsuperscript{(40)} Metakaoline is the mineral admixture that appears to have significant potential for the production of high strength and high performance concretes. The present paper attempted to quantify the 28 days cementitious efficiency of Metakaoline in concrete at various replacement levels from the data available in the literature. It was seen that the efficiency of Metakaoline in concretes can also be defined through a procedure adopted earlier for other cementitious materials like fly ash, silica fume and GGBS. The overall strength efficiency was found to be a combination of two parameters, one depending on the age and the other depending on the %age of replacement as is the case with other pozzolona.

Metakaoline is a supplementary cementitious material with pozzolonic properties. Its activation by tricalcium silicate (C\textsubscript{3}S), tricalcium aluminates (C\textsubscript{3}A) and ordinary Portland cement is reported by Jean Ambrose, Sandrine Maximilien and Jean Pera\textsuperscript{(35)}. The early hydration period of pastes containing Metakaoline was investigated using isothermal calorimetry and Conductivity Differential Thermal analysis, X-ray diffraction and Fourier transform infrared spectrometry were used to follow the consumption of calcium hydroxide (CH) and identify the products of reaction – compressive strength porosity were also determined.

Blended cements containing upto 30% MK can easily be developed in countries where pozzolonic admixtures become scarce. At upto 30% replacement, MK acts as an accelerating agent, the pore size distribution is displaced towards small values, the CH content is considerably reduced
and comp. strength are not affected. The ability of MK to quickly consume CH was used by the authors to develop new cement matrices that allowed their reinforcement by E-glass fibers, usually destroyed in OPC. Other fields of applications are still being investigated: improvement of concrete durability in severe environments, development of high strength concrete and formulation of colored concrete without efflorescence.

According to David Trejo & Ceki Halmen (19) the objective to evaluate critical performance characteristics of cement based materials containing Metakaoline MK235 & MK349. Five durability tests were performed on samples prepared from concrete mixtures containing two types of Metakaoline, silica fume and control samples. Concrete mixtures were prepared at three different w/cm levels (0.4, 0.5 & 0.6) for all tests with the exception of ASTM G 109 test, where all samples had a w/cm of 0.5. The freeze-thaw resistance of samples containing different supplementary cementitious materials was evaluated using 48 samples. Comp. strength of all the mixtures was determined at 7, 28 & 90 days using 4 x 8 inch. Cylinders.

The comp. strength results indicated that at all w/cm levels samples containing both types of Metakaoline exhibited statistically significantly higher comp. strength values at early ages compared to the control samples, although at later ages the differences in compressive strength values decreased to insignificant values. This is a significant finding as higher early strength is a desirable characteristic for precast, pretension products. The freeze-thaw results indicate that at a w/cm of 0.4, silica fume and Metakaoline containing samples exhibited statistically significantly higher durability factors compared to the control samples. At a w/cm of 0.4, the samples containing MK 349 performed statistically significantly better.
compared to the samples containing MK 235. Also at a w/cm of 0.5, samples containing SCMs performed better compared to the control samples, however the difference between the samples containing the two types of Metakaoline were not statistically significant. Although the mean durability factor observed for the samples containing SCMs at w/cm of 0.6 was higher compared to the control samples, the differences were not statistically significant.

The performance of two Metakaoline as SCMs was evaluated at 8% by wt. of cement replacement by Justice J.N. et al (39). Performance of Metakaoline mixtures was compared to control mixtures at w/c of 0.4, 0.5 & 0.6 where no SCM had been used and two mixtures where silica fume had been used as a partial replacement for cement. In both mixtures containing Metakaoline compressive strength, splitting strength and flexural strengths increased, as well as elastic modulus as compared to control mixtures. Additionally, considering durability, both Metakaoline reduced rapid chloride ion permeability and expansion due to alkali-silica reaction when compared to control and silica fume mixtures.

With regard to workability and setting time, both Metakaoline examined generally required more super plasticizer and shortened setting time of pastes as compared to control mixtures and silica fume mixtures. Increased concrete strength as compared to both control and silica fume mixtures was measured for concrete produced with both Metakaoline. However the finer Metakaoline fineness was more apparent at lower w/cm. Concrete produced with the finer Metakaoline also exhibited an increased rate of strength gain. With regard to the durability tests reported here, concrete produced with Metakaoline at 8% by wt, if cement exhibited reduced permeability, as measured by rapid chloride permeability test
(RCPT) with very low measurements at w/cm if 0.4, low measurements at 0.5 AND moderate measurements at 0.6. The coarser Metakaoline generally produced greater reductions in permeability at all three w/cm examined.

E. Badogiannis, G. Kkali & S. Tsivilis \(^{(26)}\) have focused on the optimization of the thermal treatment conditions of kaolin and their effect on the reactivity of the produced Metakaoline.

Metakaoline is an adequate pozzolonic addition for lime mortars, providing adequate mechanical and water absorption characteristics for application in conservation of mortars. A further advantage of lime/pozzolona mortars is for their lower environmental impact when compared to cement mortars. An important conclusion that arises is that the use of greater percentages of pozzolona in a mortar does not necessarily imply improved characteristics. For each particular pozzolonic product there are specific formulations that produce better results for the applications those are being considered.

Cement/Cementitious material used by V.y.Garus, K.E. Kuritis \(^{(74)}\) in concrete is in the powder form, hence particle size, shape, surfaces, particle size distribution (particle characteristics) have effected on the property of concrete(final product) packing arrangements. Powder consists of a no. of particles each in contact with its neighbours. If we assume that powder particles in given sample are of uniform size and spherical then packing arrangement could be (1) Rehmoheral packing (closed) (2)Cubic packing (most open, loosest). A theoretical porosity of 26% is possible in the closed packing while 48% in loosest packing. In fact powder sample do not have uniform size and spherical particles and hence total porosity is between 30% to 50%. Porosity is nothing but fraction of total
volume occupied by the free space between the particles. When particles of varying sizes are present, porosity lower than the theoretical minimum of 26% is also possible. This is because of smaller particles fit in the void space thereby giving reduced porosity.

Jiping Bai, Albinas Gaillius (36) has presented statistical models for predicting the consistency of concrete incorporating PC, FA & MK from the experimental results of standard consistency tests.

2.2.7 Role of Silica fume

The role of silica fume as a cementitious byproduct is reported in terms of its historical and experimental aspects. Silica fume is found to be 100 nm in size and therefore is the finest component ever to be used to make cements or concrete so far. Its average particle size when compared to that of Portland cement (10 µm - 15µm) is almost 100 times smaller in diameter(size of the particle), which enhanced compressive strength from the use of silica fume at 28 days was found. The compressive strength was found to increase significantly with increasing level of silica fume used in the mixture. Greatest increase in strength can be seen in the concrete mix with silica fume at 20%. This is thought to be due to improved densification of the cement matrix and also to stronger bonding in the interfacial zone between the cement paste and aggregates.

In the experimental investigation, V. Bhikshma, K Nitturkar & Y. Venkateshan (70) have considered the mechanical properties of high strength concrete of grades M_{40} and M_{50} at 28 days characteristic strength with different replacement levels of cement with silica fume or micro silica of grade 920 D are considered. Standard cylinders (diameter 150mm and height
300mm) and Standard prisms (100 mm x 100 mm x 550 mm) were considered in the investigation. In all, 144 specimens were casted with or without silica fume. The mechanical properties viz. compressive strength and stress strain characteristics of high strength concrete with various replacement of silica fume viz. 3%, 6%, 9%, 12%, & 15% has been considered. The investigations revealed that the use of waste materials like silica fume improved the mechanical properties of high strength concrete which is otherwise hazardous to the environment and thus may be used as a partial replacement of cement.

Cement replacement upto 12% with silica fume leads to increase in compressive strength, splitting strength and flexural strength for both M40 & M50 grade concrete. Beyond 12% there is a decrease in compressive strength, splitting strength and flexural strength for 28 days curing. It is observed that the comp. strength, splitting strength and flexural strength of M40 grade concrete is increased by 16.37%, 36.06% and 16.40% respectively and for M50 grade concrete 20.20%, 20.63% and 15.61% respectively over controlled concrete.

There is an increase in Young’s modulus of concrete as silica fume content increases. This increase is again upto a replacement level of 12%. The Young’s modulus at this replacement level is Ec = 32.19 GPa, for M40 grade concrete which is 28.06% higher than conventional concrete. There is a decrease in workability as the replacement level increases and hence water consumption will be more for higher replacements. The ratio of cube strength to cylinder is found as 1.22 & 1.24 respectively for M40 and M50 grades where as for the conventional concrete is 1.20. The maximum replacement level of silica fume is 12% for M40 and M50 grades of concrete.
As high performance Portland Cement (PC), flyash (FA) and Metakaoline (MK) concrete have been developed in wide applications.

The objective of the programme was to establish a relation between w/cm ratio and comp. strength of concrete with silica fume by L.V.A. Seshasayi & M. Sudhakar\(^{(45)}\). In the silica fume concrete, cement was replaced with 9% of equal wt. of silica fume in all the corresponding mixtures. The 9% value was fixed because it was found to be an optimum replacement value from previous results of the programme unpublished report from REC, Warangal. Further, a review of literature show that the maximum dosage recommended for use of silica fume was 10% only. Ten values of w/cm. ratio were taken ranging from 0.30 to 0.52. A total of forty mixtures were tested to obtain the 150 mm cube comp. strength.

The silica fume used in this investigation exhibits good pozzolonic properties and can be used in the production of high strength concrete. The relation between comp. strength (MPa) and w/cm ratio of silica fume concrete with 9% replacement of cement by silica fume can be formed. Micro silica is very reactive of effective pozzolonic material. It is mainly used in concrete for enhancing mechanical properties, improving durability, enhancing constructability. The use of micro silica or silica fume in production of high strength and high performance concrete has been looked widely and proved by reputed institutions like SFA. Special use of micro silica is the production of high performance concrete structures like bridges where the strength and durability properties of concrete are critical. Micro silica can be used to replace cement in a given concrete mixture by R.H.Nair\(^{(61)}\). The relative costs of two materials do not make this a practical approach for saving cement. If cost saving is the goal, fly ash or blast furnace slag is better replacement material for cement.
It is high time that our engineering and design fraternity start including micro silica – a wonder mineral that imparts strength, durability, weather proofing corrosion control etc. in one go at the time of construction itself. Ensuring huge time and cost savings to the client and thereby improving the specifying agency’s and builder’s reputation. Micro silica has also been used to provide increase resistance for concrete exposed to a variety of aggressive chemicals. In such applications, the amount of micro silica is typically much greater than that used for other durability applications usually 15% by mass of cement or higher.

### 2.2.8 Limit of replacement of Cement

The manufacture of OPC is a costly and energy intensive process, besides polluting the environment heavily. OPC production is associated with emission of carbon dioxide, which is a major source of global warming. Also to produce one ton of OPC nearly 1.5 tons of earth minerals are being used and at the same time, one ton of CO$_2$ is emitted to the atmosphere. Due to growing environmental concerns and to conserve energy and natural resources of our earth, efforts have been made to utilize industrial and agro waste products in the construction industry as a pozzolonic mineral admixture to replace OPC partially. Rice Husk (RH) is one of such materials which constitute about one fifth of the 300 million metric tons of rice produced annually in the world. RH contains about 20% of ash by wt. when incinerated at a temperature not exceeding 800°C for one hour. Because of their high ash content and the silicon dioxide (SiO$_2$), it is used as a SCM in concrete.
The objective of the investigation according to K Ganeshan, K Rajagopal, K Thangavel and R Several & V Saraswathi (41) to evaluate RHA (both open air fired ash and burnt at controlled temp.) as SCM for cement and to evaluate the threshold limit of replacement of cement. Uniform water to binder (w/b) ratio of 0.55 was adopted for different Cement Replacement Levels (CRL). Maximum CRL was 35%, even at this CRL and in absence of super plasticizer in the mix, the workability was not affected. However, if the surface area of Standard Rice Husk Ash (RHA) is increased, further mix may need more water, as RHA is hygroscopic in nature. Workability of the mix containing open air burnt and controlled fired ashes are not affected significantly up to 35% CRL with the water binder ratio of 0.55. This is due to the lubricating effect of the RHA particles while mixing. As the percentage of CRL is increased, the cube comp. strength is gradually reduced for the mixes containing open air fired RHA. On the other hand in the case of specimens containing controlled fired RHA, a gradual increase in strength was observed upto 30% CRL.

Cylinder compressive Strength of specimens was gradually increased as the percentage of CRL is increased from 5% to 30% when both the category of RHA is mixed. This is due to the column effect provided by the cellular structure of the active silica present in the RHA in cylindrical specimens. Cube comp. strength, cylinder comp. strength, splitting strength and direct tensile strength data showed a threshold level of replacement as 30% and both open air fired ash and controlled thermally treated RHA.

Water absorption, effective porosity, permeable voids and coefficient of water absorption data showed that controlled thermally treated RHA blended mortars improved the micro structural characteristics to a greater extent when compared to the mix made with open air fired RHA.
This indicates that the activity of amorphous silica was improved by controlled burning of RHA. The carbon present in open air fired ash decreased the impermeability characteristics.

The RCPT data indicates a considerable decrease in permeability with increasing CRL for both open air fired ash and thermally treated ash blended mortars. This was observed due to higher silica reactivity leading to increase of C-S-H gel formation and decrease of capillary pores in the blended mortars. Concrete is the most widely used construction material because of its flowability in to complicated forms i.e. its ability to take any shape while wet and its strength development characteristics when it hardens. In concrete fine and coarse aggregates constitute about 75% of the total volume. To describe completely the ingredients of the concretes by loosing the numerical values of the important characteristics. The loss on ignition (LOI) of mineral admixtures is usually expressed as percentage loss of mass. LOI of rice husk ash (RHA) is 1.5 gms/cc, how this is computed and what would be the valued in percentage terms.

According to M.C. Nataraja and B.M. Ramalinga Reddy\(^{(46)}\) by using the draft IS 10262 “mix design calculation by absolute volume method”, that it doesn’t require the information of air content of concrete to be used in the calculations and this aspect is always considered in the mix design guidelines given by many prominent institutions such as ACI\(^{(4,5)}\). They have given the computations for the contents of 15% RHA concrete mix and mentioned them as cement: FA:CA = 372:630:1128 kg/m\(^3\). The quantity of 372 kg/m\(^3\) mentioned consists of cement of 316.2 kg/m\(^3\) and RHA of 55.8 kg/m\(^3\). Regarding the water content of concrete for computation of w/c ratio or water binder ratio, the engineers have to note that the actual water content in SP (Super Plasticizer) is also to be accounted.
The Mineral Admixtures (MA) have ability to act as cementing material recognizing that MA’s contribution to concrete strength comes mainly from its ability to react with free calcium hydroxide produced during cement hydration. \(^{(31,68,40)}\). The rate of this reaction called a pozzolonic reaction (PR), when compared to Cement Hydration Rate (CHR) determines the value of ‘k’. The need for reducing the no. of trials using rational approaches such as Abram’s Law. The cementing efficiency of RHA and Bolomey equation is for comp. strength of concrete. The strength of cement concretes (CCs) are generally less than that of RHA Concretes (RHACs) and therefore ‘k’ of RHA < 1, However, it is seen that at equal water binder ratios, the difference between CC & RHACS reduces water indicating that ‘k’ of RHA increases with age.\(^{(61)}\)

2.2.9 Challenges to concrete industry

The world is passing through difficult and troubled times and we live in a rapidly changing world. The construction industry is facing many challenges – global warming, climate change forces and the capability to achieve sustainable development and economic progress without damaging our environment. The concrete industry in particular faces further challenges. There is extensive evidence to show that concrete materials and concrete structures all over the world are deteriorating at a rapid rate and that we are unable to ensure their long term durable service life of performance. To confound this situation, there is an urgent need to regenerate our infrastructure systems to eradicate poverty and provide a decent quality of life for all the people of the world. The current emphasis on high strength and very high strength and the design philosophy of durability through strength for concrete materials and concrete structures is fundamentally due to this
misleading concept and vision that is primarily responsible for the lack of durable performance of concrete in real life environments.

The concrete materials must be manufactured for durability and not for strength. This concept of strength through durability can be achieved through careful design of the cement matrix and its microstructure. If concrete is to be an eco-friendly and sustainable driving force and construction material for social change, the need is to produce durable concrete with strengths of 30 MPa to 60 MPa to 80 MPa rather than very high strength concrete without an assured durable performance. High strength concretes should be seen in relation to the overwhelming evidence of alarming and unacceptable rate of damage and deterioration of concrete structures all over the world, when they are exposed to real and aggressive environments. The fact that structures seldom fail due to lack of intrinsic strength and the fact that the major problems confounding concrete structures is not lack of strength but lack of durable service life strongly implies that the concept of durability through strength, implicit in ultimate strength design approach is invalid, flowed and indeed unattainable.

For a variety of reasons, the concrete construction industry is not sustainable. First, it consumes huge quantities of virgin materials. Second, the principal binder in concrete is Portland cement, the production of which is a major contributor to greenhouse gas emissions that are implicated in global warming and climate change. Third, many concrete structures suffer from lack of durability which has an adverse effect on the resource productivity of the industry. Because the high volume fly ash concrete systems addresses all three sustainability issues, its adoption will enable the concrete construction industry to become more sustainable\(^{(55)}\).
The high volume fly ash concrete system overcomes the problems of low early strength to a great extent through a drastic reduction in the water cementitious materials ratio by using a combination of methods, such as taking advantage of the super plasticizing effect of fly ash when used in a large volume, the use of a chemical super plasticizer, and a judicious aggregates grading. Consequently, properly cured high volume concrete products are very homogeneous in microstructure, virtually crack-free and highly durable. Because there is a direct link between durability and resource productivity, the increasing use of high volume concrete will help to enhance the sustainability of the concrete industry.

The high volume fly ash concrete offers a holistic solution to the problem of meeting the increasing demands for concrete in future in a sustainable manner and at a reduced or no additional cost and at the same time reducing the environmental impact of two industries that are vital to economic development namely the cement industry and the coal fired power industry. The technology of high volume fly ash concrete is especially significant for countries like China and India. Where, given the limited amount of financial and natural resources, the huge demand for concrete needed for infrastructure and housing can be easily met in a cost effective and ecological manner.

There is high alkali activation effectiveness of new silica fume activator. As it has been shown it significantly overcomes the current alkali activators like Sodium hydroxide and water glass according to Vladmir Z Ivica.

Rheological tests on cement paste were used successfully to select the type and dosage of mineral admixtures that improved concrete
workability by Chiara F Ferraris, Karthik H Obla, and Russell Hill \(^{(18)}\).

Among the six different mineral admixtures tested, UFFA was determined to give the best results by reducing the yield stress and viscosity. These improved rheological properties were not achieved by increasing the water demand and/or the High Range Water Reducer (HRWR) admixtures dosage. Therefore addition of UFFA improved the concrete flow without a potential decrease of the hardened properties or an increase in cost.

The ability of the concrete to resist the ingress of exterior deleterious agents is a very important indicator of the durability of concrete. The ease or difficulty with which gas can migrate through the hardened concrete mass is referred as gas permeability. The permeability of two classes of different High Performance Concrete (HPC) containing High Reactivity Metakaolin (HRM) to oxygen permeation is determined by Cembureau method according to Mehralad Mehoutran, Mehdi Bakhshi and Aboozer Bonakdar \(^{(48)}\). The experimental results showed that adding HRM by 5\%, 10\% & 15\% decreased gas permeability of two classes of HPC (w/b = 0.38, w/b = 0.26) upto 2, 3 & 6 times respectively to achieve a more durable concrete. The permeability coefficient of dry HPC conforming Cembureau regime was in the range of \(6.3 \times 10^{-18}\) to \(1.1 \times 10^{-16}\) m\(^2\). These values are at the middle of the range of values generally expected for structural concrete.

By partial replacement of cement content with Metakaoline, the gas permeability of concrete decreased and comp. strength of concrete increased. Therefore, the durability of concrete improved and such a concrete with high durability characteristics would be proper for severe conditions such as Persian Gulf environment. The suitable percentage of cement replacement by metakaolin for reaching to the low permeability and high
comp. strength was 15%. By replacing this percentage, the gas permeability of concrete decreased about 70%.

RHA from parboiling plants and Micro Silica (MS) from the ferrosilicon industries were posing a serious environmental threat and ways were being thought of to dispose them. These materials were actually super pozzolona since they were rich in silica and have about 85% to 90% silica content. A good way of utilizing these materials was to use them for making “High Performance Concrete”. Lot of research has been carried out in this context and it has been beyond doubt that they utilizing these super pozzolonic materials even in small amounts (5% to 10% cement replacements) can dramatically enhance the workability; strength and impermeability of concrete mixes as a result of the concretes were highly durable to chemical attacks, abrasion and reinforcement corrosion. The performance of concrete in terms of water permeability was improved with the addition of MS or RHA. Due to shortage of cheap electric power, MS is not produced in Asian countries.

Siliceous agricultural wastes such as RHA should therefore be utilized as important source for durable concrete according to Ms. Nazia Pathan. Obviously, the rice crop residues have a great role in socioeconomic development of rural area. In the last decades, the use of residue in civil construction, especially in addition to concrete has been subjected to many researches to reduce the environmental polluter’s factors; it may lead several improvements of the concrete properties. The world rice harvest is estimated 500 million tons per year and Brazil is the 8th producer. Considering the 20% of the grain is husk, and 20% of the husk after combustion is converted into ash, a total of 20 million ton of ash is obtained.
How different contents of RHA added to concrete may influence was physical and mechanical properties. Samples with dimensions of 10cm x 20 cm were tested with 5% to 10% RHA, replacing in mass the cement. Adding RHA to concrete, decreasing water absorption was verified. An increment of 25% was obtained when added 5% of RHA. According to the results of splitting test, all the replacement degrees of RHA researched, achieves similar results. As samples studies have a similar result in elastic modulus. A deceasing in the modulus was realized when the levels of RHA were increasing the functions of mortars which were used for block laying in masonry walls are:

(i) To bond units of masonry (ii) to distribute loads (iii) to absorb like sludge from marble processing and Cement Kiln Dust (CKD). The use of this waste was proposed in different percentages both as an addition and instead of cement for the production of self leveling mortar. Two mixtures containing natural aggregates were also prepared for comparison purposes: one using lime stone powder as a mineral addition and the other with no addition. A total of sixteen different mixtures were prepared containing 10%, 20% & 30% waste compared to the total quantity of aggregates and 10%, 15% & 20% compared to the amount of cement.

It is possible to use both the wastes in the manufacturing of self leveling. When the wastes were employed in addition to cement and in partial substitution of aggregates upto 30% can be used to provide mortars of higher physical and mechanical properties than the reference ones.

To study much larger on the strength, durability and cost of low cost high performance concrete mixtures, fly ash, slag and silica fume to replace portions of the cement were used.
2.3 Mineral Admixture:

Mineral Admixtures have changed the concept of making durable and special concrete in last four decades. Mineral admixtures can be broadly divided into two groups; the reactive type and inert type. The latter has no cementitious value while the first type has cementitious value. The first type is further categorized into cementitious material such as Ground Granulated Blast furnace Slag (GGBS), Class C fly ash or Supplementary Cementitious Material (SCM) such as Silica Fume (SF), Rice Husk Ash (RHA), Metakaoline and Class F Fly Ash as Pozzolonic. Materials which have high reactivity are known as super pozzolona e.g. Silica Fume (SF), Rice Hush Ash (RHA), Metakaoline (Mk).

ASTM defined pozzolona as “Siliceous or siliceous and aluminous material which in itself possesses little or no cementitious value but which will in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperature to form compounds possessing cementitious properties” Use of ground granulated blast furnace slag, fly ash, silica fume have become tradition for all high strength, high performance concrete.

Super pozzolonic materials are properly enhancing material. It is not a replacement material for Portland cement. Fly ash or ground granulated blast furnace slag (GGBS) can be used as cement replacement. These materials are frequently used in combination with Portland cement and super pozzolona. Properties improved by pozzolonic material.
Figure: 2.1 Fresh concrete property of Metakaoline

The reaction between a pozzolona and calcium hydroxide is called the pozzolonic reaction. There are two physical effects of the chemical reaction between the pozzolonic particles and calcium hydroxide (i) pore size refinement (ii) grain refinement. The formation of secondary hydration products (mainly calcium silicate hydrate) around the pozzolona particles tends to fill the large capillary voids with micro porosity and therefore a low density material. The process of transformation of a system containing large
capillary voids into a micro porous product containing numerous fine pores is referred to as pore size refinement. Also nucleation of calcium hydroxide around the fine and well distributed particles of the pozzolona will have the effect of replacing large and oriented crystals of calcium hydroxide with numerous, small and less oriented crystal plus poorly crystalline reactions products. The process of transformation of system containing large grains of a component into a product containing smaller grains is referred to as ‘grain size refinement’. Both the pore size and grain size refinement strengthen the transition zone, thus reducing the micro cracking and increasing the impermeability of concrete.

Adding super pozzolona and UFFA brings millions of very small particles to a concrete mixture. Just like fine aggregates fill the space between coarse aggregates, cement particles fill the space between the fine aggregates. UFFA will fill the space between cement grains. Super pozzolona will fill the space between UFFA, resulting in dense cementitious paste. Even if pozzolonic material did not react chemically, the micro filler effect would bring about significant improvements in the nature of the concrete. Over and above these properties, use of fly ash and Ground granulated blast furnace slag will improve the workability; class F UFFA also reduces water demand.

2.3.1 Silica Fume

American Concrete Institute (ACI) defines silica fume as ‘very fine, non crystalline silica produced in electric arc furnaces as a byproduct of the production of elemental silicon or alloys containing silica. (ACI 116R) Production of silicon metal or alloys containing silicon is highly energy intensive. Hence production units are generally established where electrical energy is very cheap. (Out of all power, hydro power is the cheapest). In
India Hydropower generation is negligible resulting in low production of silicon metal and its alloys. So in India requirement of silica fume is fulfilled by importing it from near by countries like Bhutan, Norway and Denmark.

Silica Fume is usually grey coloured amorphous powder. Its particles are very small with more than 95% particles being less than 1µm

Physical and Chemical Properties:

Table 2.3 Chemical properties of silica fume

<table>
<thead>
<tr>
<th>Property</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amorphous</td>
<td></td>
</tr>
<tr>
<td>Silicon Dioxide &gt; 85%</td>
<td></td>
</tr>
<tr>
<td>Trace elements depending upon type of fume</td>
<td></td>
</tr>
</tbody>
</table>

Table 2.4 Physical properties of silica fume:

<table>
<thead>
<tr>
<th>Property</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle Size (Typical)</td>
<td>&lt; 1 µm</td>
</tr>
<tr>
<td>Bulk Density</td>
<td></td>
</tr>
<tr>
<td>(as produced):</td>
<td>130 to 140 Kg/m³</td>
</tr>
<tr>
<td>(Densified):</td>
<td>480 to 720 Kg/m³</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>2.2</td>
</tr>
<tr>
<td>Specific Surface</td>
<td>15000 to 30000 m²/kg</td>
</tr>
</tbody>
</table>

Table 2.5 Comparison of size of silica Fume particles and other concrete Ingredients

<table>
<thead>
<tr>
<th>Material</th>
<th>Nominal Size</th>
<th>SI units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica fume particle</td>
<td>NA</td>
<td>0.5 µm</td>
</tr>
<tr>
<td>Cement grain</td>
<td>No. 325 sieve</td>
<td>45 µm</td>
</tr>
<tr>
<td>Sand Grain</td>
<td>No. 8 sieve</td>
<td>2.36mm</td>
</tr>
<tr>
<td>Coarse aggregate particle</td>
<td>¾ inch sieve</td>
<td>19.0 mm</td>
</tr>
</tbody>
</table>
2.3.2 Metakaoline:

Kaoline is a fine, white clay mineral that has been traditionally used in the manufacture of porcelain. When kaoline – hydrated aluminium disilicate \([\text{Al}_2\text{Si}_2\text{O}_3(\text{OH})_4]\) is calcined between 500\(^0\)C-800\(^0\)C for a definite period of time. Dehydroxylisation (Loss of water) is known as Metakaoline. Thoroughly roasted (but never burnt) kaolinite result in disordered amorphous state, which is highly pozzolonic. Metakaoline (used as super pozzolona) must be processed to remove non reactive impurities and ground down 1.5µ.

**Table 2.6 Typical chemical properties of SCMs**

<table>
<thead>
<tr>
<th>Ingradiend</th>
<th>SiO(_2)</th>
<th>Al(_2)O(_3)</th>
<th>Fe(_2)O(_3)</th>
<th>CaO</th>
<th>MgO</th>
<th>LOI</th>
<th>Na(_2)O</th>
<th>K(_2)O</th>
<th>SO(_3)</th>
<th>IR</th>
<th>TiO(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flyash</td>
<td>57.1</td>
<td>27.1</td>
<td>7.4</td>
<td>2.1</td>
<td>1.2</td>
<td>1.3</td>
<td>0.22</td>
<td>2.2</td>
<td>0.1</td>
<td>82.3</td>
<td>1.2</td>
</tr>
<tr>
<td>GGBS</td>
<td>33.7</td>
<td>14.4</td>
<td>1.5</td>
<td>39.3</td>
<td>6.6</td>
<td>2.8</td>
<td>0.24</td>
<td>0.45</td>
<td>-</td>
<td>-</td>
<td>0.37</td>
</tr>
<tr>
<td>SF</td>
<td>89.5</td>
<td>0.8</td>
<td>1.7</td>
<td>0.1</td>
<td>1.0</td>
<td>4.5</td>
<td>0.6</td>
<td>1.7</td>
<td>-</td>
<td>-</td>
<td>0.03</td>
</tr>
<tr>
<td>Metakaoline</td>
<td>52.3</td>
<td>44.6</td>
<td>0.6</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>0.8</td>
<td>0.16</td>
<td>0.06</td>
<td>0.1</td>
<td>31.4</td>
<td>1.3</td>
</tr>
</tbody>
</table>

**Table 2.7 Physical properties of Metakaoline**

<table>
<thead>
<tr>
<th>Properties</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET Specific surface, m(^2)/g</td>
<td>18.3</td>
</tr>
<tr>
<td>Retention on 45 µm sieve, %</td>
<td>0.9</td>
</tr>
<tr>
<td>D50, micron</td>
<td>1.5</td>
</tr>
<tr>
<td>Accelerated Pozzolonic Index, %</td>
<td>97</td>
</tr>
</tbody>
</table>
Table 2.8 Pozzolonic reactivity of various SCMS

<table>
<thead>
<tr>
<th>Material</th>
<th>Pozzolonic reactivity (mg Ca(OH)$_2$ per gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bauxite (Calcined)</td>
<td>534</td>
</tr>
<tr>
<td>Silica Fume</td>
<td>427</td>
</tr>
<tr>
<td>Blast furnace slag</td>
<td>300</td>
</tr>
<tr>
<td>PFA</td>
<td>875</td>
</tr>
<tr>
<td>Metakaoline</td>
<td>1000</td>
</tr>
</tbody>
</table>

It is concluded that

(i) There are three elementary factors which influence the contribution that Metakaoline makes to the concrete strength when it partially replaces cement in concrete. These are filler effect, the acceleration of OPC hydration and Pozzolonic reaction of MK with Calcium Hydroxide (CH).

(ii) The filler effect was immediate, the acceleration of OPC had its major impact within the first 24 hours and maximum pozzolonic reaction occurred between 7 days and 14 days.

(iii) The positive contribution which Metakaoline made to strength enhancement of concrete did not continue beyond about 14 days irrespective of the replacement level.

Comparing the different pozzolonic materials, initially the rate of pozzolonic reaction of Metakaoline is greater than that of silica fume.
Table 2.9 Degree of reaction of blended cement pastes (Poon et al.)\(^{(59)}\)

<table>
<thead>
<tr>
<th>Mix</th>
<th>Degree of reaction of pozzolonas (%age)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3 days</td>
</tr>
<tr>
<td>5% Metakaoline</td>
<td>20.56</td>
</tr>
<tr>
<td>10% Metakaoline</td>
<td>15.34</td>
</tr>
<tr>
<td>20% Metakaoline</td>
<td>9.38</td>
</tr>
<tr>
<td>5% Silica Fume</td>
<td>15.86</td>
</tr>
<tr>
<td>10% Silica Fume</td>
<td>10.32</td>
</tr>
<tr>
<td>20% Flyash</td>
<td>3.98</td>
</tr>
</tbody>
</table>

Hence Initial permeability is very low.

Polo m et al. (1999)\(^{(58)}\) Investigated that alkali activation of metakaoline is a way of producing high strength cementitious material. The alkaline activation with concentrated NaOH solutions produced an amorphous material. Alonso and Polomo (2001\(^{(6)}\)) found that when Metakaoline activation was carried out with high concentrated alkaline solution in the presence of calcium hydroxide, the main reaction product was sodium aluminosilicate similar to the one obtained when metakaoline was activated in the absence of calcium hydroxide. Additionally there was a formation of CSH gel as a secondary product. The solid ratio (Metakaoline/Ca (OH)\(_2\)) did not influence larger product precipitation; It was produced when solid ratio increased.

Based on the investigation it is concluded that when NaOH concentration was 5M or lower then Metakaoline activation in calcium hydroxide presence, main product formed was CSH gel. When activation was carried out with 10M or higher NaOH concentration, the main reaction product is alkaline aluminosilicate. And secondary reaction product (between 20% and 30%), CSH gel was obtained.
2.3.3 Fly Ash

Fly Ash is composed of non combustible mineral portion of coal consumed in a coal fueled power plant. Fly ash particles are glassy, spherical in shape, ranging in dia from < 1µm to 150 µm. Finer size, spherical shaped glass bead acts like ‘ball bearing’ resulting in ease of flowability.

ASTM classify fly ash into two (1) Class C (2) Class F. Depending upon the amount of CaO contained.

Class C  CaO > 10%
Class F  CaO < 10%.

Class ‘C’ fly ash is cementitious in nature. While classes ‘F’ fly ash is pozzolonic in nature. Some class ‘C’ fly ash may posses both cementitious and pozzolonic property. Fly ash increases workability in three ways.

(1) Finer size, spherical shaped, glass bead acts like ball bearing resulting in ease of flowability. Fly ash has a lower unit weight (compared to OPC) contributing 30% more volume of cementitious material per kg versus cement. Thus Fly Ash products have more cementitious paste. The greater the amount of fly ash in paste, higher the ball bearing action (higher quantity of ball), better lubrication effect on aggregate resulting better concrete flows.

(2) Fly ash creates more paste. Due to its spherical shape and dispersive action makes the cement paste slippery in nature. Finishers notice the ‘creamier’ texture when working. Higher initial setting time helps us in retaining the slump.

(3) Cement particles are electrically charged due to broken bond. They tend to flocculate. Fly ash particles, normally smaller than cement particles get adsorbed on the surface of the cement grains and act as very powerful
dispersant to the cement particles like lingo sulphonate. Combining all the above three effects reduces water demand for workability. Every 10% addition of ultrafine fly ash will result in 4%-5% reduction in water demand. Most of the current coded, fly ash particles limit usage to 15% to 40% which gives about 7% to 15% reduction in water. With 50% replacement of cement with ultrafine fly ash, water requirement are reduced by 30% as compared to the reduction of 25%-30% obtained with expensive super plasticizer. Fly ash reduces the amount of water needed to produce given slump. This will contribute in decreasing permeability. Fly ash will help in pore filling and pore refinement (result of pozzolonic reaction). Further more durable C-S-H will fill capillaries and bleed water channels occupied by water soluble lime (calcium hydroxide). Reduction in segregation and bleeding will result in lower air voids, rock pockets and big holes.

Thus fly ash will be helpful in making concrete impermeable. In short Fly Ash addition will result in

1. Lowering the amount of soluble lime (calcium hydroxide)
2. Converting soluble lime into insoluble C-S-H gel.
3. Decreasing in rate of heat of hydration.
4. Reduction in shrinkage cracks, air voids, capillary pores, micro cracks at the transition zone.
5. Decrease in chlorine penetration. These will contribute in (a) higher corrosion protection (b) Increase the sulphate resistance. (c) Increase resistance to sea water. (d) Reduce alkali silica expansion.

2.4. Durability

Designers of concrete structure have been mostly interested in the strength of characteristics of the material. What is concern in practice is to ensure a satisfactory performance over a sufficiently long period of time. This
performance over-time whether due to initial good quality or to repeated repair of a not so good structure may be termed as the service life of structure.

Fig: 2.2 Relation between concrete performance and service life

Hence concrete structure should be designed and constructed with the aim of satisfying a set of functional requirements over a certain period of time without causing unexpected costs for maintenance and repair. This period of time constitutes the anticipated design service life of structure.

The decline and fall of unsatisfactory structure can be divided into four phases.

(a) Phase A- Design and construction.
(b) Phase B-Pre Corrosion Phase.
(c) Phase C- Local active corrosion.
(d) Phase D- Generalized Corrosion.
Fig: 2.3 The law of fives\textsuperscript{14}, $t_0$ marks the onset of generalized corrosion; $t_1$ marks the end of service life

The accessibility of the reactive substance in the concrete is the rate determining factor when aggressive substance enters. The rate increasing effect of increasing temperature is due to the effect on transport rate. (Higher temperature result in higher mobility of ions and molecules). A simple rule-of-thumb is that an increase in temperature 10\textdegree{}C causes doubling of the rate of reaction. Depending on the type of reaction, the accessibility will be determined by the permeability of still sound concrete or by the passivating layer of the reaction products.
A precondition for chemical reaction to take place within the concrete at a rate which has any importance in practice in the presence of water in some form (liquid or gas)

The common examples of aggressive substances which may be present in moisture are

1. Carbon Dioxide – Necessary for carbonation
2. Oxygen – Necessary for corrosion
3. Chlorides – Necessary for corrosion
4. Acids - Dissolve cements
5. Sulphates – Give expansive reaction with cement
6. Alkalis - Give expansive reaction with aggregates
2.4.1 Sulphate Attack:

Sulphate attacks to only certain components in cement. Sulphate attack is characterized by the reaction of sulphate ions with the aluminates components and ions of sulphates, calcium and hydroxyl of hardened Portland cement or cement containing Portland clinker, forming mainly ettringite and to a lesser extent gypsum. Formation of ettringite after hardening causes expansion of concrete, leading to cracking with irregular pattern. This gives easier access to further penetration and so process continues to complete disintegration.

Cements potentially containing a little or no calcium hydroxide on hydration perform much better (with reference to sulphate attack) for instance, high alumina cement, Portland blast furnace slag cement with more than 70% slag and Portland pozzolana cements with at least 25% pozzolana. (Natural Pozzolana) calcined clay or low calcium fly ash.

On the basis of his work, Dunstan concluded that lignite and sub bituminous fly ash concrete generally exhibited reduces resistance to sulphate attack. The basic postulate of Dunstan’s thesis is that CaO and Fe₂O₃ in fly ash is the main contributor to the resistance or susceptibility of fly ash concrete to sulphate attack. Dunstan\(^{(25)}\) noted that as calcium oxide content of ash increases above a lower limit of 5% or as ferric oxide content decreases, sulphate resistance is reduced. Dunston proposed the use of Resistance factor (R), calculated as follow.

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

C= Percentage of CaO, and

F is the percentage of Fe₂O₃.
The findings of Dunstan’s work were summarized in terms of selection of fly ash for sulphate resistance concrete as follow.

<table>
<thead>
<tr>
<th>R Limits</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>

\( a = \) at 25% cement replacement

\( b = \) Relative to ASTM type II cement of water/cement of 0.45

### 2.4.2 Alkali attack:

The pH value 12.5 to 13.5 of the pore fluid in Portland cement paste, represents a caustic or strongly alkaline liquid in which some acidic rocks (aggregates composed of silica & siliceous mineral) do not remain stable on long exposure. This may lead to destructive expansion. The main parameters influencing the expansion in practice are

1. The reactivity of the aggregates which is based on the presence of amorphous silica.
2. The amount and grain size of reactive aggregates.
3. Alkali and calcium concentration in pore water (Internal amount of aggressive substances).
4. The type of cement (rate of transport)
5. Exposure conditions (external amount of aggressive substances)
6. The amount of water available

Depending upon the degree of disorder in the aggregate structure and its porosity and particle size, alkali silicate gels of variable chemical
composition are formed in the presence of hydroxyl and alkali-metal ions. The mode of attack in concrete involves depolymerisation or brake down of silica structure. It is observed that when a large amount of a reactive material is present in a finely divided form (i.e. under 75µm), there may be considerable evidence of the reaction, but expansion to any significant extent do not occur. In addition to the reduction in the effective alkali content, the use of pozzolonic admixture results in the formation of less expansive alkali-silicate products with a high silica/alkali ratio.

Hydration of crystalline MgO or CaO when present in substantial amount in cement can cause expansion and cracking in concrete.

2.4.3 Concrete Deterioration by corrosion of embedded steel

Corrosion of steel in concrete is an electro chemical process corrosion cell may be generated in two ways.

(1) Corrosion cells may be formed when two dissimilar metals are embedded in concrete such as steel rebars and aluminium conduit pipes or when significant variation exists in surface characteristics of the steel.

(2) Corrosion cell may be formed due to differences in concentration of dissolved ions in the vicinity of steel, such as alkalis, chlorides and oxygen.

As a result, one of the two metals or some parts of the metal when only one metal is present) becomes anodic and other cathodic.

Anode Fe $\rightarrow 2e^- + Fe^{+2}$ (metallic ion)

Cathode: $\frac{1}{2} O_2 + H_2O + 2e^- \rightarrow 2(OH^-)$

Rust has higher volume than metallic iron may be as high as 600 percent of the original metal.
Anodic reaction involving ionization of metallic iron will not progress far unless the electron flow to the cathode is maintained by the consumption of electron at cathode; for this the presence of both air and water at the surface of the cathode is absolutely necessary. Also ordinary iron and steel products are covered by thin iron-oxide film which becomes permeable and strongly adherent to the steel surface in alkaline environments thus making steel passive to corrosion.

In the absence of chloride ions in the solution, the protective film on steel is stable as long as pH of solution says above 11.5 when calcium hydroxide is carbonated or neutralized by an acidic solution the pH in the vicinity of steel is reduced below 11.5. This will destroy the passivity of steel and setting the stage for corrosion process.

In the presence of chloride ions depending on the Cl-/OH⁻ ratio, protective film may be destroyed even at pH values considerably above 11.5 when Cl⁻/OH⁻ molar ratio higher than 0.6, steel seems to be no longer protected against corrosion. Common source of chloride in concrete are admixtures, salt contaminated aggregates and Cl⁻ penetration of deicing salt solution or sea water.

2.4.4 Concrete in Seawater:

Most seawater is fairly uniform in chemical composition having 3.5 percent soluble salts by weight. The ionic concentration of Na⁺ and Cl⁻ are typically 11000 and 20000 mg/litre. Respectively concentration of Mg²⁺ and SO₄²⁻ are typically 1400 mg/litre and 2700 mg/litre. The pH of seawater
varies between 7.5 and 8.4. The average value in equilibrium with the atmospheric CO$_2$ being 8.2. Under exceptional conditions (i.e. in shelter bays and estuaries). pH value lower than 7.5 may be observed, due to higher concentration of dissolved CO$_2$. Which makes the sea water more aggressive to Portland cement concrete.

Deterioration of concrete exposed to marine environment is a result of combined effects of chemical action of sea water constituents on cement hydration products, alkali aggregate expansion (when reactive aggregates are present). Crystallization pressure of salts within concrete if one face of structure is subjected to wetting and other drying conditions, frost action in cold climates, corrosion of embedded steel in reinforced or prestressed members and physical erosion due to wave action and floating objects. Attack on concrete due to any one of these causes tends to increase the permeability. This will make the material progressively more susceptible to further action by the same destructive agent but also other types of attack. It should be noted in permeable concrete the normal amount of CO$_2$ present in sea water is sufficient to decompose the cementitious products

(1) Calcium silicate into $\rightarrow$ Calcium silico carbonate
(2) Calcium hydroxide into $\rightarrow$ calcium carbonate
(3) Calcium Aluminates hydrates into calcium carbo aluminate hydrates.

Deleterious interactions of serious consequence between constituents of hydrated Portland cement and sea water takes place when sea water is not prevented from penetrating into interior of concrete.

Pores and micro cracks already exist in the interfacial zone, but their enlargement through variety of phenomena other than corrosion must
take place for significant corrosion of embedded steel in concrete. A progressive escalating cycle of cracking corrosion more cracking begins leading to complete deterioration of concrete. Depending on the cation type present in the sulphate solution (i.e. Na\(^+\) or Mg\(^{+2}\)) both calcium hydroxide and C-S-H may be converted to gypsum by sulphate attack.

\[
Na_2SO_4 + Ca(OH)_2 + 2H_2O \rightarrow CaSO_4.2H_2O + 2NaOH
\]

\[
MgSO_4 + Ca(OH)_2 + 2H_2O \rightarrow CaSO4.2H_2O + Mg(OH)_2
\]

\[
3MgSO_4 + 3CaO.2SiO_2.3H_2O + 8H_2O \rightarrow 3(CaSO_4.2H_2O) + 3Mg (OH)_2 + 2SiO_2.H_2O
\]

In the case of sodium sulphate attack, formation of sodium hydroxide as a byproduct of the reaction ensures, the continuation of high alkanality in the system which is essential for the stability of the main cementious phase. (C-S-H)

In the case of magnesium Sulphate attack conversion of Calcium hydroxide to gypsum is accompanied by the formation of the relatively insoluble and poorly alkaline magnesium hydroxide. Thus the stability of the C-S-H in the system is reduced and it is also attacked by the sulphate solution. This magnesium sulphate attack is more severe.

It is proposed that entrigitite expansion is suppressed in environment where (OH\(^-\)) ions have essentially been replaced by Cl\(^-\) ions. This proves that alkaline environment is necessary for swelling of ettringite by water absorption.
Unless concrete is very permeable, no damage results from chemical action of sea water on cement paste because the reaction products, being insoluble, tend to reduce permeability and stop further ingress of sea water into interior of the concrete. This kind of protective action would not be available under condition of dynamic loading and in the tidal zone, where reaction products are washed away by wave action as soon as they are formed.

2.5. Accelerated Curing

Hossam E.H.Ahmed (32) has discussed Warm water curing technique at 35°C to accelerate the strength gain of concrete for the early prediction of the 28 and 90-day compressive strength. Various concrete mixes in terms of cement type, cement replacement materials, micro silica and fly ash were considered. Super plasticizer admixtures type G and type F was also applied. The compressive strength values were determined at ages of 24 and 48 hours for accelerated cured specimens and at 1, 3, 7, 28 and 90-days for standard water cured specimens. The results revealed that the standard water curing 28 and 90-day compressive strength values can be predicted at age of 24-hour in warm water curing, at 35°C through mathematical model with a confidence level of 90%. When the warm water curing period is extended to 48-hour, the 28 and 90 days compressive strength can be predicted in confidence level of 95%. He considered number of fourteen concrete mixes to investigate the reliability of the warm water curing technique at 35°C for twenty four hours in predicting the 28-days and 90-days compressive strength. Also, in this research work a warm water-curing regime for 48 hours is applied.
He compared the results of the 24-hour warm water curing with the corresponding one-day standard water curing reveals that increasing the curing temperature from 20°C to 35°C resulting in an increase in the compressive strength by a ratio varies from 40% up to 90%, depends on the applied constituent materials. He also concluded that an increase in curing temperature has a more favourable effect on the strength gain of concrete with cement replacement materials due to the direct effect of the temperature on activating the pozzolonic activity.

Accelerated curing through warm water curing technique at 35°C for 24 hours is convenient, simple and safe for early prediction of the 28 and 90 days compressive strength. Extending the warm water curing period to 48 hours enhance the prediction accuracy. Mathematical models for early prediction of the 28 and 90-days compressive strength after warm water curing at 35°C for 24 or 48-hour are proposed. The concept of warm water curing is suggested to be introduced in the Egyptian Specification.

\[
\begin{align*}
F_{c28} &= 1.44 \ F_{c\text{acc.24}} + 165 \\
F_{c90} &= F_{c\text{acc.24}} + 330 \\
F_{c28} &= 0.92 \ F_{c\text{acc.48}} + 190 \\
F_{c90} &= 0.90 \ F_{c\text{acc.48}} + 270
\end{align*}
\]

Various methods currently available for accelerating the curing of concrete, particularly for precast concrete applications were discussed by Brent vollenweider\(^{(12)}\).

Two distinct methods for accelerating the curing process exist: (1) the use of physical processes and (2) the use of admixtures to act as
catalysts for the hydration process resulting in the achievement of high compressive strengths in relatively short periods of time.

The use of admixtures in order to accelerate the curing process can be further subdivided into the use of mineral and chemical admixtures. Calcium Chloride has proven to be an extremely effective accelerator; however, due to corrosion concerns, its use in concrete with embedded metal is not recommended. The most common mineral admixture used as an accelerator was micro silica or silica fume. While fly ash is frequently used in order to improve other properties of concrete. It has a retarding effect on the initial set and early strength gain of concrete and should not be used for accelerated curing purposes. Some chemical admixtures such as high-range water reducers (HRWR) or super plasticizers have been used as indirect accelerators, primarily due to their ability to reduce the water demand for a given mix. At last he concluded that the major methods that exist for the purpose of accelerating the curing process of concrete can be divided into two categories: physical processes and admixtures. As a result, this is the primary method currently employed by commercial precast manufacturers.

Denny Meyer (21) suggested Accelerated curing results, obtained after only 24 hours, and is used to predict the 28 days strength of concrete. He made attempt to compare two accelerated curing methods using two historical data sets. The first data set consists of Warm Water accelerated 24-hour strengths and the corresponding 28-days strengths collected during the period 1993-1995 in Auckland. The second data set consists of Hot Water accelerated 24-hour strengths and the corresponding 28-days strengths collected during the period 1986-1990 in Wellington. And finally he concluded that the Warm and Hot Water accelerated curing methods to environmental variability, cement chemistry variation in particular. This
comparison is complicated by the fact that the Warm and Hot Water tests were run in different years and in different locations using different aggregates. This meant that the aggregates effect was confounded with the method of accelerated curing. By considering only concretes with a strength of less than 45Mpa the only known result of this confounding has been removed.

In the first attempt a straight line was fitted to the Warm and Hot Water data. It was found that the residual variance for the Warm Water Method was smaller than that for the Hot Water Method, suggesting that the Warm Water Method was more accurate or there was more environmental variation for the Hot Water test than for the Warm Water test.

The second attempt involved a dynamic linear model which allowed the parameter estimates to change over time, in response to changes in cement chemistry (and ambient weather conditions). This method removed the effect of long-term variability by allowing the regression parameters to vary over time. The greater standard deviations associated with the Warm Water regression parameters suggested that there was actually less environmental variation for the Hot Water test than for the Warm Water test. The residual variance for this model was again smaller in the case of the Warm Water Method, confirming that this method may indeed be more reliable than the Hot Water Method.

These results suggested that the simpler Warm Water Method of accelerated curing is preferable to the Hot Water Method and that the equation used to predict 28-days strengths needs to be regularly checked, and recalibrated if necessary. However, this study has also suggested three additional methods for improving the accuracy of 28-days concrete strength
predictions. Most importantly it is suggested that cement chemistry should be included as a predictor in the prediction equation. In addition it is suggested that a dynamic model which permits changes in the regression parameters over time is more appropriate than a static model.

Finally, it is suggested that a single straight line model is not appropriate when the compressive strength of super-strength concrete is to be predicted. In view of the limited number of high strength batches it is probably not feasible to develop separate equations for these high strength concretes. Consequently a quadratic model is recommended to describe the relationship between accelerated 24 hour and 28 days strengths when high strength concretes are to be included in the analysis.

W. Calvin McCall\textsuperscript{(78)}, suggested that internal concrete temperature is the most important factor affecting early compressive strength. He suggested three methods for curing,

- Steam and heated-air curing.
- Curing by jacketed heating
- Curing by electrical heating

**Benefits:**

The findings from this study will be very beneficial to precast yards in terms of the mass production of concrete members with silica fume concrete, quick turn around of such precast concrete members and overall resulting economy from such efforts. Currently accelerated curing techniques such as steam curing were not allowed for FDOT concrete products containing silica fume. The currently approved moist curing techniques took longer time than the steam curing approach. This study has shown that steam
curing, 12-24 hours in duration, can be effectively used for FDOT concrete with silica fume. Short-duration steam curing techniques can drastically improve the turnaround times for the subject precast prestressed concrete products. Precast yards already used steam curing techniques for FDOT concrete products without silica fume. Applying steam curing techniques to the production of silica fume concrete products would allow the precast yards to streamline their production process. The expected result would be increased rates of production and related cost savings, which should translate into economic benefits for FDOT. (Florida Department of Transportation).