CHAPTER 1

INTRODUCTION

1.1 GENERAL

Concrete structures in marine environment show a significant amount of distress even well before their expected service life. Structures in marine environment need to satisfy two basic requirements viz., strength and durability. These two may not always be obtained with the techniques and materials adopted for producing conventional concrete. Even the higher strength concrete, higher shrinkage and heat of hydration may lead to poor performance in such aggressive environment (Biczok 1972).

In recent years many researchers have established that the use of supplementary cementitious materials (SCM) like fly ash, blast furnace slag, silica fume, activated metakaolin, rice husk ash etc., can improve the various properties in fresh and hardened states of concrete. In fresh concrete, these SCMs improve workability and reduce the heat of hydration, whereas in hardened concrete they reduce the porosity by the pozzolonic reaction thus increasing the durability (ACI 226.3R-87, ACI 226.1R-87). In addition to the cost saving by the replacement of considerable amount of cement, SCMs reduce the CO₂ emission during the manufacture of Portland cement. The use of industrial by-products is another reason for using these SCMs in concrete (Malhotra 1999). The performance of SCMs are mainly depending upon the percentage incorporation of these materials in cement. Variation also exists in the incorporation of these materials in concrete. For example, in many
advanced countries these are usually added during mixing at the batching plant. In our country, where majority of the construction is carried out by adopting labour intensive techniques, the cement manufacturers supply factory produced ‘Blended cements’. As per ASTM specification blended hydraulic cements can be defined as “a hydraulic cement consisting of two or more inorganic constituents (at least one of which is not Portland cement or Portland cement clinker) which separately or in combination contribute to the strength gaining properties of the cement” (ASTM C219-94). It was recently reported that the concrete made with intergrinding blended cement gains more strength more rapidly than site blended cement (Detweiler 1996). Examination of the microstructure of the intergrinding cements showed that the process of intergrinding breaks up agglomerates of these fine particles rather than fracturing the particles themselves.

Two types of blended cements, namely Portland Pozzolana Cement (PPC) and Portland Slag Cement (PSC) are available in our country. Out of the total cement production of 156 million tonnes in 2006-07, the PPC contributed to 60 % whereas PSC contributed to 8 % (Ghosh 2007). The increase in production in PPC during 2000-07 is 340 %. The SCMs are mainly industrial by-products from thermal power plants and steel plants. These are also termed as ‘mineral admixtures’.

1.2 MINERAL ADMIXTURES

Mineral Admixtures are fine divided siliceous materials, which are added to concrete in the range of 20-50 % by weight of Portland cement.
1.2.1 Fly Ash

According to ACI 116 R-85 (1985), fly ash is a finely divided residue resulting from the combustion of ground or powdered coal which is transported from the firebox through the boiler by flue gases. Fly ash possesses pozzolanic property and comes under the category of artificial pozzolan. As per ACI 116 R-85, a Pozzolan is a siliceous or siliceous and aluminous material that in itself possesses little or no cementitious value but in the presence of moisture it chemically reacts with calcium hydroxide at ambient temperature to form compounds possessing cementitious properties.

Fly ashes contain approximately 60-85 % glass, 10-30 % crystalline compounds and up to 5-10 % unburnt carbon. Most of the particles in fly ash occur as solid spheres of glass, but sometimes a small number of hollow spheres called cenospheres also occur. Spheres that contain smaller particles of ash are known as plerospheres (Lane 1982, Lauf 1982). The fly ash particles are translucent to opaque, slightly to highly porous and vary in shape rounded to elongated. Particle size varies from < 1 μm to 100 μm in diameter. The fly ash containing less than 10 % CaO is ‘Class F fly ash’ which is generally a product of combustion of anthracite and bituminous coals. The ash containing 15-35 % CaO is ‘Class C fly ash’ which is a product of combustion of lignite and sub-bituminous coals (ASTM C618). Normally the optimum blend of ash with Portland cement that produces sufficient strength at 28 days is 15- 25 % for class F fly ash and 15-35 % for class C fly ash (Cook 1983).

1.2.2 Ground Granulated Blast - Furnace Slag

According to ACI 116 R-85 (1985), granulated blast-furnace slag is defined as, ‘the glassy granular material formed when molten blast furnace
slag is rapidly chilled, as by immersion in water. It consists essentially of silicates and alumino silicates of calcium and other bases. The cementitious action of a slag is dependent to a large extent on the glass content. When compared to rapidly cooled slags, slowly cooled slags are predominantly crystalline and therefore do not possess significant cementitious properties. The glassy structure of slag mainly consists of clear isotrophic transparent grains with rough texture.

Slag mainly consists of oxides of silica, alumina, lime and magnesia (Lea 1971). The particle size of slag is normally less than 45 μm. As per ASTM C989 (1995) the slags are classified as grades 120, 100, 80 based on the slag-activity index corresponding to minimum strength of 115%, 95%, 75% in the 28 days cured OPC mortars respectively (ASTM C989, 1995). The optimum blend of GGBF slag that produces sufficient strength at 28 days is 50 % (Hogan 1981).

1.3 STANDARDS AND SPECIFICATIONS

1.3.1 IS Standards

The performance of the blended cement concrete depends upon the physical and chemical characterisation of mineral admixtures (Hogan 1981, Tikalsky 1988, Monk 1983). In view of this, each country has its own specifications. In India, IS 456:2000 clause 5.2 permits blending these mineral admixtures as part replacement with cement. For RCC constructions IS 456 permits Portland pozzolana cement conforming to IS 1489 (Part-I) and Portland slag cement conforming to IS:455. In the case of pozzolana cement it permits fly ash conforming to grade I of IS:3812 for blending with Portland clinker with possible addition of gypsum. As per IS:3812 (1981) the fly ash should have a specific surface area of 3200 cm$^2$/g and having minimum lime
reactivity index of 4 MPa at the end of 7 days. It also recommends that the fly ash constituent shall not be less than 10% and not more than 25% by mass of Portland pozzolana cement. The chemical requirements of fly ash as per IS 3812:1981 is given in Table 1.1.

Table 1.1 Chemical requirements of fly ash

<table>
<thead>
<tr>
<th>Sl.No.</th>
<th>Chemical Composition</th>
<th>Requirement (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>SiO$_2$+ Al$_2$O$_3$ + Fe$_2$O$_3$, Min</td>
<td>70</td>
</tr>
<tr>
<td>2.</td>
<td>SiO$_2$, Min</td>
<td>35</td>
</tr>
<tr>
<td>3.</td>
<td>MgO, Max</td>
<td>5</td>
</tr>
<tr>
<td>4.</td>
<td>SO$_3$, Max</td>
<td>2.75</td>
</tr>
<tr>
<td>5.</td>
<td>Available alkalis as Na$_2$O, Max</td>
<td>1.5</td>
</tr>
<tr>
<td>6.</td>
<td>Loss on ignition, Max</td>
<td>12</td>
</tr>
</tbody>
</table>

The IS specification does not mention about the CaO content. But the level of replacement and early strength behaviour of fly ash added concrete mainly depends upon the CaO content.

In the case of slag cement, IS 456 permits slag conforming to IS: 12089 for blending with Portland cement clinker. It recommends that slag content shall not be less than 50% by mass of Portland slag cement. The chemical requirement of slag as per IS 12089: 1987 is given in Table 1.2.
Table 1.2 Chemical requirements of slag

<table>
<thead>
<tr>
<th>Sl.No.</th>
<th>Chemical composition</th>
<th>Requirement ( %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>SiO$_2$, Min</td>
<td>30</td>
</tr>
<tr>
<td>2.</td>
<td>Al$_2$O$_3$, Min</td>
<td>7</td>
</tr>
<tr>
<td>3.</td>
<td>MgO, Max</td>
<td>10</td>
</tr>
<tr>
<td>4.</td>
<td>SO$_3$, Max</td>
<td>4</td>
</tr>
<tr>
<td>5.</td>
<td>Sulfide as sulfur, Max</td>
<td>2.5</td>
</tr>
<tr>
<td>6.</td>
<td>Total alkalis as Na$_2$O, Max</td>
<td>0.90</td>
</tr>
<tr>
<td>7.</td>
<td>Loss on ignition, Max</td>
<td>2</td>
</tr>
</tbody>
</table>

1.3.2 ASTM Specifications

1.3.2.1 For fly ash and slag

ASTM (C618) classifies the fly ash as Class C and Class F fly ash based on CaO content and total amount of SiO$_2$+ Al$_2$O$_3$ + Fe$_2$O$_3$. Class C fly ash having CaO content more than 10% and SiO$_2$+ Al$_2$O$_3$ + Fe$_2$O$_3$ is 50% (min) whereas Class F fly ash having SiO$_2$+ Al$_2$O$_3$ + Fe$_2$O$_3$ is 70% (min). The fineness of fly ash is maximum of 34% (wt retained on 45µm sieve). In the case of slag, ASTM classifies Grade 80, 100 and 120 (ASTM C989) based on lime reactivity index. It shall have minimum lime-reactivity index of 35 MPa at the end of 28 days. The fineness of slag is (wt retained on 45 µm sieve) is 20% (max).
1.3.2.2 For blended cements

ASTM also specifies a standard C595M for blended hydraulic cements (ASTM C595M). It classifies the blended cements as follows:

i) Portland blast furnace slag cement: In this, the replacement level of slag is between 25-70%.

ii) Slag Modified Portland Cement: In this, the slag content is less than 25%.

iii) Portland pozzolana Cement: In this, the pozzolana constituent varies between 15-40%.

iv) Pozzolana Modified Portland Cement: In this, the pozzolana content is less than 15%.

From this it can be seen that no standard specifies the optimum replacement level of mineral admixtures in blended cements with regard to durability in aggressive marine environment. Further the corrosion performance of rebar in chloride- contaminated concrete under long term conditions has not been studied in detail earlier.

1.4 NEED FOR THE STUDY

Prediction of service life: There is no detailed investigation is carried out on the quantitative estimation of service life of concrete using blended cements. Service life of concrete structures is mainly affected by corrosion of rebar and deterioration of concrete. Accordingly, prediction of service life due to chloride induced corrosion of rebar and deterioration of concrete by sulphate has been carried out as given in Table 1.3.
### Table 1.3 Prediction of service life

<table>
<thead>
<tr>
<th>Chloride attack on steel</th>
<th>Sulphate attack on concrete</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Laboratory Evaluation studies</strong></td>
<td><strong>Laboratory Evaluation studies</strong></td>
</tr>
<tr>
<td>(a). Macrocell corrosion studies</td>
<td>In 10% MgSO₄ solution</td>
</tr>
<tr>
<td>(b) Salt spray studies in chloride contaminated/ uncontaminated concrete</td>
<td></td>
</tr>
<tr>
<td><strong>Field exposure studies</strong></td>
<td><strong>Field exposure studies</strong></td>
</tr>
<tr>
<td>In the tidal zone of sea, Tuticorin, Tamil Nadu, India.</td>
<td>In the tidal zone of sea, Tuticorin, Tamil Nadu, India.</td>
</tr>
</tbody>
</table>

### 1.4.1 Service Life Prediction of Concrete due to Chloride Induced Corrosion

As per the model suggested by Tutti (1982), corrosion-induced deterioration of reinforced concrete involves three component steps: (1) time for corrosion initiation, \( T_i \); (2) time, subsequent to corrosion initiation, for appearance of a crack on the external concrete surface (crack propagation), \( T_p \); and (3) time for surface cracks to progress into further damage and develop into spalls, \( T_d \), to the point where the functional service life, \( T_f \), is reached. Figure 1.1 illustrates these schematically as a plot of cumulative damage versus time.
Figure 1.1  Schematic illustration of the various steps in deterioration of reinforced concrete due to chloride-induced corrosion

$T_i$ - corrosion initiation, $T_p$ - crack propagation, $T_d$ - time to spall,

$T_f$ - functional service life

1.4.1.1 Prediction of time to corrosion initiation

By chloride diffusion model: The time to initiation of corrosion is normally calculated from diffusion coefficient of chloride ($D_{eff}$) using Fick’s second law. When only natural diffusion is involved different conditions/methods lead to different diffusion coefficients. After concrete has hardened, the diffusion of chloride ions is predominantly controlled by the composition and microstructure of the concrete. Diffusion of chloride is a time dependent process. It will decrease with time since the capillary pore system will be altered as hydration products continue to form. In addition to this, some chloride ions will become chemically or physically bound as they penetrate through the pore system and form complex salts (Friedel’s salt). As such it is difficult to precisely predict the diffusion coefficient. It is reported that the short term migration tests give much higher D values. The most common method widely adopted is the measuring of chloride profile after a
predetermined time and fitting this profile in Fick’s second law of diffusion. Determination of concentration of chloride by volumetric method is laborious and destructive in nature. A non-destructive method that is applicable also in actual field structures needs to be evolved. In the present study using EIS technique, from Warburg-Nyquist plot (under diffusion controlled reaction) the $D_{eff}$ was calculated and compared with the value determined using Fick’s second law.

**By corrosion rate model:** To arrive the time to initiation of corrosion from $D_{eff}$, the threshold chloride concentration of rebar for initiation of corrosion is assumed as 0.4% chloride by weight of cement. But both laboratory and field investigation revealed that the value varies from 0.2-1.4% chloride by weight of cement. So far no single value has been arrived on chloride threshold value because of the numerous influential variables including type of cement, cement alkalinity, concrete mix design, environmental factors, potential, reinforcement composition and microstructure (Glass 1995). Due to above foresaid reasons in chloride diffusion method, the service life prediction based on corrosion rate model shall be more appropriate. In the present investigation, as proposed by the European concrete committee and others (CEB 1997, Khatri 2004), the time to corrosion initiation is calculated if the $R_p$ value is less than 130 KΩ-cm$^2$ whereas the propagation period ends when the $R_p$ value reaches 25 KΩ-cm$^2$. The propagation period corresponding to significant corrosion and just before the appearance of the rust stains on the concrete surface.

**1.4.1.2 Prediction of propagation period and time to spall**

The propagation period is calculated by determining the time to reach a corrosion rate of 0.01 mmpy (Andrade 1993). Using Electrochemical impedance technique (EIS) the corrosion rate is calculated non destructively.
The time for cracking of cover concrete to spalling is usually estimated based on either mathematical model or finite element model. Of the three phases, the estimation of initiation and propagation period are more important for service life prediction.

**Studies on corrosion of rebar:** The corrosion of steel rebar embedded in concrete structures induced by chloride ion contamination is a major problem. The high alkalinity of cement paste offers satisfactory protection against corrosion due to the existence of self-generating protective layer γ-Fe₂O₃ at the steel-concrete interface. The K⁺ and OH⁻ ions are believed to be mainly contributing to the formation of passive layer. Consumption of free calcium hydroxide [Ca(OH)₂] by pozzolanic reaction, leaching of OH⁻ ions and dilution of cement alkalis caused by replacement of fly ash/slag causes the reduction of OH⁻ ions in concrete. The reduction of OH⁻ ions concentration raised the concern over the long-term durability of rebar embedded in chloride contaminated concrete. Only limited information is available on the long-term performance of rebar embedded in blended cements concrete in presence of added chloride. The bound chloride may present a corrosion risk and contributes to the reservoir of available chloride at the steel concrete interface as similar to free chloride in concrete. The acidification, which occurs at an incipient anode in the corrosion process, releases the bound chloride increasing the local chloride activity above its initial value. Compared to ordinary Portland cement concrete, blended cement concrete bound more chlorides. The reduction of hydroxyl ions may release the bound chloride and may accelerate the corrosion of rebar after long exposure under marine environment. This necessitates a thorough understanding on the durability performance of rebar embedded in blended cement concrete under marine environmental conditions. With the increased use of blended cement in various structures in India, the systematic studies on their durability characteristics under sea water become inevitable.
1.4.2 Service Life Prediction of Concrete due to Concrete Deterioration

In the deterioration model, total functional service life is characterized by 0.1% expansion as the tolerable limit in the case of sodium sulphate attack and loss of compressive strength in the case of magnesium sulphate attack. In the present study, 20% reduction in strength, which is corresponding to 1% mass loss, is being taken as the failure of the concrete.

**Deterioration due to magnesium and sulphate ions:** Structural concrete components undergo degradation when exposed to sulphate bearing environments. The intensity and rate of sulphate attack depends upon the mineralogical phases of cement, type of cation (Na\(_2\)SO\(_4\) or MgSO\(_4\)) and concentration of the solution, quality of concrete and exposure conditions. A characteristic feature of the magnesium ions attack on Portland cement paste is that the attack is eventually extended to the C-S-H (Calcium- Silicate-Hydrate) gel which is the principal cementitious constituent and hence when compared to sodium sulphate attack, magnesium sulphate attack is more severe on concrete. The concentration of magnesium sulphate in sea water is more than that of sodium sulphate.

It is believed that when compared to Portland cement, blended cements perform better in sulphate environment The reasons are, (i) because of pozzolanic reaction the consumption of portlandite [Ca(OH)\(_2\)] reduces the formation of gypsum, (ii) the formation of secondary C-S-H leads to the densification of pore structure thus reducing the permeability of sulphate ions and (iii) OPC is replaced by a pozzolanic material entails a reduction of C\(_3\)A content (dilution effect) which reduces the aluminate bearing phases by as much as 30% by weight of the cementitious material. Even if ettringite is formed because of the reduction of pH the ettringite becomes less expansive.
Hence the sulphate resistance of blended cements are by both pozzolanic as well as by dilution effect. But $\text{Al}_2\text{O}_3$ content of blended cements are comparatively more than the Portland cement and this constituent in cement is more susceptible to attack by sulphates. The chemical analysis of a composite material does not yield a satisfactory estimate of its sulphate resistance, there is a need to carry out detailed investigation on the effect of magnesium and sulphate ions on the deterioration behaviour of blended cement concretes.

### 1.5 SCOPE OF THE INVESTIGATION

The chloride attack on steel and sulphate attack on concrete will reduce the service life of concrete structures. So far, no reliable correlation has been established between accelerated short-term tests and long term performance to predict the service life. Accordingly, the scope of the present investigation consists of the following:

1. Evaluation of the corrosion resistance of rebar embedded in PPC and PSC was carried out under substructure condition (Splash Zone) by creating macro cell corrosion condition in the laboratory. By creating chloride ion concentration gradient in concrete, the galvanic corrosion was induced due to external chloride (from outside) which accelerated the corrosion process. The experiment was conducted over a period of 1376 days.

2. Evaluation of the corrosion resistance of rebar under simulated marine aggressive atmospheric condition was carried out in chloride contaminated concrete in the laboratory. To create this environment, 0.5 and 1 % $\text{Cl}^-$ by weight of cement was added at the time of mixing of concrete (internal chloride) and then the
specimens were subjected to salt-spray exposure. The experiment was conducted over a period of 1765 days.

3. Under each test, the progress of corrosion was assessed periodically by measuring the potential, macrocell corrosion current, polarization resistance by EIS technique. Estimation of free and bound chloride from the concrete samples was done using Volumetric method.

4. Non-destructively using EIS technique, the progress of corrosion process such as passivation, initiation of corrosion and uniform corrosion of rebar embedded in concrete was followed.

5. The diffusion coefficient of chloride was determined non-destructively using Warburg coefficient from the Nyquist plot and compared with the value determined using Fick’s law.

6. The enhanced service life of concrete structures using blended cements was estimated based on corrosion rate model using electrochemical impedance technique. The initiation and propagation of corrosion of rebar can be followed by observing distinct Nyquist plot from EIS technique. The service life of concrete was estimated in presence of external (from outside) and internal (added) chlorides.

7. Sulphate resistance of blended cements was evaluated by exposing the concrete specimens (without rebar) in 10% MgSO₄ solution for a period of 36 months. The sulphate resistance was assessed by change in compressive strength, mass loss and resistivity. By conducting the thermogravimetric analysis the expansive products were identified.
8. The effect of conjoint presence of chlorides and sulphates on the durability performance of blended cement was evaluated by exposing the concrete specimens in the tidal zone of sea (Bay of Bengal) of OPMEC (Offshore Platform & Marine Electrochemical Centre), Tuticorin. The concrete deterioration by sulphates and rebar corrosion by chlorides, were evaluated by exposing the plain and rebar embedded concrete specimens.

9. The pore size refinement of blended cement was done quantitatively by estimating calcium hydrates content and pore size. The formation of additional calcium hydrates by pozzolanic reaction in blended cements concrete was quantitatively estimated by differential thermal analysis. Using resistance measured from EIS technique, the pore size was calculated.

The durability factor of rebar in blended cements concrete in terms of corrosion resistance was computed both under laboratory and field conditions. In marine environment, the effect of carbonation-induced corrosion is less compared to chloride induced corrosion and sulphate attack. Due to this, the effect of carbon-di-oxide is not studied. In the evaluation of all the above aspects, three grades of concrete namely 20, 30 and 40 MPa have been used. The mix design is based on same cement content and w/c ratio for blended cement concretes as well as OPC concretes.
1.6 ORGANIZATION OF THESIS

The thesis consists of six chapters:

Chapter 1 gives a general introduction to the mineral admixtures and blended cements. Need for the study, scope of the investigation and the organization of thesis are also presented.

Chapter 2 provides the review of literature on the effect of addition of fly ash and slag added concrete on the behaviour of strength, water, chloride ion permeability.

Chapter 3 discusses the method of experimental procedures carried out to assess the durability performance of rebar embedded in blended cement concretes under marine environmental conditions.

Chapter 4 presents the results and discussion of the experimental studies carried out.

Chapter 5 documents the service life prediction of blended cements concrete based on corrosion rate model.

Chapter 6 summarises the conclusions and scope for future work.

The list of references and vitae are given at the end of the thesis.