CHAPTER 3

EXPERIMENTAL PROCEDURES

For quantifying service life of blended cements, the experiments were designed which simulate the splash zone and atmospheric zone condition of a marine environment under laboratory condition. Studies were carried out on concrete having a strength of 20, 30 and 40 MPa. The cover of concrete studied were 25, 30 and 40 mm. Long term data will be essential to conclusively establish the service life in medium strength concrete. Accordingly the experiments were carried out for a period of more than 3 years.

Using Electrochemical Impedance Spectroscopic (EIS) technique, the initiation and propagation of corrosion was assessed in chloride contaminated/uncontaminated concrete. Deterioration of concrete was carried out in 10% MgSO$_4$ solution. Using thermogravimetric analysis the pore structure refinement of blended cements was done by estimating calcium hydrates content. The details of materials used, experimental methods, exposure conditions and techniques used are discussed below:

3.1 MATERIALS AND THEIR CHARACTERISATION

3.1.1 Cement

In this investigation, the following three types of cement commercially available in the market have been used:
i) Ordinary Portland cement (43 grade) conforming to IS 8112
ii) Portland pozzolana cement (Fly ash based) conforming to IS: 1489 Part1
iii) Portland slag cement conforming to IS: 455.

Cement was obtained from single source and single batch from a reputed firm. The chemical composition details as furnished by the supplier are reproduced and given in Table 3.1. From the table, it can be seen that loss on ignition is highest in pozzolana cement whereas in OPC and PSC it is quite less. CaO content is maximum in OPC i.e., 62-63% whereas it is in the range of 41-46% in both PPC and PSC cements. SiO₂ content is only 20-21% in OPC whereas it is the range of 26-32% in PPC as well as PSC cements.

3.1.2 Particle Size

The particle size distribution of three cements was analysed in a Malvern particle size analyzer. Figure 3.1 compares the particle size distribution of three cements. From the figure it can be seen that in OPC and PPC cements, all the particles are less than 25 µm in size whereas in PSC 25% of particles lies in the range of 21-16 µm and 55% particles lies in the range of 10-8 µm and 20% lies in the range 4-3 µm. It has been reported that the particle size fraction below 3 µm has been found to have the predominant effect on the 1day strength while 3-25 µm has a major influence on the 28 day strength (Lea 1974). It is reported that cement particles larger than 45 µm are difficult to hydrate and those larger than 75 µm never hydrate completely. From the results it can be seen that in all the three cements most of the particles are less than 25 µm in size.
Table 3.1 Chemical composition of three types of cement

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ordinary Portland Cement (%)</th>
<th>Portland Pozzolana Cement (%)</th>
<th>Portland Slag Cement (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon -di-Oxide (SiO₂)</td>
<td>20-21</td>
<td>28-32</td>
<td>26-30</td>
</tr>
<tr>
<td>Aluminium Oxide (Al₂O₃)</td>
<td>5.2-5.6</td>
<td>7.0-10.0</td>
<td>9.0-11.0</td>
</tr>
<tr>
<td>Ferric Oxide (Fe₂O₃)</td>
<td>4.4-4.8</td>
<td>4.9-6.0</td>
<td>2.5-3.0</td>
</tr>
<tr>
<td>Calcium oxide (CaO)</td>
<td>62.-63</td>
<td>41-43</td>
<td>44-46</td>
</tr>
<tr>
<td>Magnesium oxide (MgO)</td>
<td>0.5-0.7</td>
<td>1.0-2.0</td>
<td>3.5-4.0</td>
</tr>
<tr>
<td>Sulphur – tri-Oxide (SO₃)</td>
<td>2.4-2.8</td>
<td>2.4-2.8</td>
<td>2.4-2.8</td>
</tr>
<tr>
<td>Loss on ignition</td>
<td>1.5-2.5</td>
<td>3.0-3.5</td>
<td>1.5-2.5</td>
</tr>
</tbody>
</table>

**Bogue compound composition**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ordinary Portland Cement (%)</th>
<th>Portland Pozzolana Cement (%)</th>
<th>Portland Slag Cement (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tricalcium Silicate (C₃S)</td>
<td>42-45</td>
<td>Not applicable</td>
<td>Not applicable</td>
</tr>
<tr>
<td>Dicalcium Silicate (C₂S)</td>
<td>20-30</td>
<td>-do-</td>
<td>-do-</td>
</tr>
<tr>
<td>Tricalcium Aluminate (C₃A)</td>
<td>7.0-9.0</td>
<td>-do-</td>
<td>-do-</td>
</tr>
<tr>
<td>Tetra Calcium Alumino Ferrite (C₄AF)</td>
<td>11-13</td>
<td>-do-</td>
<td>-do-</td>
</tr>
</tbody>
</table>

**Physical Properties**

| Pozzalanic Material used (%)                 | 0                            | Around 25% Flyash (Metturthermal power station) | Around 50% GGBS (Vizag steel plant) |
| 28 Day Compressive Strength (MPa)            | 62                           | 48                                           | 53                                     |
| Fineness (m²/kg)                              | 295                          | 363                                          | 385                                    |
3.1.3 Aggregates

Well graded river sand and good quality crushed blue granite were chosen as fine and coarse aggregate respectively. The different size fractions of coarse aggregate (20 mm down graded and 12.5 mm down graded) were taken and recombined to get a specified grading. The sand was sieved through a 4.75 mm sieve. Sieve analysis data are presented in Table 3.2. The aggregate grading was selected in accordance with the ACI mix design procedure. The fineness modulus of coarse aggregate was 7.5 and that of fine aggregate was 2.43. The grading of fine aggregate falls in the grading Zone II as per IS: 383 (1963).
Table 3.2 Grading of coarse and fine aggregate

<table>
<thead>
<tr>
<th>Sieve size (mm)</th>
<th>Coarse aggregate</th>
<th>Fine aggregate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cumulative % retained</td>
<td>Cumulative % retained</td>
</tr>
<tr>
<td>20</td>
<td>0</td>
<td>4.75</td>
</tr>
<tr>
<td>16</td>
<td>25</td>
<td>2.36</td>
</tr>
<tr>
<td>12.5</td>
<td>52</td>
<td>0.600</td>
</tr>
<tr>
<td>10</td>
<td>72</td>
<td>0.300</td>
</tr>
<tr>
<td>4.75</td>
<td>100</td>
<td>0.150</td>
</tr>
<tr>
<td></td>
<td>&lt;0.150</td>
<td>100</td>
</tr>
</tbody>
</table>

3.1.4 Water

Potable water has been used for casting concrete specimens. The water is free from oils, acids, alkalis and have a water soluble chloride content of 340 mg/lit. As per IS 456:2000, the permissible limit for chloride is 500mg/lit for reinforced concrete, hence the amount of chloride present is less than the permissible limit.

3.1.5 Steel

High yield strength cold twisted deformed bar of grade Fe 415 conforming to IS: 1786 has been used. The details of chemical composition of the steel rebar grade Fe 415 is Carbon-0.17%; Manganese-0.66%; Silicon-0.11%; Sulphur-0.017%, Phosphorus-0.031% and Fe-Balance.
3.1.6 Mechanical Properties

Mechanical properties were tested by conducting the standard tensile test in the Universal Testing Machine (UTM). Tests were carried out on duplicate specimens and average value was reported. They are as follows:

- Yield strength: 474 N/mm²
- Ultimate tensile strength: 582 N/mm²
- % of elongation (30 cm gauge length): 16%

3.2 MIX PROPORTIONING

The quality of concrete mainly depends upon the proportioning of its constituent materials. The permeability of concrete, which would allow environmental ingress into the concrete and cause corrosion is mainly influenced by the mix proportioning. Rather than a nominal mix, design mix is more appropriate to know the exact behaviour of corrosion of steel. 20, 30 and 40 MPa grades of concrete were designed as per the recommendations of ACI 211-91. A slump of 25-50 mm has been used. The detailed information on the concrete mixes used in the investigation is given in Table 3.3. From the table it can be seen that for each grade, proportions have been kept constant for OPC, PPC and PSC concretes. Same water content as well as same coarse aggregate content has been maintained in all the mixes. In this way, the variations in the mix design have been kept to a minimum. The influence of each type of cement on various aspects can thus be distinctly followed and analyzed.
Table 3.3 Detail of concrete mix proportions

<table>
<thead>
<tr>
<th>Grade</th>
<th>Type of cement</th>
<th>w/c ratio</th>
<th>Cement (kg/m$^3$)</th>
<th>Water (kg/m$^3$)</th>
<th>Fine aggregate (kg/m$^3$)</th>
<th>Coarse aggregate (kg/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M20</td>
<td>OPC</td>
<td>0.67</td>
<td>284</td>
<td>190</td>
<td>770</td>
<td>1026</td>
</tr>
<tr>
<td></td>
<td>PPC</td>
<td>0.67</td>
<td>284</td>
<td>190</td>
<td>770</td>
<td>1026</td>
</tr>
<tr>
<td></td>
<td>PSC</td>
<td>0.67</td>
<td>284</td>
<td>190</td>
<td>770</td>
<td>1026</td>
</tr>
<tr>
<td>M30</td>
<td>OPC</td>
<td>0.54</td>
<td>352</td>
<td>190</td>
<td>739</td>
<td>1026</td>
</tr>
<tr>
<td></td>
<td>PPC</td>
<td>0.54</td>
<td>352</td>
<td>190</td>
<td>739</td>
<td>1026</td>
</tr>
<tr>
<td></td>
<td>PSC</td>
<td>0.54</td>
<td>352</td>
<td>190</td>
<td>739</td>
<td>1026</td>
</tr>
<tr>
<td>M40</td>
<td>OPC</td>
<td>0.42</td>
<td>452</td>
<td>190</td>
<td>655</td>
<td>1026</td>
</tr>
<tr>
<td></td>
<td>PPC</td>
<td>0.42</td>
<td>452</td>
<td>190</td>
<td>655</td>
<td>1026</td>
</tr>
<tr>
<td></td>
<td>PSC</td>
<td>0.42</td>
<td>452</td>
<td>190</td>
<td>655</td>
<td>1026</td>
</tr>
</tbody>
</table>

3.3 MIXING, COMPACTION AND CURING

Good concrete can be obtained only through uniform and thorough mixing, better compaction and adequate curing. In the laboratory, the concrete was mixed by hand mixing. All the constituent materials were weighed and dry mixing was carried out for about 5 minutes and then water was added. The mixing was continued till concrete of uniform consistency was obtained. The specimens were compacted using a table vibrator. After casting, the specimens were demoulded and kept immersed in curing tank containing potable water till the required curing period.
3.4 LABORATORY EVALUATION: MACROCELL CORROSION STUDIES

3.4.1 General

In marine environment, either chloride ion and or oxygen ion concentration gradient formed in the cover concrete leads to the formation of macro galvanic cells on the rebar. The chloride ions depassivate the steel and cause dissolution of the metal at the location called an ‘anode’ or ‘active zone’. Active zone is surrounded by a ‘passive zone’ called ‘cathode’ where oxygen reduction takes place (Sagues 2001). The cell constituting separate anodic and cathodic regions is termed as ‘macrocell’. This creates relatively large-scale potential gradients between anode and cathode causing flow of corrosion current (Rengaswamy 1987). These cells are more prevalent in chloride-contaminated concrete with a spatial separation of 100 mm or more between anodes and cathodes in the same rebar (Broomfield 1995). To simulate marine substructure condition in the laboratory, studies were made by forming chloride ion concentration gradient in concrete, which accelerated the corrosion (Rendell 1990, Suzuki 1990) The corrosion rate of rebar under this condition is a function of the difference in potential between anode and cathode, ohmic resistance of the concrete and polarisation resistance of the rebar (Andrade 1991). The effect of damages on the performance of various coatings such as fusion bonded epoxy coating, cement slurry coating and galvanizing using accelerated macro cell corrosion test were investigated (Kahhaleh 1994, Sagues 1994, Vedalakshmi 2000). In actual field structures, long term corrosion monitoring of concrete structures had also been attempted by creating macro cell corrosion condition either by embedding the stainless steel electrodes or by embedding the steel in high chloride concrete (Broomfield 1995). ASTM (G109-92) has evolved a standard for this type of macro cell corrosion studies to evaluate the chemical admixtures in chloride-
contaminated concrete. Brown et al (1999) modified the prism for evaluating the different types of corrosion inhibiting admixture. In the present study modified ASTM G109-94 a corrosion test prism was used.

3.4.2 Specimen Details

Concrete specimen of size 400 × 250 × 150 mm as shown in Figure 3.2(a) was used. In each specimen, a 320 mm long rebar of 16 mm diameter was embedded at 30 mm cover from the top. Two 450 mm long rebars of 16 mm dia were embedded at 15 mm cover from the bottom. While embedding these bars at bottom, they were kept in such a way that 80 mm lengths of these bars protruded outside of the concrete specimen. Before embedding, the rust as well as scale was removed from the all bars by chemical cleaning in inhibited hydrochloric acid and then dried. Initial weight of the top rebar was measured. After measuring the initial weight, a stem of size 6 mm diameter and 100 mm long was taken and screwed on the top of the rebar as shown in Figure 3.2(b) and from this, electrical leads were taken. Thus, the top rebar fully embedded inside the concrete and not directly exposed to outside atmosphere. By means of this, at the end of the exposure, after removing the stem the final weight of the top rebar could be made accurately for calculation of corrosion rate. After demoulding, the specimens were cured for 28 days. After curing, electrical leads were taken from all the three bars. The rod protruding outside the specimen was sealed by using epoxy compound in order to eliminate the crevice corrosion at these locations. A bund of 345×195×13 mm in size was constructed on the top of the each specimen using 1:1 cement mortar and was sealed in all sides using epoxy resin. All the specimens were taken to the exposure yard and kept on concrete blocks. The arrangement is shown in Figure 3.3.
Figure 3.2(a) Modified ASTM G109-94a corrosion test prism

Figure 3.2(b) Rebar end and protection details
Figure 3.3 Concrete specimens under macro cell corrosion test

3.4.3 Method of Exposure

The specimens were subjected to an alternate wetting in 3% NaCl solution and drying test. 3% NaCl solution was ponded on the top of each specimen for 4 days and allowed to dry for 3 days and thus 7 days constituted one cycle of alternate wetting and drying. During exposure to salt solution, chloride ions tend to diffuse through the cover concrete and cause the corrosion of the top rebar. During the entire exposure period, the chloride concentration is higher at the top of the specimen when compared to the bottom of the specimen and thus a chloride ion concentration gradient gets created. Because of higher chloride concentration at the top, the top rebar acts as the anode and bottom bars act as the cathode. The area of the anode to cathode ratio has been kept as 1:2 so as to accelerate the galvanic corrosion. The experiment was conducted over a period of 1376 days.

3.4.4 Method of Measurement

The initial half-cell potential measurements were made on top rebar using high input impedance multimeter. Saturated calomel electrode was used
as a reference electrode. Then all the rebars were electrically short-circuited. The galvanic current also called macro cell current flow between top and bottom bars was measured once in a month at the end of wet cycle as per procedures outlined in ASTM G109-94a. A 100-ohm resistor was placed between the top and bottom rebars and the potential difference was measured. The current was calculated from this potential difference as:

\[ I_c = \frac{V}{100} \]  

(3.1)

Anodic current of the order of 0.1 \( \mu \text{A/cm}^2 \) indicates the initiation of corrosion. After measuring the current, at the end of each cycle the bars were disconnected. Then the half-cell potential of the top rebar was measured for each specimen after 1 hour thus allowing depolarization of rebar to reach the steady state. At the end of 300, 847, and 1376 days, the specimens were broken open and both the top and bottom rebars were taken out and examined visually.

### 3.4.5  Visual Observation and Scanning Electron Microscopic Studies

During the exposure, the initiation of rust stains on the top of the concrete specimen was monitored periodically. This indicates that the rebar embedded inside the concrete gets corroded. After breaking open the specimens, the rebars were taken and the extent of rust on the rebars was examined visually and photographs were taken.

Scanning electron microscopic studies were carried on the exposed surface of the rebar after 300 days of macrocell corrosion test. From the corroded rebar, 2.5 cm length was cut and examined using Hitachi S3000H scanning electron microscope. The experiment was conducted only in 20 MPa
- OPC, PPC and PSC concretes as there is no significant change are observed on the rebar embedded in 30 and 40 MPa concrete at the end of 300 days.

3.4.6 Corrosion Rate from Gravimetric Weight-loss

The stem was removed from the top rebar in all the specimens. After pickling the rebars in inhibited hydrochloric acid as specified in ASTM G1 (1995), the final weight was measured. From the initial and final weight, the corrosion rate in mmpy was calculated using the following formulae,

\[
\text{Corrosion rate in mmpy} = \frac{87.6 \times w}{D \times A \times T}
\]  

(3.2)

where  
- \( w \) - loss in weight, mgms
- \( D \) - Density of iron, gm/cm\(^3\)
- \( A \) - Area, cm\(^2\)
- \( T \) - Time, hrs

3.4.7 Determination of \( \text{Cl}^- \) and \( \text{OH}^- \) ions Concentration

3.4.7.1 \( \text{OH}^- \) ions concentration

The concentration of \( \text{OH}^- \) ions was determined from the powdered concrete sample by decantation method. For this, the concrete core samples up to a depth of 120 mm were taken from one of the duplicate specimens. Then the sample was sliced at every 30 mm depth up to a depth of 90 mm. The core samples taken from the concrete specimens are shown in Figure 3.4. Each slice was powdered and sieved through a 600 \( \mu \)m sieve. Then this powder was mixed with distilled water at the ratio of 1:3 by weight. This mixture was taken in a closed glass tube and shaken for 10 minutes and kept
for 48 hrs to dissolve the OH⁻ and Cl⁻ ions completely. After 48 hrs, the solution was filtered and used to determine the OH⁻ ion concentration. A known amount of solution was titrated against 0.1 N H₂SO₄ using phenolphthalin as an indicator and from the titrated value, the OH⁻ ion concentration was calculated.

![Image](image.png)

**Figure 3.4 Core samples after 847 days of exposure**

### 3.4.7.2 Cl⁻ ions concentration

The water-soluble chloride content was determined by volumetric analysis using silver nitrate method (Mangat 1991, Muralidharan 2005). The decanted solution filtered for OH⁻ ion concentration was used for chloride determination also. 5 ml of solution was titrated against 0.01 N silver nitrate using potassium chromate as an indicator. From the titrated value, the Cl⁻ ion concentration was calculated.

### 3.4.8 Determination of Diffusion Co-efficient of Chloride

When chloride ion diffusion into the concrete is in uni direction, it obeys the Fick’s second law of diffusion. This enables the prediction of the apparent diffusion coefficient, if the chloride concentration at the concrete
surface as well as chloride concentration at any known depth are known. Fick’s second law of diffusion is given below:

\[
\frac{\partial c}{\partial t} = D_a \frac{\partial^2 c}{\partial x^2} \tag{3.3}
\]

An analytical solution to the Equation (4.3), assuming that the flux of chlorides at any time is proportional to the chloride concentration gradient in the concrete of a semi-infinite medium is as follows (Browne 1980, Berke 1994).

\[
C_x = C_s \left[1 - \text{erf} \left( \frac{x}{2 \sqrt{D_a t}} \right) \right] \tag{3.4}
\]

where

- \(C_x\) - the chloride ion concentration at depth \(x\), \(\text{mol/lit}\)
- \(x\) - thickness of concrete, \(\text{cm}\)
- \(t\) - exposure time, \(\text{sec}\)
- \(C_s\) - surface chloride concentration at the concrete surface, \(\text{mol/lit}\)
- \(D_a\) - the apparent chloride diffusion co-efficient, \(\text{cm}^2 /\text{sec}\)
- \(\text{erf}\) - the Gaussian error function.

It is widely accepted that the transport behaviour of chloride ions in concrete is a more complex and complicated process that can be described by Fick’s law of diffusion. This approach, therefore, characterized as semi empirical resulting in the calculation of an ‘apparent effective diffusivity’.

From the chloride concentration determined at various depths \((C_x)\), the chloride profile curve was established. Taking 3% NaCl (ponding solution) as the surface chloride concentration \((C_s)\), the \(D_a\) was calculated by
fitting the chloride profile curve in Equation (3.4). Using the Non-linear square curve fit method, the best ‘D_a’ was calculated.

3.5 SALT SPRAY EXPOSURE STUDIES

3.5.1 General

In offshore, concrete structure is normally exposed to four different zones viz., (a) atmospheric zone (b) tidal zone (c) immersion zone and (d) mud zone. Among the four zones, tidal zone is the most aggressive zone. Atmospheric zone is also aggressive because of periodic salt spray exposure. Compared to the above two zones immersion and mud zones are less aggressive. There is no standard test procedure to simulate the marine atmospheric zone in laboratory condition. Different researchers have adopted their own simulation procedures. For example, Sorn et al (2001) exposed the concrete specimens in 48 hrs hot salt-spraying (3% NaCl solution, 50°C) followed by 24 hrs of hot air drying (50°C). The same author conducted another test by spraying seawater twice a week for a period of 2-3 minutes in addition to exposing the specimens on pier of a marine environment. Sideris et al (2001) conducted the experiment by exposing the specimens on the coast 150 m away from the sea. It came to know that there is no standard test procedure and researchers adopted their own exposure condition to simulate the marine atmospheric condition in the laboratory.

In similar way marine atmospheric zone has been simulated by subjecting the reinforced concrete test cubes to periodic salt spray i.e., one spray per day. Resistivity of the concrete was measured with a view to assess the hardening process. Potential of the embedded reinforcements was periodically monitored to ascertain the active or passive condition of rebar. Impedance measurements were also periodically carried out to assess the polarization resistance of the rebar.
3.5.2 Specimen Preparation

150 × 150 × 150 mm size concrete cubes as shown in Figure 3.5 were cast. 100 mm long CTD (cold twisted deformed) rods of 16mm dia were taken and pickled in inhibited hydrochloric acid solution to remove the initial rust product. In each specimen three rods of similar dimension were embedded at 25 mm cover from one side of the specimen. For electrochemical measurement, copper wire was brazed at one end of a particular rod and that was sealed. Impedance measurement was carried out over an exposed length of 8 cm and the remaining area was sealed using epoxy compound. For determining the corrosion rate from weight-loss measurement, another two rods were embedded near to the previous one as shown in Figure 3.5. Before embedding, the initial weight of the rods were recorded. In one set of specimens, no chloride was added (0%) to the concrete and in another set of specimens, 0.5% and 1% chloride by weight of cement was added at the time of casting. While casting all the three rebars were embedded vertically with a 25 mm cover both at the top and bottom. Four specimens were cast for each grade/cement. The specimens were cured for 28 days in potable water.

Figure 3.5 Arrangement of rebar in concrete specimen
3.5.3 Exposure Condition

After 28 days of curing, the specimens were exposed in the exposure yard. Synthetic seawater was prepared as specified in ASTM D-1141 (1998). The composition of synthetic seawater is given in Table 3.4. As shown in Figure 3.6, 20 ml of synthetic seawater was sprayed horizontally using spray gun once in a day for 5 days on one side of the specimen and then the specimen was air dried for the next 2 days. Thus 7 days constituted one cycle of wetting and drying. This test procedure simulates the atmospheric exposure of concrete structures in marine environment. The temperature and relative humidity and other parameters prevailing at the exposure site are given in Table 3.5. To accelerate the corrosion process as well as to arrive at the chloride tolerable limit, Cl⁻ ions were added during the casting of concrete specimens. Since the atmospheric salinity at the exposure site is quite less and a considerable amount of chloride added during casting of specimens will be bound as Friedel’s salt, periodic salt spray was resorted to. The experiment was conducted over a period of 1765 days.

Table 3.4 Composition of synthetic seawater

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>gms/lit</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>24.5</td>
</tr>
<tr>
<td>MgCl₂</td>
<td>5.2</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>4.09</td>
</tr>
<tr>
<td>CaCl₂</td>
<td>1.16</td>
</tr>
<tr>
<td>KBr</td>
<td>0.101</td>
</tr>
<tr>
<td>KCl</td>
<td>0.695</td>
</tr>
</tbody>
</table>
Table 3.5 Meteorological data at the exposure site

<table>
<thead>
<tr>
<th></th>
<th>Max</th>
<th>Min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (average)</td>
<td>33°C</td>
<td>21°C</td>
</tr>
<tr>
<td>Relative Humidity</td>
<td>80%</td>
<td>65%</td>
</tr>
<tr>
<td>Rainfall (average)</td>
<td>180 mm</td>
<td></td>
</tr>
<tr>
<td>SO₂</td>
<td>Nil</td>
<td></td>
</tr>
<tr>
<td>Salinity</td>
<td>38 mg/m².day</td>
<td></td>
</tr>
</tbody>
</table>

3.5.4 Experimental Technique: A.C. Impedance Technique

**Principle:** Electrochemical impedance technique is used by several authors for studying the corrosion kinetics of the steel rebars embedded in concrete (John 1981, Crenstil 1992, Ping Gu 1997, Hachani 1994). The main advantage of this technique compared to other DC techniques such as linear polarization and Tafel extrapolation is that the resistance of the concrete can be computed in this method directly. In this technique, an A.C signal is applied to the embedded rebar and the response is monitored in terms of the
phase shift of the current and voltage components and their amplitude. This is done in the frequency domain using a frequency response analyser. The analysis can be done by assuming appropriate equivalent circuit. Many equivalent circuits have been proposed to describe the stages of the steel/concrete corrosion process including active, passive and diffusion controlled processes (Feliu 1998, Newton 1998, Brantervik 1983). Recently a modified electrical equivalent circuit has been proposed (Feliu 1998, PingGu 1992). This equivalent circuit consists of three parallel combination of a pure resistor and a frequency dependent capacitor (which is also called a constant phase element) to represent concrete matrix, interfacial film and corrosion of rebar. Impedance ‘Z’ is the ratio of A.C. voltage to A.C. current. An alternating voltage of about 10 to 20 mV is applied to the rebar and the resultant current and phase angle are measured for various frequencies.

\[
|Z| = R_c + \frac{R_{ct}}{1 + j\omega C_{dl} R_{ct}} \tag{3.5}
\]

where 
- \(\omega\) - \(2\pi f\) 
- \(j\) - \(\sqrt{-1}\) 
- \(R_c\) - resistance of concrete 
- \(C_{dl}\) - double layer capacitance 
- \(R_{ct}/R_p\) - charge transfer resistance 
- \(|Z|\) - \(R_c + R_{ct}\) (low frequency) 
- \(\omega \rightarrow \infty\) 
- \(|Z|\) - \(R_c\) (High frequency)

Hence the subtraction of cell impedance \(Z\) at low frequency from that of high frequency gives \(R_{ct}\). This charge resistance can be related to the extent of corrosion. European concrete committee (CEB 1997) has proposed
one such criteria. If the charge transfer resistance is more than 130 kΩ-cm², then the rebar is in passive condition and if it is less than 25 kΩ-cm², then the bar is in active condition.

3.5.5 Method of Measurement

The potential of the rebar was measured periodically using a high input impedance multimeter. Saturated calomel electrode was used as a reference electrode. Impedance measurement was made using three electrode arrangements. Stainless steel electrode of size 10 mm × 80 mm was used as an auxiliary electrode and saturated calomel electrode was used as a reference electrode. Rebar embedded in concrete acted as a working electrode. The electrode assembly was kept on a wetted sponge. The experimental set up is shown in Figure 3.7. The length of the counter electrode is more than the exposed length of the rebar and by means of this, current was distributed uniformly throughout the length of the rebar. Chloride solution was used as a contacting solution to reduce the contact resistance between the electrode assembly and the concrete. A small sinusoidal voltage signal of 20 mV was applied over a frequency range of 100 KHz to 10 mHZ using a computer controlled electrochemical analyzer (Model 6310: E G and G Instruments, Princeton applied research). Measurements were made periodically. The impedance values were plotted on the Nyquist plot. From the Nyquist plot, using the software ‘z view’ the $R_c$ and $R_p$ value were calculated from the diameter of the high and low frequency semi-circle. For calculating $R_c$, the frequency range between 100 kHz - 100 Hz was used whereas for calculating $R_p$, 100 Hz –10 mHz has been used (Feliu 1998). By assuming B as 26 mV (Andrade 1978), the $I_{corr}$ was calculated using the Stern-Geary relation (Stern 1975),

$$I_{corr} = \frac{B}{R_p}$$  (3.6)
where  

\[ B \] - Stern-Geary Constant, 26 mV for both active and passive state of rebar

\[ R_p \] - Polarization resistance, ohms-cm²

\[ I_{corr} \] - Corrosion current, µA/cm².

From the \( I_{corr} \), the corrosion rate of rebar was calculated using the following formulae,

\[
\text{Corrosion rate, mmpy} = 0.0116 \times I_{corr}
\]

(3.7)

where, \( I_{corr} \) is in µA/cm².

Figure 3.7  Experimental setup for impedance measurement

3.5.6 Determination of Diffusion Coefficient of Chloride Using Warburg-Nyquist Method

**Theoretical background:** The reaction kinetics and diffusion are characterized by Faradic impedance, which is composed of the charge transfer resistance in series with the Warburg impedance (WI) describing the diffusion behaviour. The equivalent circuit for this behavior is given in Figure 3.8(a)
Typical Nyquist plot with the Warburg impedance describing the diffusion controlled reaction is shown in Figure 3.8(b). The analytical expression is,

\[ Z = R_c + \frac{R_{ct}}{1 + j\omega R_{ct} C_{dl}} \]  

(3.8)

\[
\begin{align*}
Z &= R_c + R_{ct} + \sigma_w \omega^{1/2} \\
Z' &= \sigma_w \omega^{1/2} + 2\sigma_w^2 C_{dl}
\end{align*}
\]

(3.9) \hspace{1cm} (3.10)

Elimination of \( \omega \) leads to

\[ Z' = Z' - R_c - R_{ct} + 2\sigma_w^2 C_{dl} \]

(3.11)

**Figure 3.8** Method of determining \( \sigma_w \) from Nyquist plot: (a) Equivalent circuit (b) Nyquist plot with Warburg impedance

From the plot it can be seen that, in the high frequency region, the experimental curve is a semicircle and in the low frequency region, it is a straight line of slope 1. Correspondingly, at the high frequency limit, Warburg impedance becomes unimportant. At the low frequency limit it will approach the limiting form as shown below (Shi 1999):
where, \( \sigma_w \) is the coefficient of Warburg impedance, which can be obtained from the intersection of the straight line on the real axis as shown in Figure 3.8 (b) which is below:

\[
\sigma_w = \left[ \frac{R_c + R_{ct} - x}{2C_d} \right]^{1/2}
\]  

(3.12)

where  
- \( R_c \) - the concrete resistance in ohm  
- \( R_{ct} \) - the charge transfer resistance in ohm  
- \( C_d \) - Capacitance of electrode - electrolyte interface in nF  
- \( \sigma_w \) - Warburg coefficient, ohm-m\(^2\)/\(\sqrt{\text{sec}}\)

For a reversible reaction of \( R_{ct} \rightarrow 0 \), which is controlled by chloride ions alone, then Equation (3.12) can be reduced to

\[
\sigma_w = \frac{RT}{\sqrt{2AF^2\sigma_wD_{eff}^{1/2}C}}
\]  

(3.13)

Hence, Equation (3.13) becomes

\[
D_{eff} = \left[ \frac{RT}{\sqrt{2AF^2\sigma_wC}} \right]^2
\]  

(3.14)

where  
- \( D_{eff} \) - Diffusion coefficient of chloride, m\(^2\)/sec  
- \( A \) - Area of electrode, m\(^2\)  
- \( \sigma_w \) - Warburg coefficient (ohm - m\(^2\)/sec\(^{1/2}\))  
- \( C \) - Concentration in mole m\(^{-3}\)  
- \( R \) - Gas constant, J K\(^{-1}\) mol\(^{-1}\)  
- \( T \) - Temperature, Kelvin  
- \( F \) - Faraday, Coulombs
The $D_{eff}$ calculated using Equation (3.14) was compared with the value determined with the value determined from the chloride concentration ($c_x$) at 25 mm depth from the powdered concrete sample using Fick’s law.

### 3.5.7 Corrosion rate from Gravimetric Weight-loss

At the end of 775, 1135, 1528, 1765 days of exposure, the concrete specimens were broken open and the rods were visually examined for the extent of rust. After pickling the rebars in inhibited hydrochloric acid as specified in ASTM G1 (1990), the final weight was measured. From the initial and final weight, the corrosion rate in mmpy was calculated using the Equation (3.2). Durability factor of rebar in all concretes has been arrived by comparing the corrosion rate at the end of 1765 days as follows:

$$\text{Durability Factor of rebar} = \frac{\text{Corrosion rate of rebar in OPC concrete}}{\text{Corrosion rate of rebar in PPC/PSC concrete}}$$  

(3.15)

### 3.5.8 Cl$^-$ and OH$^-$ ions Concentration

The Cl$^-$ and OH$^-$ ions concentration were measured as per procedures explained in 3.4.7.

### 3.5.9 Chloride ion Binding Capacity

Chloride ion binding may be defined as the interaction between the hydrated cement products such as C$_3$A, C$_4$AF and chloride ions leading to their effective removal from the pore solution. Generally it is believed that blended cements bound more chlorides than Portland cement and its
quantification is necessary. Hence the chloride ion binding capacity of each cement was carried out in 1% Cl\textsuperscript{-} added concrete. The powdered concrete sample was dissolved in concentrated nitric acid at 1:3 ratio. Then this mixture was kept in the water bath at 60-70\degree C for 1 hour. After filtration, the filtrate was neutralized with strong alkali to have a pH of 7. Soluble chloride ion was estimated (Vogel 1974). The concentration has been expressed as mg/g of the sample.

3.6 FIELD EXPOSURE STUDIES AT OPMEC, TUTICORIN

3.6.1 General

In hardened concrete, C\textsubscript{3}A is the relevant phase that binds chloride ions and forms calcium chloroaluminate hydrate thereby reducing the rebar corrosion. The same phase that can also react with sulphate ions to form ettringite and gypsum if the C\textsubscript{3}A content is above a certain critical level, leading to degradation of concrete. When chlorides and sulphates exist concomitantly, the sulfate resistance of concrete has been increased. It is reported that the solubility of ettringite formed was three times higher in chloride solutions than in water (Harrison, 1990). The increased sulphate resistance are due to

i) The increased solubility of ettringite formed results a non-expansive form.

ii) The transformation of aluminate hydrate phases into chloroaluminates, thereby reducing the quantity of ettringite formed.

It is reported that the sulphates contained in sea water do not appear to be directly responsible of degradation of concrete, although the sulphates
concentration is high (Mehta 1999, Thomas 1999); deterioration of concrete in marine environment are due to dissolved carbon-di-oxide and magnesium ions, with chloride ions leading to reinforcement corrosion.

In the foregoing discussion it is inferred that the effect of the conjoint presence of chlorides and sulphates on the durability performance of ordinary Portland cement and blended cement in actual marine environment will prove their performance in such environments. In addition to deterioration by aggressive pollutants, when the specimens exposed to tidal zone, they were also subjected to erosion by wave action. The durability performance of OPC and blended cements were evaluated by exposing the specimens in the tidal zone of Bay of Bengal, OPMEC, Tuticorin. For assessing the chloride resistance, rebar embedded concrete specimens were used whereas for assessing the sulphate deterioration, plain concrete cubes (without rebar) were used.

3.6.2 Chloride Induced Corrosion

3.6.2.1 Specimen preparation and method of exposure

For field exposure studies, the same specimen preparation as described in 3.5.2 has been used. After 28 days of curing in potable water, all the specimens were transported to OPMEC, Tuticorin. The specimens were tied in the net and exposed in the tidal zone of Sea, Tuticorin. To avoid the attachment of biorganisms, which may hinders the intrusion of chloride and sulphate ions, the specimens were tied in the net and then exposed. Because of low and high tide level, the specimens were subjected to 8 hrs drying and 16 hrs wetting in sea water for every day. This exposure study was conducted over a period of 852 days.
3.6.2.2 Method of measurement

**Potential and electrical resistivity measurement:** Potential of rebar was carried out periodically using high impedance multimeter. Saturated calomel electrode was used as a reference electrode.

Electrical resistivity of concrete is an important parameter, which can be related to various other aspects such as strength, porosity and deterioration. The reason is that resistivity is the parameter characterizing pore connectivity. Hence its measurements are an interesting way to assess concrete durability from the point of view of assessing the transport properties (Castellote 2002). In the present study, four probe resistivity meter based on Wenner-probe principle was used (Millard 1990, Rengaswamy 1987, Gjorv 1977) which produces frequency-independent resistivity measurements. The electrodes of the resistivity meter were in the form of spring-loaded 3 mm diameter probes of copper rod surrounded by wetted sponge. The spacing between the electrodes was adjustable; however, for the present study, the spacing (a) was maintained at 25mm. A known current ‘I’ is impressed on the outer probes and the resulting potential drop ‘V’ between the inner probes was measured. Resistance ‘R’ is given by V/I. From this, the resistivity can be calculated as,

$$\text{Resistivity of concrete (}\rho\text{)} = 2\pi a R$$  \hspace{1cm} (3.16)

Four measurements were taken on each side of the cube (except top and bottom face of the cube), and then averaged to obtain a mean value. During the measurements, the contact surfaces of the probes were maintained in a moist state to ensure good electrical contact with the concrete surface. By pressing the four probes on the concrete surface, the resistivity of concrete up
to a cover of 25 mm was displayed in the meter directly. The resistivity was measured at the end of 470 and 850 days of exposure.

**Determination of corrosion rate:** After 852 days of exposure, the specimens were brought to the laboratory. The rebar embedded concrete cubes were broken open and the rods were visually examined for extent of rust spots. The rods were then pickled. From the loss in weight, corrosion rate in mmpy was calculated using Equation (3.2).

### 3.7 LABORATORY EVALUATION: SULPHATE ATTACK

#### 3.7.1 General

Structural concrete components undergo degradation when exposed to sulphate bearing environments. The seawater, soil, and ground water contain high concentrations of calcium, sodium and magnesium salts of sulphates. Dissolved sulphates intrude concrete pore structure by diffusive or advective flow. This will cause progressive precipitation of sulphate bearing phases such as ettringite and gypsum in the internal micro structure of the concrete (Lawrence 1990, Mangat 1995, Marchand 2002). This change leads to swelling, spalling and cracking of concrete and causes a significant reduction in the cross-sectional area of the structural components and also decreases the strength (Wee 2000, Irasser 1996, Al-Amoudi 1994, Brown 1981, Tikalsky 1992, Mathews 2001, Al-Amoudi 1999). The intensity and rate of sulfate attack depends upon the mineralogical phases of cement, type of cation ($\text{Na}_2\text{SO}_4$ or $\text{MgSO}_4$) and concentration of the solution, quality of concrete and exposure conditions. The mechanisms by which the various sulfates attack on concrete are still a matter of some controversy (John 1999).
When compared to sodium sulphate attack, magnesium sulphate attack is more severe on concrete (Al-Amoudi 1999, Mehta 1999a). 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. The reactions are as follows;

\[
\text{MgSO}_4 + \text{Ca(OH)}_2 + 2 \text{H}_2\text{O} \rightarrow \text{CaSO}_4 \cdot 2 \text{H}_2\text{O} + \text{Mg(OH)}_2 \hspace{1cm} (3.17)
\]

\[
\text{MgSO}_4 + \text{CaO} \cdot \text{SiO}_2 \cdot 3 \text{H}_2\text{O} + \text{H}_2\text{O} \rightarrow (\text{CaSO}_4 \cdot 2\text{H}_2\text{O}) + \text{Mg(OH)}_2 + \text{SiO}_2 \cdot \text{H}_2\text{O} \hspace{1cm} (3.18)
\]

\[
\text{Mg(OH)}_2 + \text{SiO}_2 \cdot \text{H}_2\text{O} \rightarrow \text{MgO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O} + \text{H}_2\text{O} \hspace{1cm} (3.19)
\]

Magesium hydroxide (brucite) produced in Equation (3.17) is extremely little soluble and its saturated solution has a pH value of about 10.5 (Rasheeduzzafar 1994). Such a low pH destabilizes both ettringite and C-S-H and because of this, secondary ettringite will not form (Lea 1974). Then magnesium sulfate react with C-S-H as per Equation (3.18) thereby producing gypsum, brucite and silica gel (SiO\textsubscript{2}.H\textsubscript{2}O). This gel is less cementitious than the original cementing C-S-H gel (Rasheeduzzafar 1994). C-S-H tends to liberate more lime to raise the pH and to establish its equilibrium. This process is known as decalcification of C-S-H. The Mg(OH\textsubscript{2}) formed reacts further with hydro silicates thereby producing magnesium-silicate hydrate (M-S-H) as given in Equation (3.19) which is non-cementitious and has no binding properties (Rasheeduzzafar 1994, Brown 2000). It is reported that when compared to Portland cement, blended cement performed better in sulphate environment by both pozzolanic effect as well as by dilution effect.
A widely recognized test to assess the sulfate resistance of concrete does not exist yet. However three test methods are being widely adopted by many researchers. They are: (i) measurement of the expansion of mortar or concrete specimens (ASTM C1012, 2000) (ii) determining the loss of strength through mechanical or ultrasonic tests (Ju 1999). (iii) the measurement of the weight change of the specimen (Kropp 1995). Since the expansion appears to be the main phenomenon in the case of sodium sulfate attack, and loss of strength the one in the case of magnesium sulfate attack, it is suggested that the corresponding tests be applied taking into account the nature of the cations (Al-Amoudi 1995).

In the present study, the effect of w/c ratio, influence of cement type and cement content of concrete on magnesium sulphate attack has been investigated in 10% MgSO₄ solution. The rate of deterioration was assessed by measuring the change in resistivity, compressive strength and mass loss. The ettringite and gypsum formation was identified using differential thermal analysis (DTA).

### 3.7.2 Specimen Preparation and Method of Exposure

100 mm size cubical plain concrete specimens (without rebar) were cast. After 24 hrs, all the specimens were demoulded and kept immersed in the curing tank for 28 days. After 28 days, the specimens were removed from the curing tank and were kept immersed in 10% MgSO₄ solution. The ratio of the volume of the solution to the volume of the specimen was kept at 4:1. During exposure, the pH of the solution was in the range of 7 to 8.5. The solution was renewed once in 3 months. At the end of 6, 9, 15, 21, 30 and 36 months, the specimens were tested for change in mass loss, resistivity and compressive strength.
3.7.3 Measurements

3.7.3.1 Visual appearance

The progress of deterioration due to sulphate was assessed by visually examining the surface of the concrete specimens at the end of each exposure period for the presence of cracks, softening, corner attack and edge failure. The external condition of the specimen was judged by a visual rating proposed by Malhotra (1987).

3.7.3.2 Mass loss

The initial weight of each specimen was measured to an accuracy of 1 gm. At the end of the exposure, final weight of the specimen was recorded. From the loss in weight, the decrease in mass loss was calculated.

3.7.3.3 Compressive strength

The percentage increase/decrease in compressive strength in the sulphate solution was calculated by comparing with the corresponding compressive strength in potable water. This is called sulphate deterioration factor (SDF). To assess the deterioration by sulphate attack, the change in compressive strength of the cubes after a specified immersion period in 10% MgSO₄ was carried out in conformity with IS: 516 (1959). The SDF at the end of 6 and 9 months in sulfate solution was assessed by comparing the corresponding compressive strength of cubes kept immersed in potable water at the end of 6 and 9 months. For 15, 21, 30, 36 months, the compressive strength at the end of 12 months in potable water was compared since increase in compressive strength in potable water is not significant after
12 months. For each duration, duplicate specimens were tested and values obtained.

3.7.3.4 Differential Thermal Analysis (DTA)

After testing the compressive strength at the end of 9, 15 and 30 months, the samples from the top layer up to 3 mm depth of the specimen were taken, powdered and sieved through 75 µm sieve for DTA analysis. DTA was done using polymer laboratories (UK), Thermal Science Division STA 1500 thermal analyzer. It has a balance with a resolution of 0.01 mg. Type ‘R’ thermocouple (Pt-13% Rh/Pt) was used for temperature measurement. The sample was taken in a ceramic crucible and heated from room temperature to 600\(^0\) C at a heating rate of 20\(^0\) C /min using nitrogen as medium under static conditions. The ettringite and gypsum were identified by observing an endothermic peak at 80-100\(^0\) C and 110-130\(^0\) C respectively (Chang 1999, Li 2000, Wee 2000, Manu Santhanam 2003).

3.8 FIELD EXPOSURE STUDIES AT OPMEC, TUTICORIN: SULPHATE ATTACK

3.8.1 Specimen Preparation and Method of Exposure

100 mm size plain cubical concrete (without rod) specimens were cast. After 24 hrs, the specimens were demoulded and kept immersed in the curing tank for 28 days. After 28 days of curing, the specimens were removed from the curing tank. All the specimens were transported to OPMEC, Tuticorin. The specimens were tied in the net and exposed in the seashore of Sea, Tuticorin.
3.8.2 Resistivity and Mass Loss Measurement

Using four probe resistivity meter the change in resistivity is measured at the end of 470 and 862 days of exposure. The initial weight of the each specimen was measured to an accuracy of 1 gms. At the end of the exposure final weight of the specimens were measured. From the loss in weight the decrease in mass loss was calculated.

3.9 PORE STRUCTURE CHARACTERISATION OF BLENDED CEMENT CONCRETE

3.9.1 Determination of Calcium Hydrates Content Using Thermogravimetric Analysis

3.9.1.1 General

During hydration, compounds present in the cement such as $\text{C}_3\text{S}$ and $\text{C}_2\text{S}$ react with water and form calcium hydrates ($\text{C}_3\text{S}_2\text{H}$ and $\text{C}_2\text{A}_2\text{H}$) and calcium hydroxide. These can be determined either directly by microscopic examination of the hydrated material or indirectly from determination of combined water or changes in density. Hubbert et al (2001) estimated the $\text{C}_3\text{S}_2\text{H}$ phase indirectly with hydration time using the molybdate method by estimating unreactive $\text{SiO}_2$ in the hydrated cement powder. Thermogravimetric analysis (TG/DTA) can be used in pozzolanic reaction and hydration of blended cement pastes by estimating $\text{Ca(OH)}_2$ content and calcium hydrates content quantitatively (Bhatty 1986, Hussain 1994, Monzo 2001, Sha 2001). Hussain et al (1994) conducted TG/DTA analysis on fly ash blended cement pastes after hydration for 180 days and reported that $\text{Ca(OH)}_2$ content was reduced by 53% when compared to OPC paste. Feldman et al (1991) conducted TG/DTA analysis in fly ash blended and portland cement pastes and investigated the effect of w/c ratio and hydration time on the
variation of Ca(OH)$_2$ content. But the effects of pozzolanic reaction are more important in concrete than in hydrated cement paste. The presences of microcracks in the transition zone make the concrete more permeable than paste and mortar. The process of pore size refinement strengthen the transition zone, thus increasing the impermeability of concrete. Though the presence of sand particles will dilute the cement phase but studies in concrete is more realistic than in paste and mortar. In the preset study TG/DTA analysis were carried out on powdered concrete samples obtained from concrete specimens.

### 3.9.1.2 Specimen preparation

Concrete specimens of size 100 × 100 × 100 mm size were cast. After 28, 90, 365 days of curing in potable water, the specimens were broken and concrete samples were collected from the interior portion of the specimen. Samples were powdered and sieved through 75 µm. Sieve. At the end of each hydration period, about 1 gram of sample was collected in a closed plastic container from 20, 30 and 40 MPa concrete.

### 3.9.1.3 Method of measurement

TG/DTA was done with Polymar Laboratories (UK), thermal science Division STA 1500 thermal analyzer with a resolution of 0.01 mg. Type R thermocouple (Pt-13% Rh/Pt) is used for temperature measurement. Sample of known weight was taken in a ceramic crucible and heated from a room temperature to 900°C at a heating rate of 20°C/min using air as a medium under static condition. Alumina powder was used as a reference material and both TG and DTA were done simultaneously. The upper temperature was limited to 900°C because of crystallization of hydrated compounds at higher temperature. The sharp endotherm in the DTA curve around 465°C indicates the decomposition of Ca(OH)$_2$ formed during
hydration (Singh 2002). The amount of Ca(OH)$_2$ was estimated quantitatively from the weight-loss measured from the TG curve between the initial and final temperature of the corresponding TG peak by considering the following decomposition reaction (Dweck 2000):

\[
\text{Ca(OH)}_2 \rightarrow \text{CaO} + \text{H}_2\text{O}
\]  

(3.20)

The total weight-loss including that due to the loss of water from other hydrates was measured from the difference in weight between 100 and 600°C (Taylor 1997). The calcium hydrates content which is a total of calcium silicate hydrate, calcium aluminate hydrate and calcium sulfoaluminate hydrate formed during hydration was calculated by deducting calcium hydroxide content from total weight-loss. Hence it is an indirect measurement of calcium hydrate content as total water content.

3.9.2 Determination of Pore Size Using Electrochemical Impedance Spectroscopic Technique

3.9.2.1 General

Most of the properties of hardened cement-based materials are related to the quantity and the characteristics of pores in the concrete. There are three types of pores in concretes: gel pores, capillary pores and air pores. The gel pores are <10 nm in size which are associated with the formation of hydration products and has a major effect on hydration rates. Macro pores or capillary pores are 10-10,000 nm in size and have major effect on transport processes but only minor effect on hydration rate. In the literature on characterization of microstructure of cementitious system, several techniques such as BET, scanning electron microscopy (SEM), mercury intrusion porosimetry (MIP), magic angle spinning and small angle x-ray scattering have been used (McCarter 2000). For pore size characterization, MIP is the
most widely used method. These techniques require the specimen to be dried, which can significantly alter the microstructure. Electrical resistance measured from EIS represent an additional and fast-developing technique in the study of cement based materials both at micro and macro scale (Zhongzixu 1993). From the engineering point of view, electrical resistance measurements could be exploited to characterize pore size in cement based materials. In blended cement the formation of additional calcium hydrates densifies the pore structure and reduces the pore size. Using EIS technique, the diameter of the interconnected pores was determined.

3.9.2.2 Specimen preparation

As shown in Figure 3.9 concrete specimens of size $100 \times 100 \times 100$ mm were cast. In each cube, two polished stainless steel electrodes of size $40 \times 40$ mm were embedded at 1 cm interval. Both the top and the bottom faces of the specimen were sealed with epoxy coating. Electrical leads were taken from the electrodes by brazing and sealed. After demoulding, the specimens were kept immersed in water and cured for different periods viz., 3, 7, 14 and 28 days. EIS experiments were carried out at the end of each curing period.

3.9.2.3 Method of Measurement of Resistance Using EIS

Measurements were carried out in the frequency range 100 kHz - 1 Hz using the electrochemical impedance analyser model No. 6310. The amplitude used was 20 mV. The impedance values were plotted in the Nyquist plot. Using the software ‘Z view’, the high frequency arc was extrapolated to a semicircle. From the diameter of this semicircle, the resistance of the concrete was calculated and converted into resistivity ‘$\rho$’ as below:
\[
\rho = \frac{r \ast a}{l}
\]  

(3.21)

where
\( \rho \) - resistivity (ohm-m)
\( r \) - resistance (ohms)
\( a \) - area of the electrode (m\(^2\))
\( l \) - distance between the driven electrodes (m)

**Figure 3.9 Experimental set-up for measuring resistance using EIS**

Using resistance measured from EIS, the average pore diameter of the OPC and PPC concrete were calculated using the following equation:

(Beaudoin 2004)

\[
R = \frac{2 L \delta}{3 S \sigma_f} \left( \frac{1}{P \ast r_{0}} \right)
\]  

(3.22)

\[
r_{0} = \frac{k}{P \times R}
\]
From Equation (3.22), it can be understood that for determining the pore size, estimation of porosity, pore solution conductivity ($\sigma_f$) and double layer thickness ($\delta$) is necessary.

**Determination of porosity:** The porosity of the concrete was determined by the oven drying method given in ASTM C642 (2000). For this test, 80 mm diameter and 40 mm thick concrete disks were cast and cured for different periods viz., 3, 7, 14 and 28 days. The specimens were dried in an oven at a temperature of $100 \pm 5^\circ$ C for 48 hours and allowed to cool to room temperature. The weight of the oven-dried specimen (A) was measured. Then the specimen was kept immersed in water continuously for 48 hrs and after wiping out the surface moisture, the increase in weight (B) was measured. The specimen was then kept immersed in boiled water continuously for a period of 5 hours and it’s weight (C) was taken after a time gap of 14 hrs. The specimen was suspended in water and it’s submerged weight (D) was determined.

To determine the % of total voids, apparent specific gravity of the specimen ($g_3$) has to be determined. The specimen was broken, crushed and powdered for this purpose. 64 grams of powdered sample were taken after
sieving through a 90 micron sieve. As per the procedure outlined in IS: 4031(1988), the specific gravity of the powdered sample was determined using a Le-chatelier flask

\[ \% \text{ of total voids} = \frac{g_3 - g_1}{g_3} \times 100 \]  

(3.23)

where

- \( g_1 \) - \( A/(C-D) \)
- \( A \) - weight of oven dried sample in air
- \( C \) - saturated weight of surface dry sample in air after immersion in water
- \( D \) - submerged weight in water
- \( g_3 \) - apparent specific gravity of the specimens.

\[ \text{Porosity, } \% = \frac{\text{Void volume of concrete}}{\text{Total volume of concrete}} \times 100 \]  

(3.24)

**Estimation of Specific Conductivity of the Pore Solution:** For estimating the pore solution conductivity, the concentration of major charge carriers of the pore fluid such as \( \text{OH}^- \), \( K^+ \), \( \text{Na}^+ \) was only taken into consideration whereas contribution from other ions such as \( \text{Ca}^{2+} \) and \( \text{SO}_4^{2-} \) were not included as their contribution to total conductivity is less than 2% (Snyder 2003). The concentrations of various ions in pore solution and their equivalent conductivities for cement mortar (Larbi 2002) having a ratio of 1:2 (cement : sand) with w/c ratio of 0.5 were used. The details are given in Table 3.6. The specific conductivity of the pore solution in the present investigation can be calculated as follows:

\[ \sigma_i = \sigma_{\text{water}} + \sum_i c_i \lambda_i \]  

(3.25)
where \( \sigma_{\text{water}} \) - specific conductivity of water = \( 1 \times 10^{-5} \text{ m}^{-1} \Omega^{-1} \)

\( c_i \) - concentration of the i-th ion

\( \lambda_i \) - equivalent conductivity of the i-th ion.

### Table 3.6 Concentration of ions in the pore solution

<table>
<thead>
<tr>
<th>Ion in pore solution</th>
<th>Concentration (c) (equiv/l)</th>
<th>Equivalent conductivity (( \lambda )) (m² equiv⁻¹/Ω)</th>
<th>Valence (z)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K⁺</td>
<td>0.57</td>
<td>0.00735</td>
<td>1</td>
</tr>
<tr>
<td>Na⁺</td>
<td>0.24</td>
<td>0.00501</td>
<td>1</td>
</tr>
<tr>
<td>OH⁻</td>
<td>0.8</td>
<td>0.0198</td>
<td>1</td>
</tr>
</tbody>
</table>

Taking into account the equivalent conductivity of ions such as OH⁻, K⁺, Na⁺ and their molar concentration, conductivity of the pore solution was calculated as \( 0.0212 \text{ m}^{-1} \Omega^{-1} \).

**Estimation of Double Layer Thickness:** Double layer thickness can be arrived at by using the relationship given by Adamson (1982)

\[
\delta = \frac{1}{\kappa} \quad (3.26)
\]

where

\[
\kappa^2 = \frac{4 \pi e^2}{\varepsilon k T} \sum_i n_i z_i^2 \quad (3.27)
\]

\( e \) - Charge on the electron (1.602*10⁻¹⁹ Coulombs)

\( \varepsilon \) - Dielectric constant of the cement paste [For M20: 5.58: M30 : 7.58: Reproduced from Ref Cabeza (2002)]
Using Equations (3.26) and (3.27), δ was calculated. By substituting the values of δ and σ_\text{i} in Equation (3.22), the K value was calculated. From this K-value, the pore size was calculated.