CHAPTER 2

REVIEW OF LITERATURE

2.1 GENERAL

The concrete should withstand the process of deterioration for which it is expected to be exposed. The life cycle cost of the buildings is increasing due to corrosion prone aggressive environment and become difficult to manage. To meet the technical and economical concerns, efforts are being made to enhance the service life of concrete structures by various method. This chapter reviews the number papers published by various researchers studied on concrete durability with regard to High strength and High performance concrete, chemical corrosion inhibitors, protective coatings on steel reinforcement (e.g. epoxy-coated or galvanized steel), corrosion-resistant steel (e.g. stainless steel), non-ferrous reinforcement (e.g. fiber-reinforced plastics), waterproofing membranes or sealants applied to the exposed surface of the concrete, cathodic protection and combinations of the above. Experimental test method such as chloride permeability, chloride diffusion, accelerated corrosion test, resistitivity, Half cell potential tests carried out to evaluate the durability properties of concrete by various researchers are reported. A number of models for predicting the service life of concrete structures exposed to chloride environments or for estimating life-cycle costs of different corrosion protection strategies have been developed recently are also discussed. The approaches adopted by the different models
vary considerably and service life prediction model for reinforced concrete structures are modelled.

2.2 HIGH STRENGTH CONCRETE

High-strength concrete is often considered a relatively new material. Its development has been gradual over many years, the development has continued and the definition of high-strength concrete has changed. The development of high strength concrete has been discussed by Russell 1997 as follows. In the 1950s, concrete with a compressive strength of 34 MPa was considered as high strength. In the 1960s, concrete with 41 and 52 MPa compressive strengths were used commercially. A book written by Michael A. Caldarone, 2009 on high strength concrete – a practical guide and given details about the development of high strength concrete. In the early 1970s, 62 MPa concrete was being produced. More recently; compressive strengths approaching 138 MPa have been used in cast-in-place buildings. For many years, concrete with compressive strength in excess of 41 MPa was available at only a few locations. However, in recent years, the application of high-strength concrete has increased, and high-strength concrete has now been used in many parts of the world. The growth has been possible as a result of recent developments in material technology and a demand for higher-strength concrete.

2.3 HIGH PERFORMANCE CONCRETE

High-performance concrete (HPC) not only have high strength but also have good durability. The high-performance concrete has very low permeability, of which permeability is about 1/100 of the conventional concrete. It is one of the main reasons to use HPC to solve the problem of corrosion of steel (Faguang Leng et al 2000). The resistance to chloride penetration is one of the simplest measures to ensure the durability of
concrete. The high-performance concrete may be defined as the concrete having high resistance to chloride penetration as well as high strength. Since high resistance to chloride penetration can be directly related to low permeability that control the deterioration process in concrete structures. This provides a firm basis for the use of high-performance concrete having very low permeability and high durability in the actual structures under severe conditions (Byung Hwan Oh et al 2002). High performance concrete (HPC) is cement-based concrete, which meets special performance requirements with regard to workability, strength, and durability, that cannot always be obtained with techniques and materials adopted for producing conventional cement concrete (Rajamane et al 2003). High Performance Concrete (HPC) provides a solution, and achieves a specified service life by enhancing the concrete characteristics such as volume stability, long term mechanical properties in terms of durability, etc (Kyong Yun Yeau et al 2004). Oner and Akyuz, 2007 has reported that the use of 55% GGBS in total binder content is the optimum point, further addition of GGBS does not improve the compressive strength.

2.4 CORROSION

Reinforcement corrosion is one of the most common causes for reinforced concrete structures deterioration. Corrosion damage to the reinforcing steel results in the build-up of voluminous corrosion products generating internal stresses and subsequent cracking and spalling of the concrete. The main causes of rebar corrosion are due to ingress of chloride ions and CO$_2$ which destroys the natural passivity of reinforcement located in alkaline concrete condition. In general good quality concrete provides excellent protection for steel reinforcement. Due to high alkalinity of concrete pore fluid, steel in concrete initially and in most cases, for sustained long periods of time, remains in a passive state. Initiation of corrosion occurs either due to reduction in alkalinity arising from the breakdown of the passive layer by the attack of chloride ions. The time to initiate corrosion is
determined largely by the amount and the quality of concrete, cover thickness as well as permeability of concrete. Once de-passivation occurs, corrosion propagation is governed by anodic, cathodic and/or electrolytic properties of corrosion cell (Pal et al 2002).

Chloride salts are highly soluble in water. The chloride ions diffuse though concrete pores. The chloride ions present in the pores of concrete are dissolved in water and penetrate. Then the chloride ions attack the passive layer due to higher concentration of chloride ions than hydroxyl ions. The chemical reaction takes place is given below.

\[
\begin{align*}
\text{O}_2 + \text{H}_2\text{O} &\rightarrow \text{OH}^- + \text{H}_2\text{O} \\
\text{Fe}^{2+} + \text{Cl}^- &\rightarrow \text{Fe}^{3+} + \text{Cl}^- \\
\text{O}_2 + \text{H}_2\text{O} &\rightarrow \text{OH}^- + \text{H}_2\text{O}
\end{align*}
\]

The passive layer is destroyed with very less drop of pH value. Chlorides act as a catalyst to corrosion when there is sufficient concentration at the rebar surface to break down the passive layer. They are not consumed in the process but help to break down the passive layer of oxide on the steel and allow the corrosion process to proceed quickly. Then the concrete reinforcement tends to corrosion and lead to concrete deterioration as shown in Figure 2.1 (Mohammad, 2007).

![Figure 2.1 Corrosion of Steel in Concrete by Chloride Attack](image)

The process of concrete structure deterioration due to chloride corrosion can be divided in to two phases. They are initiation period ($T_i$) and propagation period ($T_p$) as shown in Figure 2.2 (Tutti, 1982). During the
initiation period the chloride ions penetrate into cover concrete and accumulate around concrete reinforcement. The initiation period is determined mainly by the diffusion rate of chloride ions in concrete. Propagation period is a process in which reinforcement begins to corrode due to chloride ions. The corrosion products accumulate around concrete reinforcement and cause cracking along the reinforcement due to expansion pressure of corrosion product. The propagation depends on oxygen in dissolved state and the moisture content in the concrete.

\[
\begin{align*}
    \text{Fe} & \rightarrow \text{Fe}^{2+} + 2\text{e}^- \\
    \text{Fe}^{2+} + 2\text{Cl}^- & \rightarrow \text{FeCl}_2 \\
    \text{FeCl}_2 + 2\text{OH}^{-} & \rightarrow \text{Fe(OH)}_2 + 2\text{Cl}^- \\
    2\text{Fe(OH)}_2 + \frac{1}{2} \text{O}_2 & \rightarrow \text{Fe}_2\text{O}_3 + 2\text{H}_2\text{O}
\end{align*}
\] (2.1) (2.2) (2.3) (2.4)

The negative chloride ions promote corrosion of steel in concrete and accelerate corrosion and the chemical reaction takes place as shown below.

Figure 2.2 Service Life Model for Design Life (Tutti, 1982)
Chloride ions can enter into the concrete from de-icing salts that are applied to the concrete surface or from seawater in marine environments. Other sources include admixtures containing chlorides, contaminated aggregates, mixing water, air born salts, salts in ground water, and salts in chemicals that are applied to the concrete surface. If chlorides are present in sufficient quantity, they disrupt the passive film and subject the reinforcing steel to corrosion (Steven F Daily).

**Carbonation Attack:** Moisture content in concrete plays an important role for chemical process of carbonation. The relative humidity of concrete around 60 to 75% is favour for the progress of carbonation (Verbeck, 1958). The chemical reaction takes place as shown below.

\[
\begin{align*}
\text{CO}_2 + \text{H}_2\text{O} & \rightarrow \text{H}_2\text{CO}_3 & (2.5) \\
\text{H}_2\text{CO}_3 + \text{Ca(OH)}_2 & \rightarrow \text{CaCO}_3 + 2\text{H}_2\text{O} & (2.6) \\
\text{H}_2\text{CO}_3 + \text{CaCO}_3 & \rightarrow \text{Ca(HCO}_3)_2 & (2.7) \\
\text{Ca(HCO}_3)_2 + \text{Ca(OH)}_2 & \rightarrow 2\text{CaCO}_3 + 2\text{H}_2\text{O} & (2.8)
\end{align*}
\]

The carbon dioxide gas dissolves in the presence of moisture content and forms dilute carbonic acid (Equation 2.5). Then the carbonic acid reacts with calcium hydroxide to form calcium carbonates (Equation 2.6). If the concentration of the CO\(_2\) gas present is high enough, carbonic acid continues to form and react with the carbonates present to produce bicarbonates, (Equation 2.7). This reaction continues as long as the bicarbonates present in the solution and thus more CO\(_2\) is required. The reverse reaction takes place when any of these are lost and calcium carbonate will then be precipitated until sufficient CO\(_2\) gas has been released to stabilize the bicarbonate remaining in solution (Hewlett, 1998, Taylor, 1997).

The pH value of pore water in the hardened concrete is generally from 12.5 to 13.5 depends upon the alkali content of cement. The high alkalinity forms
a thin passivating oxide layer around concrete reinforcement and it protects from the action of water and oxygen. Due to carbonation effect the pore fluid being neutralized, the pH drops to value between 8 and 9. Then the passive layer around reinforcement is decayed and lead to concrete deterioration.

2.4.1 Effect of Chloride Ingress in Concrete

The factors related to declining concrete durability are carbonation, corrosion, alkali-silica reaction, freezing and thawing. The penetration of chloride-ions into concrete has been regarded as the major deterioration problem. Ingress of chloride-ions destroys the natural passivity of the surface of reinforcing steel, and often lead to the corrosion of steel in concrete structures (Kyong Yun Yeau et al 2004). The presence of sulfate ions in chloride environments did not affect the time-to-initiation of reinforcement corrosion. It can be concluded that protecting the ingress of chloride-ions is more useful than preventing the attack of sulfate ions in case of the coexistence of sulfate and chloride-ions. A common method of preventing such deterioration is to prevent chlorides from penetrating the structure to the level of the reinforcing steel bar using relatively impenetrable concrete (Stanish et al 2003).

2.4.2 Mode and Mechanisms of Chloride Ion Ingress in Concrete

Chloride ions can penetrate concrete though capillary absorption, hydrostatic pressure, and diffusion. In the bulk of the concrete, the pores remain saturated and the concentration gradient controls the chloride ion movement. The mode of transport though concentration gradient was called as Diffusion (Thomas et al 1995). The rate at which chloride ions penetrate into concrete determines the time period after which the passivity of reinforcing bars begins to break down for corrosion (Ampadu 1999).
2.5 IMPROVEMENT OF CONCRETE DURABILITY

2.5.1 Effect of Concrete Cover on Concrete Durability

Insufficient concrete cover or poor quality concrete lead to reinforcement corrosion. Theoretically, bars embedded in concrete structures are protected both chemically and physically against environmental corrosion using concrete cover. The high alkalinity of the pore solution of the concrete cover provides the chemical protection and the impermeability of the concrete cover is expected to provide a physical protection against the ingress of deleterious materials like chloride ions.

To control the reinforcement corrosion, the rate of chloride penetration should be minimized. Chloride penetration deeply dependays on the depth and quality of concrete cover. The resistance of steel corrosion is superior when the thickness of concrete cover is large but too much a cover could result in larger and more cracks allowing direct access of aggressive agents to the steel reinforcement (Ampadu 1999).

The impermeability of concrete depends on the depth of concrete cover, cement type, and Fly ash or GGBS content. The impermeability of concrete cover can be further improved by using high strength and durable concrete such as High Performance Concrete (Kyong Yum Yeau and Eum Kyum Kim 2004).

For a concrete cover of 70 mm, the time necessary for corrosion initiation ranges from 3 to 6 years for the synthetic seawater exposure. The cover depth of 50 mm for 3 years in the synthetic seawater, a concrete cover of at least 90 mm is required for an exposure period of 10 years in the same exposure (Erdogdu et al 2004).
2.5.2 Effect of Cement Replacement Materials on Concrete Durability

A High Performance Concrete using cement alone as a binder requires high paste volume, which often lead to excessive shrinkage and large evolution of heat of hydration, besides increased cost. A partial replacement of cement by mineral admixtures (MA), such as, fly ash, ground granulated blast furnace slag (GGBS) and silica fumes (SF) in concrete mixes overcome these problems and lead to improvement in the durability of concrete and also leads additional benefits in terms of reduction in cost, energy savings, promoting ecological balance and conservation of natural resources, etc. (Rajamane et al 2003).

GGBS, obtained as an industrial by-product from iron and steel industry, serves as a supplementary cementitious material (SCM) by forming additional calcium silicate hydrate (C-S-H) gel and thereby increases the denseness of the matrix though pore refinement. Slag hydration is hindered by formation of a protective film on the surface of GGBS particles and activation of hydration will not occur until pH of pore solution exceeds 13.2 and glass fraction of the slag is broken down by hydroxyl ions. This requires a certain amount of hydration of cement to take place. Before the cement hydration, GGBS particles serve as nuclei for precipitation of cement hydration products. At later ages, GGBS acts as an effective cementitious material.

A study conducted by Rajamane et al 2003 indicate that 8%-16% of GGBS hydrates at 3 days and 30%-37% of GGBS hydrates at 28-d. Degree of hydration is greatly influenced by fineness and glass content of GGBS, besides SO$_3$ content of cement. The resistance to chloride penetration of 50% ground granulated blast-furnace slag (GGBS) concrete was almost the same
as that of 10% silica fume concrete (Kyong Yum Yeau and Eum Kyum Kim 2004).

### 2.5.3 Effect of Cement Type on Concrete Durability

It is confirmed that chloride permeability decreases with increased volume of Supplementary Cementing Material (SCM), but Ordinary Portland Cement itself is more resistant to chloride penetration when compared to special cements such as sulfate-resisting Portland cement. (Byung Hwan Oh et al 2002).

### 2.5.4 Effect of Aggregate Properties on Concrete Durability

The rate at which chloride ion ingress into saturated concrete occurs depends on the chloride ion diffusion Co-efficient of the concrete’s cement paste and aggregate fractions and the aggregate volume concentration (Hobbs 1999).

In the limestone concrete, it appears that chlorides can be transported though the aggregate as well as though the surrounding cement paste. Carbonation and water permeability data indicate that the aggregate could play an important role in influencing chloride ingress into concrete (Page et al 2009).

The carbonation depths for Portland cement concretes of similar water-cement ratios subjected to sheltered external exposure were on an average of 90% greater for concretes containing a lightmass coarse aggregate (sintered pulverized fuel ash) than for concretes containing dense coarse aggregate. The chloride ion diffusion Co-efficient of the cement paste is dependent on w/c ratio and degree of hydration, but if its diffusion Co-efficient is lower than that of the aggregate, then, ignoring interfacial effects,
chloride ion ingress will increase with increasing aggregate volume (Hobbs 1999).

The effect of maximum size of aggregates on the chloride permeability is a important parameter but not only the maximum aggregate size but the aggregate particle size distribution and aggregate-paste volume ratio also influence on the formation of the microstructure of concrete, (Byung Hwan Oh et al 2002).

To achieve a specified working life, controls are necessary both on the quality of concrete’s paste fraction and it’s aggregate. If the diffusivity of the aggregate and paste fractions is not the same, then chloride ion mass flow and chloride ion concentration gradient are nowhere near uniform across a concrete in the normal direction of diffusion. The chloride ion diffusion Co-efficient of the aggregate ranges from 0.20 to 10 times that of a cement paste matrix (Hobbs 1999).

### 2.5.5 Importance of Water Binder Ratio for a Durable Concrete

The water cement ratio governs the porosity of the hydrated cement paste. The value of water cement ratio was relevant to many aspect of durability (Adam Neville 2000). The chloride ions diffusion Co-efficient increases with increase in w/c ratio. The diffusing paths of chloride ion into concrete have three paths: the interconnected pores in cement paste, the interconnected pores in aggregate, and the interconnected pores in the interfaces between paste and aggregate. When the permeability of aggregate was significantly lower than that of hydrated paste and the interface between aggregate and paste has no apparent deficiencies, the main diffusing path exists in the paste. Thus, the compactness and volume of paste are the two main causes affecting the diffusing velocity of chloride ions (Kyong Yum Yeau and Eum Kyum Kim 2004).
Truc et al 2000 has studied the concretes with water/cement ratio 0.55, diffusion Co-efficient, $D_c$ decreases drastically between 15 and 30 days, whereas for concrete with water/cement ratios 0.32 the values are almost constant. The concrete with water/binder ratio of 0.35 will take longer time duration for the chloride ions to migrate from the cathode chamber though the cement and cement-fly ash paste to the anode chamber than the time prescribed for the test. It could therefore be inferred that at such low water/binder ratio, fly ash or slag replacement may not cause any significant change in the diffusivity of the resulting paste at initial stage. The variation of the effective chloride ion diffusion Co-efficient $D_c$, depends on time and concrete mixture with respect to w/c ratio (Byung Hwan Oh et al 2002).

### 2.5.6 Importance of Concrete Mix

The microstructure of concrete is strongly affected by several factors including chemical composition of cement, water-to-cement ratio, types and amounts of mineral admixtures and particle size distribution of cementitious materials and aggregates, etc. In order to improve the durability of concrete, the mixture proportions of concrete should be carefully selected considering the effects on durability (Byung Hwan Oh et al 2002).

### 2.5.7 Effect of Curing Method

High-temperature curing accelerates the hydration process so that at young concrete ages, a high temperature cured concrete will be more mature and thus have a better resistance to chloride ion penetration than a normally-cured concrete. At later ages, when the normally cured concrete has a chance to hydrate more fully, it will have a lower chloride ion diffusion Co-efficient than the high-temperature-cured concrete. The coarse initial structure developed in the high-temperature-cured concrete has internal micro cracking (Stanish et al 2003).
The accelerated curing has negative impacts on the chloride resistance of concrete (even when a proper preset time is used), the use of supplementary cementing materials can be effective in terms of mitigating these negative effects (Hooton and Titherington 2004). The Diffusion Coefficient, $D_c$ was also found to decrease as the curing age increases and also as the water/binder ratio decreases. At the later ages of curing, the effect of water/binder ratio on $D_c$ becomes less significant (Byung Hwan Oh et al 2002).

2.5.8 Effect of Concrete Cover Thickness on Corrosion Initiation Period

Insufficient concrete cover or poor quality concrete lead to reinforcement corrosion. Theoretically, bars embedded in concrete structures with sufficient cover are protected both chemically and physically against environmental effects.

The high alkalinity of the pore solution of the concrete cover provides the chemical protection and the impermeability of the concrete cover is expected to provide a physical protection against the ingress of deleterious materials like chloride ions and carbon-di-oxide, etc.

To control the reinforcement corrosion, the rate of chloride penetration should be minimized. Chloride penetration deeply depends on the depth and quality of concrete cover.

The resistance of steel corrosion is high or when the thickness of concrete cover is large but too much cover could result in larger and more cracks allowing direct access of aggressive agents to the steel reinforcement (Ampadu 2002).
2.6 CONCRETE DURABILITY TEST METHOD

It is often necessary to ascertain the impermeability of concrete to chloride ions as a quality control measure and also for assessment of improvements effected in properties of new concretes (Rajamane et al. 2003). Chloride penetration in concrete is a slow process. It cannot be determined directly in a time frame that would be useful as a quality control measure. Measurement of chloride diffusion Co-efficient requires a long time. To determine the chloride penetration within a reasonable time, a test method that accelerates the process was needed (Kyong Yum Yeau and Eum Kyum Kim 2004).

The rapid chloride penetration test (RCPT) (ASTM C1202-97), was the first test proposed for rapid qualitative assessment of chloride permeability of concrete. The RCPT method measures only the total electrical charge passed though the cement-based material in the first 6 hs, the resistance of the cement-based material against chloride penetration is not clearly specified.

Norwegian test was used as an accelerated steady-state migration test, which gives the direct measure to chloride concentration with time (Yang and Cho 2003). Chloride penetration in concrete is a slow process. It cannot be determined directly in a time frame that would be useful as a quality control measure. Measurement of chloride diffusion Co-efficient requires a long time.

To determine the chloride penetration within a reasonable time, a test method that accelerates the process was needed (Kyong Yum Yeau and Eum Kyum Kim 2004). In the accelerated test method, a concrete specimen is usually placed adjacent to a chloride solution on the top face, and a chloride-free solution on the other end. A potential difference is then applied to draw chloride ions though the concrete.
2.6.1 Tests Method for Determination of Durability Properties

Table 2.1 illustrates the various existing test method and its parameters (Streicher and Alexander 1999).

### Table 2.1 Existing Durability Test Method

<table>
<thead>
<tr>
<th>Test Method</th>
<th>Considers Chloride Ion Movement</th>
<th>At a Constant Temperature</th>
<th>Unaffected Conductors in the Concrete</th>
<th>Approximate Duration for Test procedure</th>
</tr>
</thead>
<tbody>
<tr>
<td>AASHTO T259 (Salt Ponding)</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>90 d after curing and conditioning</td>
</tr>
<tr>
<td>Bulk Diffusion (Nordtest)</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>40 – 120 Days after curing and conditioning</td>
</tr>
<tr>
<td>RCPT (T277)</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>6 h</td>
</tr>
<tr>
<td>External Migration</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>Depends on Voltage and Concrete</td>
</tr>
<tr>
<td>Rapid Migration (CTH)</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>8 h</td>
</tr>
<tr>
<td>Resistivity</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
<td>30 Min</td>
</tr>
<tr>
<td>Pressure Penetration</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Depends on Pressure and Concrete (but potentially long)</td>
</tr>
<tr>
<td>Sorptivity – Lab</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
<td>1 Week and Conditioning</td>
</tr>
<tr>
<td>Sorptivity – Field</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
<td>30 Min</td>
</tr>
<tr>
<td>Propan 2-ol Counter Diffusion</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
<td>14 days with thin paste samples</td>
</tr>
<tr>
<td>Gas Diffusion</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
<td>2 – 3 h</td>
</tr>
</tbody>
</table>

The total charge passed though a specimen during a 6 h period under a 60 V potential difference is measured in AASHTO T277 test and the measured value used as the chloride permeability index. The accurate or direct chloride permeability was not measured in the AASHTO T277 (Streicher and Alexander 1999).
2.6.2 Steady State and Non Steady State Chloride Profile

The chloride concentration measured from the anode solution was plotted against time to determine the chloride flux. Steady-state and Non-steady-state are the two stages attained during the test period with respect to the change of the chloride concentration. The chloride ions will not reach the anode compartment in the non-steady-state and at the steady-state condition, the flux of chloride ions become constant. In a well-cured Portland cement-based material, the pore solution mainly contains Na$^+$, K$^+$, Ca$^{2+}$, and OH$^-$ ions. When the electrical field is applied, all the ions in the system start to move by the electrical driving force. Except for chloride ions, all other ions will achieve an equilibrium distribution and cease to move in the system.

In steady-state, most of the ions pre-existing in the specimen have been driven out that mostly Cl$^-$ and Na$^+$ ions are dominant in the specimen. The charge, $Q_s$ obtained from steady-state condition was linearly related to Days regardless of concrete mixes. The charge passed obtained from steady-state can be used to predict the steady-state diffusion Co-efficient. The values of non-steady-state charge passed and steady-state charge passed are different (Yang and Cho 2003).

To establish a steady state condition, the concentration gradient must be constant during the test. The chloride ions interaction with concrete lead to a decrease of the chloride ion penetration rate within the concrete sample. This phenomenon does not affect the value for the effective diffusion Co-efficient in steady state condition, but it increases the time lag (Truc et al 2000). The diffusion Co-efficient of the concrete sample can be determined within short period using the steady - state accelerated migration tests with the absence of chloride binding effect or chloride ion interaction (Yang et al 2002).
2.6.3 Durability Test Parameters

The various test parameters involved in determining the durability properties are Diffusion Test and RCPT are Duration, Temperature and applied Accelerating Voltage.

2.6.4 Effect of Test Duration

Duration of the test depends on various parameters such as concrete grade, w/b, ratio, amount and type of blended Supplementary Cementing Materials, applied accelerating voltage, source solution concentration, etc. Duration of the test was reduced from 25 days for the 6V sample to 7 days for the 30V sample and duration was further reduced for higher voltages (McGrath and Hooton 1996).

2.6.5 Effect of Accelerating Voltage on Chloride Profile

A potential of 12 V is applied in Norwegian test instead of 60 V in RCPT, and the passing chloride-ion concentration is measured in Norwegian test instead of charge in RCPT (Yang et al 2002). In order to accelerate the diffusion rate of chloride-ions in Norwegian test, a potential difference of 30 V DC was applied to the electrodes (Kyong Yum Yeau and Eum Kyum Kim 2004). The Diffusion Co-efficient tends to increase with increased voltage of 30V for the steady state Diffusion test (McGrath and Hooton 1996).

2.6.6 Temperature Variations During the Test Period

In the accelerated test method, the low-grade concrete specimen temperature increases due to higher voltages, but for higher-grade concrete specimen even with 30V, the temperature was not significant (McGrath and Hooton 1996). The applied electrical potential of RCPT heats up the concrete
specimen, that may affect the flow speed of chloride ions, but for accelerated Norwegian tests, the concrete specimen was not heated due to lesser source concentration (Yang and Cho 2003). The temperature effect for low-grade concrete can be solved by using higher volume container or cell (Yang et al 2002).

2.6.7 Chloride Profile and Chloride Bindings during the Test Period

To obtain an accurate value for the diffusion Co-efficient, it is necessary to measure carefully the amount of chloride ions that get into the concrete sample. During the migration test, the anode chemical reactions depend mainly on the electrode potential, intensity in the circuit, and the upstream solution pH. A part of the chloride ions that reach the anode compartment disappears as gaseous chlorine Cl (g) due to the first chemical reaction in the anode compartment.

The diffusion Co-efficient determined with this anode reaction will be wrong (Truc et al 2000). The effective diffusion Co-efficient from the upstream and downstream flux of chloride ions will be the same during the steady state condition. Generally, the chloride flux was measured in the downstream cell. A portion of the chloride ions reacts with the concrete matrix becoming either chemically or physically bound, and this binding reduces the rate of chloride diffusion. If the diffusion Co-efficient was measured after steady-state conditions, then all the binding can be presumed to have taken place and this effect will not then be observed.

If a steady state condition has not been reached, then not all the binding will have occurred and this will affect the chloride profile (Stanish et al 2003).
The binding effect does not modify the determination of the diffusion Co-efficient since it has no influence on chloride ion flux in the steady state (Truc et al 2000). The cementing materials used in the concrete controlled the chloride binding capacity. The inclusion of Supplementary cementing materials affects binding property. Replacing the OPC with fly ash and slag reduces the chloride-binding ability (Mohammed and Hamada 2003).

### 2.6.8 Concrete Diffusion Co-efficient

Diffusion Co-efficient of chloride ion increases with the rise of the water/binder ratio and decreases with the rise of quantity of fly ash or blast furnace slag. That is to say, the diffusion Co-efficient of chloride ions is not only related to the water/binder ratio but also to the quantity and the type of additive. Both the fly ash concrete and blast furnace slag concrete have good resistance to chloride ions. Their diffusion Co-efficient of chloride ions are lower than \(10^{-9}\) cm\(^2\)/s. The extent of decrease in chloride ion diffusion Co-efficient of blast furnace slag concrete is higher than that of fly ash concrete.

The chloride ion diffusion Co-efficient of fly ash and blast furnace slag concretes may be as lower than \(10^{-13}\) m\(^2\)/s (Faguang Leng et al 2000).

Concretes with high impermeability are expected to have effective chloride diffusion Co-efficient of the order of \(10^{-12}\) m\(^2\)/s (Rajamane et al 2003). The diffusion Co-efficient of chloride ions values for cement-fly ash pastes lie within the range of \(10^{-7}\) and \(10^{-9}\) cm\(^2\)/s (Ampadu 1999).

Increasing the w/c ratio or curing at elevated temperature increases the chloride diffusion Co-efficient (Detwiler and Fapohunda 1993). The apparent chloride diffusion Co-efficient obtained are in the range of \(6.4\times10^{-8}\) to \(12.4\times10^{-8}\) cm\(^2\)/s for concrete exposed in the seawater. The average chloride
diffusion Co-efficient was $8.2 \times 10^{-8}$ cm$^2$/s for an average exposure period of 142 days (Erdogdu et al. 2004).

Diffusion Co-efficient tended to increase with increased voltage of 30V in steady state test method (McGrath and Hooton 1996). The effective diffusion Co-efficient can be calculated from the upstream flux or from the downstream flux of chloride ions, but the result during the steady state was same (Truc et al. 2000). The charge passed obtained from steady-state was used to predict the steady-state diffusion Co-efficient (Yang and Cho 2003).

2.6.9 Diffusion Co-efficient from Profile Method and the Migration Co-efficient from Colorimetric Method

The diffusion Co-efficient obtained from ponding test, $D_p$, is determined based on measurements of the chloride content profile. The migration Co-efficient obtained from colorimetric method determined based on measurements of the depth at which the color change, and a constant value of $C/C_0 = 0.07/0.52$ is used. A correlation between the diffusion Co-efficient of $D_p$ and the migration Co-efficient $M_{col}$ is determined. By linear regression, the empirical relationship between $D_p$ and $M_{col}$ is statistically derived as,

$$M_{col} = 3.54D_p + 0.46 \times 10^{-12} \quad (2.9)$$

where $D_p$ and $M_{col}$ are expressed in m$^2$ s$^{-1}$. By linear regression, the correlation Co-efficient R2 for the model is 0.968. It appears that $D_p$ correlate linearly with $M_{col}$. The 90-d salt ponding test is a long-term test for measuring the penetration of chloride into concrete. Using the good experimental correlation in, the measurements of the colorimetric method after ACMT provide a time saving and easy way to obtain the transport property of concrete.
This study shows that the diffusion Co-efficient obtained from ponding test linearly correspond well with the migration Co-efficient obtained from ACMT, but the migration Co-efficient measured by ACMT is higher than the diffusion Co-efficient measured by the ponding test. Further study is needed to find this reason.

2.6.10 Diffusion Co-efficient based on RCPT

From the RCPT, the Q value was applied in the Berke’s equation (2.10) to calculate Diffusion Co-efficient, Dc values (Andrade and Whiting 1996). Chloride diffusivity is one of the important properties of concrete affecting durability of reinforced concrete structures, especially when the structure is built in a marine environment. The diffusivity of ions in concrete is determined conventionally by using diffusion cells. Since the conventional chloride diffusion test for the cement-based materials is time-consuming (Dhir and Byars 1993), accelerated chloride ion diffusion test methods were developed. Applying an external electrical field to accelerate chloride penetration has been often used in recent years to evaluate the permeability of concrete.

The rapid chloride permeability test (RCPT), designated as ASTM C1202-97, was the test proposed for rapid qualitative assessment of chloride permeability of concrete. The RCPT method has been used to investigate the effect of mineral admixture on resistance to chloride ion penetration (Wee et al 2000), the influence of aggregate fractions (Wee et al 1999), and curing conditions and pore size (Aldea et al 2000) related to the penetration of chloride ions. Detwiler et al (1994) used the accelerated steady-state migration test, to study the influence of different curing conditions on concrete permeability.
Yang and Su (2002) introduced an accelerated chloride migration test (ACMT) to determine the chloride diffusivity of the interfacial transition zone. Since the accelerated migration test needs to take liquid samples for the chlorides to be analyzed, this kind of test is laborious and expensive (Castellote et al 2001). In order to avoid the sampling and analyzing of chlorides during the test, Castellote et al (2001) correlated the chloride concentration and conductivity in the anodic compartment of a migration test in steady state.

\[
D_c = 0.0103 \times 10^{-8} \times Q^{0.84}, \text{ cm}^2/\text{s}
\]  

(2.10)

2.6.11 Initiation Period Based on Diffusion Co-efficient

The initiation period was calculated from the Diffusion Co-efficient of the concrete. The mathematical model for service life prediction presented here for existing reinforced concrete structures exposed to natural environment incorporated Fick’s second law of diffusion and a term for accelerated diffusion, and is also associated with the absorption of chloride ions by concrete. In this report, the Co-efficient of chloride diffusion are assumed to be time-dependent constants.

The theoretical model can be used to estimate the service life (defined as the initiation period) of reinforced concrete structures. The prediction of service lifetime for existing reinforced concrete structures may be used for planning future maintenance and repair of reinforced concrete structures.

The IS-456-2000 recommends the minimum cover depth for concrete exposed to different environment exposure condition. Some conservative service life predictions were calculated with the diffusion Co-efficient in this research program. Despite the fact that these predictions
ignored chloride binding which is assumed to be higher in fly ash modified concretes, (Arya et al 1990) it was still predicted that it takes 3 times longer for corrosion to begin in the high volume fly ash concretes, primarily due to the lower diffusion Co-efficient. It must be remembered that long term extrapolation of short term test data should be viewed with caution due to the lack of maturity at the time of testing, and that other mechanisms of concrete deterioration are being ignored. Other deterioration mechanisms may be irrelevant if chloride induced corrosion is the sole cause of failure, but it is far more likely that an interaction of related events will contribute to failure.

The Fick’s diffusion theory is that the corrosion Initiation period $t_o$ refers to the time during which the passivation of steel is destroyed and the reinforcement starts actively corroding.

2.6.12 Corrosion Initiation Period Based on Chloride Diffusion Co-efficient

The initiation period was calculated from the Diffusion Co-efficient of the concrete. The mathematical model for service life prediction presented here for existing reinforced concrete structures exposed to natural environment incorporated Fick’s second law of diffusion and a term for accelerated diffusion, and is also associated with the absorption of chloride ions by concrete.

In this report, the Co-efficient of chloride diffusion co-efficient are assumed to be time-dependent constants. The theoretical model can be used to estimate the service life (defined as the initiation period) of reinforced concrete structures. The prediction of service lifetime for existing reinforced concrete structures may be used for planning future maintenance and repair of reinforced concrete structures.
2.7 RELATIONSHIP BETWEEN CHLORIDE DIFFUSION RATE AND CHARGE PASSED RATE

Chloride diffusivity is one of the important properties of concrete affecting durability of reinforced concrete structures, especially when the structure is built in a marine environment. The diffusivity of ions in concrete is determined conventionally by using diffusion cells. Since the conventional chloride diffusion test for the cement-based materials is time-consuming (Dhir et al 1996), accelerated chloride ion diffusion test method were developed. Applying an external electrical field to accelerate chloride penetration has been often used in recent years to evaluate the permeability of concrete. The rapid chloride permeability test (RCPT), designated as ASTM C1202-97, was the test proposed for rapid qualitative assessment of chloride permeability of concrete. The RCPT method has been used to investigate mineral admixture effect on resistance to chloride ion penetration (Wee et al 2000), the influence of aggregate fractions (Wee et al 1999), and curing conditions and pore size (Aldea et al 2000) related to the penetration of chloride ions. Detwiler et al (1993) used the accelerated steady-state migration test, to study the influence of different curing conditions on concrete permeability. Yang and Su (2002) introduced an accelerated chloride migration test (ACMT) to determine the chloride diffusivity of the interfacial transition zone. Since the accelerated migration test needs to take liquid samples for the chlorides to be analyzed, this kind of test is laborious and expensive (Castellote et al 2001). In order to avoid the sampling and analyzing of chlorides during the test, Castellote et al (2001) correlated the chloride concentration and conductivity in the anodic compartment of a migration test in steady state.

The chloride migration rate and the charge passed rate obtained in the steady state are linearly correlated regardless of concrete mixes, or the experimental conditions of power source and the thickness of the
specimen. The chloride migration rate can be determined from charge passed to avoid sampling and analyzing chlorides during the accelerated chloride migration test (Tsai-Lung Weng and Chung-Chia Yang 2004).

Ampadu et al (1999) studied relationship between chloride diffusion, $D_c$ and resistivity, and observed good co-relation between $D_c$ and electrical resistivity. The outcome of the study can be useful for simple measurement. Yang et al (2002) studied relationship between $D_c$ and RCPT and observed good co-relation between $D_c$ and RCPT. The outcome of the study can be useful for simple measurement.

2.7.1 Model for Concrete Cover Cracking due to Rebar Corrosion in RCC Structures

Assessment of structural behavior of corrosion affected structures is an important issue; which would help in making certain decisions pertaining to the inspection, repair, strengthening, replacement and demolition of such structures. Depending on the level of oxidation of metallic iron, corrosion products may have much greater volume than the original iron which gets consumed by the process of corrosion (Kapilesh Bhargavaa et al 2006). This volume expansion is mainly responsible for the though thickness cracking of the cover concrete; which would indicate the loss of service life for the corrosion affected structures. An analytical model is proposed to predict the time required for cover cracking and the mass loss of reinforcing bars in corrosion affected reinforced concrete structures. The proposed model also incorporates the modeling aspects of the residual strength of cracked concrete and the stiffness contribution from the combination of reinforcement and expansive corrosion products. An attempt has also been made to arrive at reasonable estimates of the various parameters in the model related to the composition and properties of expansive corrosion products based on the
available published experimental data. It has been found that the model is quite capable of providing the estimates of predicted time to cover cracking and mass loss of reinforcing bars that are in reasonably good agreement with the experimentally observed values as well as the analytical predictions of other researchers. It has also been found that both predicted time to cover cracking and mass loss of reinforcing bars are significantly influenced by tensile strength of cover concrete, annual mean corrosion rate and modulus of elasticity of reinforcement plus corrosion products combined.

2.7.2 Reinforcement Corrosion in Concrete Structures, its Monitoring and Service Life Prediction

Shamsad Ahmad 2003, has discussed about the corrosion of reinforcement in concrete structures, its monitoring and service life prediction. Reinforcement corrosion has been widely reported in the literature over the last two to three decades. It is one of the major durability problems, mainly when the rebar in the concrete is exposed to the chlorides either contributed from the concrete ingredients or penetrated from the surrounding chloride-bearing environment.

Carbonation of concrete or penetration of acidic gases into the concrete, are the other causes of reinforcement corrosion. Besides these, there are few more factors, some related to the concrete quality, such as w/c ratio, cement content, impurities in the concrete ingredients, presence of surface cracks, etc. and others related to the external environment, such as moisture, oxygen, humidity, temperature, bacterial attack, stray currents, etc., which create reinforcement corrosion. The assessment of the causes and extent of corrosion is carried out using various electrochemical techniques. Prediction of the remaining service life of a corroding RC structure is done with the help of empirical models and experimental method.
2.7.3 Effect of Chloride Binding on Service Life Predictions

One of the major causes of deterioration of reinforced concrete structures is chloride-induced corrosion of the reinforcing steel. The magnitude of the damage is especially large in structures exposed to marine environments and de-icing salts. The capacity of the concrete cementitious system to bind chloride ions has an important effect on the rate of chloride ionic transport in concrete and on the corrosion initiation of the steel reinforcement. Martín-Pérez et al. 2000 discussed on the mathematical models used in the literature to describe chloride binding in concrete. The impact of the different binding relations on the time-dependent chloride penetration profiles is investigated by solving the chloride mass conservation statement with a finite-difference approach. Results were presented for a concrete structure subjected to two different exposure conditions: submerged in seawater and exposed to de-icing salts. The implication of accounting for chloride binding in service life estimations was discussed.

For chloride-induced corrosion, an equation giving the required concrete cover as a function of the chloride concentration has been derived for a chosen time of service. Helland (1999) showed how the remaining service life of existing concrete structures was assessed based on the chloride ingress and taking into account a decreasing chloride diffusion over time. Hong (2000) considered the degradation of reinforced concrete structures due to both aggressive environment and in-service loading for service life prediction. Teply (1999) dealt with practically all variables influencing the service life of a reinforced concrete beam (variations in beam properties and degradation) corrosion due to carbonation and chloride attack).

Liang et al. (2001) used a multiple layer fuzzy method model for the assessment of the service life of bridges. Vu and Stewart (2002) used a
reliability model which includes the spatial and random variability of both chloride diffusion, concrete cover and concrete strength. CIB / RILEM technical committee (CIB W080 / RILEM TC 175-SLM) was created a method of service life prediction of building materials and components in September 1996.

2.7.4 Critical Review about Service Life Concepts of Reinforced Concrete Structures

The definition of service life of concrete involves more considerations than thirty years ago. Among several reasons, this is because only mechanical parameters were taken into account by then and, now a days, there are other like durability that are being commonly used to define service life. It was in the 80´s when Tutti thought about a concrete damage model and has the vision, at that time, of what we know as the initiation and propagation periods of structure damage. As a result of his work, several contributions to improve his model have been developed that incorporate the advances from then to now. This is why several codes about cement and concrete have adopted durability terms and consider, among other things that the service life of a structure finishes when the environmental aggressive agents reach the reinforcement.

During the last 30 years the evolution of concepts has allowed interesting ways to define and calculate service life in function of the cracking or not of a concrete structure, to take into account the limitations of the initiation and propagation period, to validate probabilistic and deterministic prediction models, to introduce residual life models and definitions and, recently, to introduce durability indexes. According with the literature consulted, the main conclusion from this review is that there is a need to work
in order to obtain a guiding model to divide the whole life of the structure in several stages. Each of them must be analyzed in an isolated form from the others in such a way that the prediction models be more precise.

2.8 CONCLUDING REMARKS

In this chapter, the development of high strength and high performance concrete has been discussed. Corrosion of reinforcement in concrete is a serious problem due to the external environmental effect and reducing the life of the structure has been discussed by many researchers. From the literature study, it has been observed that several researchers have been attempted to improve the concrete properties by addition of mineral and chemical admixtures. The type of tests carried out by various researchers has been studied. The effect of concrete cover thickness on corrosion initiation period was discussed. Some of the researchers have studied the correlation between the chloride diffusion and RCPT values. It has been seen that the service life estimation of RCC structures has been obtained based on chloride diffusion. Several studies have been conducted on improvement of concrete durability and also developed a method for estimating the service life of structure. But, all these studies have been touched upon various durability parameters and have not correlated with each other. Therefore, it was felt necessary to study further and focus towards the correlation among different durability parameters and to develop a tool for service life estimation of reinforced concrete structures, particularly with respect to chloride ions ingress.