CHAPTER II



THEORICAL BACKGROUND

2.1 Mechanism of corrosion in concrete:

Generally speaking, corrosion means deterioration of a material due to a reaction which returns the metal to compounds that are similar to the minerals from which it was extracted in the first place. In reinforced concrete structures, rebar do not normally corrode. Firstly, the concrete cover forms a nature barrier which significantly reduces the penetration rate of exterior aggressive agents. Secondly, concrete is highly alkaline causing embedded steel bars to be covered with a passivation layer, a thin and dense impermeable film of iron oxide (Bijen, 1989).

In general, the most important deterioration mechanism of reinforcement corrosion involves chloride ions, as found in salts. Chloride ions may be contained in the original constituents of concrete, from mixing water, aggregate or admixtures or they may be absorbed from the environment into the concrete during the service life of the structure. In current practice, efforts are generally made to minimize the amount of chloride in concrete constituents, so the majority of chloride that results in deterioration is derived from the environmental sources such as chloride include seawater, ground water, or deicing salt. Over time, chloride ions or compounds penetrate through the cover concrete to the depth of the reinforcement through chloride diffusion process.

The resulting presence of chlorides and the loss of the alkaline environment cause the embedded steel to loose its surface passivity. Accumulated corrosion products, which occupy more volume than the reactants, cause cracking of the protective concrete cover. Steel corrosion in concrete is an electrochemical process where corrosion cells are generated due to differences in electrochemical potentials. Some areas of the bar become anodes, and some cathodes. The chemical half-cell reactions occurring at the anodic and the cathodic areas are as follows (Mehta and Kumar, 1993):

Anode:
$$Fe \rightarrow Fe^{2+} + 2e^{-}$$
 (2.1)

Cathode:
$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$
 (2.2)

The hydroxyl ions arriving at the anodic area will electrically neutralize the Fe^{2+} ions dissolved in pore water and form a solution of ferrous hydroxide (Bazant, 1979):

Anode:
$$\operatorname{Fe}^{2^+} + 2\operatorname{OH}^- \to \operatorname{Fe}(\operatorname{OH})_2$$
 (2.3)

The product further reacts with available oxygen and water and forms red rust:

Anode:
$$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_2$$
 (2.4)

Red rust is not the only product of corrosion of steel in concrete. Compounds such as black rust, Fe_3O_4 , green rust, $FeCl_2$, and other ferric and ferrous oxides, hydroxides, chlorides, and hydrates are also formed. Their composition depends on the availability of pore water, its pH and composition, and oxygen supply. Corrosion products are very dangerous to concrete elements because their volume is much larger than the metallic iron (Sorensen and Ernst 1982). The black rust volume is twice as large as that of steel, and red rust volume is four times as large (Bazant 1979). The increase in volume causes tensile stresses in concrete which crack the cover concrete.

2.2 Corrosion deterioration model:

Cady and Weyers 1984, as well as Tuutti and Kyosti 1982, have presented conceptual models for predicting the service life of reinforced concrete structures, when chloride related corrosion is considered as the primary deterioration mechanism. In general, such models divide the service life into three major phases: diffusion, corrosion and deterioration. Figure 2.1 illustrates graphically such service life model.

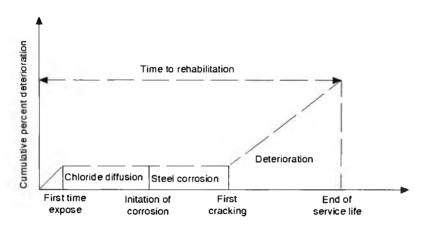


Figure 2.1 Service life model relative to corrosion deterioration (Cady and Weyers, 1984)

The diffusion phase, or time-to-corrosion, can be thought of as initiating either when the concrete structure is first placed into service or first exposed to a source of chloride contaminant. This phase represents the period of time during which chloride diffuses through the cover concrete and accumulates at the surface of the reinforcing steel. Although in most cases diffusion of chloride continues and concentrations continue to increase at the steel surface, the diffusion phase is generally considered to end at the point at which the amount of chloride at the steel surface is sufficient to initiate corrosion. Hence, the corrosion phase begins.

The corrosion phase, or time-to-cracking, involves the steady build-up of corrosion product around the surface of reinforcing steel in the concrete. Corrosion continues until sufficient corrosion product has been produced to cause cracking of the

5

cover concrete. During the final deterioration phase, or time to end of functional service life, the concrete deteriorates to a point deemed unacceptable for use. The diffusion and corrosion phases are discussed in detail in the following sections.

2.3 Chloride diffusion in concrete:

Capillary absorption and diffusion are the means by which chloride ions can penetrate concrete. The most familiar method is diffusion which is the movement of chloride ions under a concentration gradient. For this to occur the concrete must have a continuous liquid phase and there must be a chloride ion concentration gradient. The second common transport method is absorption. As a concrete surface is exposed to the environment, it will undergo wetting and drying cycles. When water usually containing chlorides encounters a dry surface, it will be drawn into the pore structure though capillary suction. Absorption is driven by moisture gradients. Typically, the depth of drying is small, however, and this transport mechanism will not bring chlorides to the surface of the reinforcing steel unless the concrete is of extremely poor quality and the rebar is shallow (Thomas et al. 1995). In addition, the effect of absorption is typically limited to a shallow cover region. In the bulk of the concrete, the pores remain saturated and chloride ion movement is controlled by concentration gradients.

Chloride movement into concrete is an ionic diffusion process following Fick's second law (Klieger el al 1994, Cady el al 1983, Page el al 1981 and Frey el al 1994). Fick's second law of diffusion represents non-steady state diffusion and is expected in a form of a partial differential equation:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$$
(2.5)

Where:

C = chloride concentration

D = chloride diffusion coefficient

t = time

 $\mathbf{x} =$ cover thickness.

The above partial differential equation has many solutions based on the boundary conditions. The most popular solutions used in the analysis are the ones with a boundary condition of surface chloride concentration C_0 being constant as follows:

$$C(x,t) = C_0 \left[1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \right]$$
(2.6)

Where:

erf(y) is the error function, a mathematical construct found in math tables or as a function in common computer spreadsheets.

2.4 Performance assessment methods:

Many studies have been performed under both laboratory and field conditions to assess the method of corrosion deterioration and to attempt to predict the time necessary for corrosion to occur and sufficient damage to accumulate to render the structurally or functionally deficient. Through laboratory studies of concrete reinforcement corrosion, several generally accepted types of test specimens have evolved, which attempt to simulate the reinforced concrete environment, and provide accelerated testing for chloride induce corrosion.

2.4.1 Standard method of test for resistance of concrete to chloride ion penetration (AASHTO T259):

The AASHTO T259 test (commonly referred to as the salt ponding test) is a long- term test. The test requires three slabs at least 75 mm thick. The sides of the slabs are sealed but the bottom and top face are not. After the conditioning period, a 3 percent NaCl solution is ponded on the top surface for 90 days, while the bottom face is left exposed to the drying environment (see Figure 2.2). At the end of this time the slabs are removed from the drying environment and the chloride concentration of 0.5-inch thick slices is then determined.

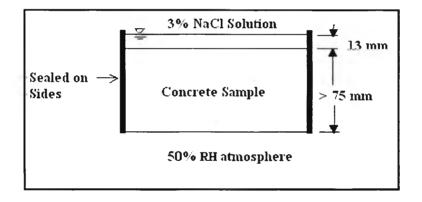


Figure 2.2 AASHTO T259 test setup (Stanish el al)

2.4.2 Bulk diffusion tests (Nordtest NT Build 443):

Nordtest is the first formally standardized version of the bulk diffusion test. In the test, specimen is saturated with limewater. This prevents any initial sorption effects when the chloride solution is introduced. All three faces of specimen are coated and leaving one face exposed to a 2.8 M NaCl solution (see figure 2.3). It is left for 35 days before evaluation.

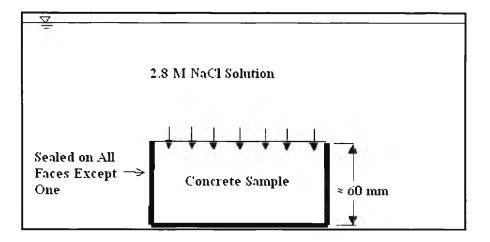


Figure 2.3 Nordtest NT build 443 test setup (Stanish el al)

To evaluate the sample, the chloride profile of the concrete is determined by mounting the sample. The sample is level in perpendicular to the surface of the sample. A pass is made at each depth with increments 0.5 mm to grind the concrete sample into dust, which is then collected. The chloride content of the powder is then determined according to AASHTO T260. The error function solution of Fick's Second Law is then fit to the curve and a diffusion value and surface chloride concentration is determined.

2.4.3 Electrical Indication of Concrete's Ability to Resist Chloride Ion Penetration (AASHTO T277 and ASTM C1202):

In the AASHTO T277 or ASTM C1202 test, a water-saturated, 50-mm thick, 100-mm diameter concrete specimen is subjected to a 60 V applied DC voltage for 6 hours using the apparatus shown in figure 2.4. In one reservoir is a 3.0 % NaCl solution and in the other reservoir is a 0.3 M NaOH solution. The total charge passed is determined and this is used to rate the concrete according to the criteria included as table 2.1

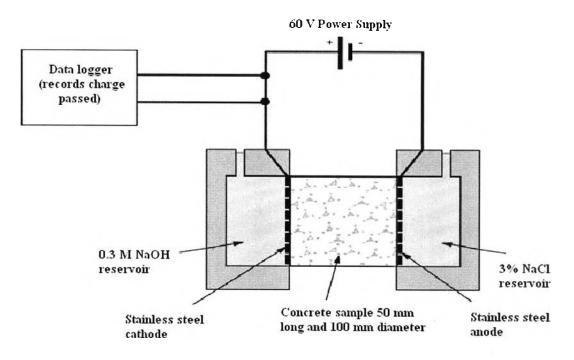


Figure 2.4 AASHTO T277 or ASTM C1202 test setup (Stanish el al)

Charge passed (coulombs)	Chloride ion penetrability	
> 4,000	High	
2,000 - 4,000	Moderate	
1,000 - 2,000	Low	
100 - 1,000	Very low	
< 100	Negligible	

 Table 2.1 ASTM C1202 ratings

2.4.4 Electrical migration techniques:

Electrical migration tests are performed in a two-chamber cell with the concrete sample as shown in figure 2.5. The concrete sample can be of any size, but is usually a disk of 100 mm diameter and length about 15 to 50 mm. The thickness of the disk will affect the duration of the test, but a sufficient size is required to avoid aggregate interface influences. Initially, the cathode chamber contains chloride ions, but the anode chamber is chloride-free. The host solution varies, but is typically either distilled water or limewater. A voltage is then applied to drive the chloride ions through the concrete while the chloride concentration of the downstream (anode chamber) solution is monitored. The change of chloride concentration with time allows the calculation of diffusion coefficients.

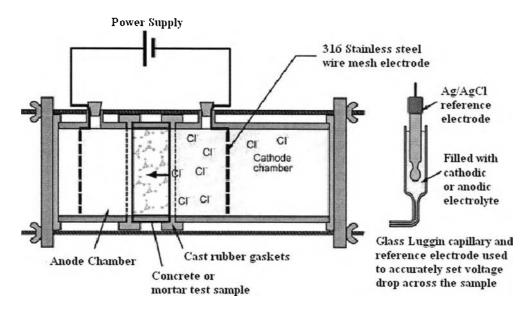


Figure 2.5 Typical chloride migration cells (Stanish el al)

2.4.5 The Rapid Migration Test:

A migration cell is set up with a specimen 50 mm thick and 100 mm in diameter, and an applied voltage of 30 V, as shown in figure 2.6. The experiment proceeds as usual for an electrical migration test, except that the chloride concentration of the downstream solution is not monitored. After a specified duration, the samples are removed and split, and the depth of chloride penetration is determined in one half of the specimen using a colorimetric technique in which a silver nitrate solution is used as a colorimetric indicator. When a silver nitrate solution is sprayed on a concrete containing chloride ions, a chemical reaction occurs. The chlorides bind with the silver to produce silver chloride, a whitish substance. In the absence of chlorides, the silver instead bonds with the hydroxides present in the concrete, creating a brownish color. This depth of penetration can be used to determine a chloride ion diffusion coefficient. Using the following equation derived from the Nernst-Einstein equation (Tang and Nilsson 1991):

$$D = \frac{RT}{zFE} \times \frac{x_{f}}{t}$$
(2.7)

Where:

D = chloride diffusion coefficient.

R = the universal gas constant.

T = the temperature.

 x_f = the inflection point of the chloride ion profiles that needs to be related to the depth given by the colorimetric technique.

z = the valence of ionic species.

F = Faraday's constant.

E = the applied electrical potential.

t = time.

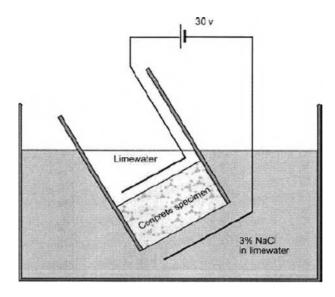


Figure 2.6 Rapid migration cells (Stanish el al)

Similar to the more usual migration cell, the rapid migration test is capable of addressing the criticisms of the rapid chloride permeability test related to examination of actual chloride ion movement and temperature rise. However, as in the case of a typical migration test, inclusion of conductive materials, such as metal or carbon, could short-circuit the rapid migration cell, with the current being carried by the conductor rather than the ions in pore solution. If the conductor does not short-circuit the cell (i.e. if a piece of steel is parallel to the surface), there is the possibility of it reacting with the chloride ions and affecting ion movement in that manner. However, if the chloride ions do not penetrate to the depth of the steel, this would not be a problem. Also, if a conductive ionic species, i.e. calcium nitrite, is present, the current will be carried by the more highly ionically mobile nitrite ions instead of the chloride ions. The chloride ions would effectively experience a lower potential gradient, reducing the distance they would travel. This effect may be minor in the concentrations of nitrite ions found in practice.

2.4.6 Pressure penetration techniques:

Another method to accelerate the flow of chloride ions into concrete is by exposing one face of the concrete to a solution containing chloride that is under pressure. This will serve to drive the chlorides into the concrete under both convection and diffusion (see figure 2.7). The concrete sample is pre-saturated with water and placed in a permeability cell. A chloride-containing solution is introduced to one face of the concrete and a pressure is applied. This pressure is maintained for a given period of time after which the concrete sample is removed from the cell and tested for chlorides. This method can be used in two ways. First, the solution to the differential equation can be fitted to a chloride profile. This concept has the disadvantage of requiring chloride profile grinding and great numerical complexity. An alternative is to determine the depth of penetration of a known concentration of chloride at a specific time. This depth can be used to rate different concretes tested under identical conditions. The depth to a known chloride concentration can be conveniently determined using a colorimetric technique such as the silver nitrate spray procedure described previously in rapid migration test.

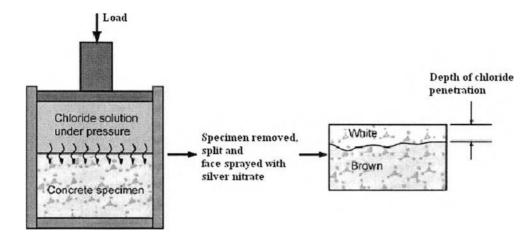


Figure 2.7 Pressure penetration test procedure (Stanish el al)

Table 2.2 provides a summary of the test methods described earlier, grouped into two main categories (long term and short term). A summary of some of the advantages and disadvantages to each testing procedure is provided in the table. An examination of Table 2.2 reveals each test has strengths and weaknesses. For example, the Nordtest and AASHTO T259, each model the actual chloride ingress well, however as long-term tests they are not suitable for use as a quality control test during construction. Other methods, like the rapid chloride permeability test, have a more nebulous relationship with what actually occurs in the concrete, but have the advantage of a short duration. Finally, some tests fall between these two extremes.

Test	Method	Considers Chloride Ion Movement	At a constant Temperature	Unaffected by Conductors in the Concrete	Approximate Duration of Test Procedure
Long Term	AASHTO T592 (salt ponding)	Yes	Yes	Yes	90 Day after curing and conditioning
	Bulk Diffusion (Nordtest)	Yes	Yes	Yes	40 - 120 Days after curing and conditioning
Short Teim	RCPT (T277)	No	No	No	6 hours
	Electrical Migration	Yes	Yes	No	Depends on Voltage and Concrete
	Rapid Migration (C'TH)	Yes	Yes	No	8 hours
	Pressure Penetration	Yes	Yes	Yes	Depends on Pressure and Concrete (but potential long)

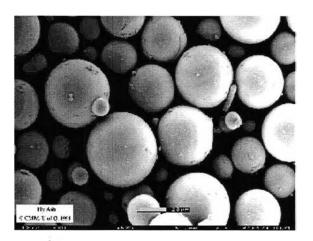
 Table 2.2 Summary of chloride penetration test method (Stanish el al)

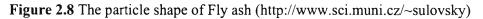
2.5 Pozzolans:

Pozzolans are materials that have little or no hydraulic activity of their own; however, they act as hydraulic cement when mixed with water in the presence of calcium hydroxide. Hydration of pozzolan, when compared with hydration of silicates in Portland cement, is a slow reaction. Hydration of silicates in Portland cement results in the formation of C-S-H and calcium hydroxide (CH). In pozzolanic reactions, pozzolan reacts with CH from the Portland cement hydration, and water, and forms C-S-H. The C-S-H produced in the pozzolanic reaction has lower density than from the Portland cement hydration. However, since the reaction is much slower, the products of the pozzolanic reaction fill the already existent capillary spaces in the cement paste. It improves strength and durability. Bentz and Garboczi stressed that the pozzolanic mineral admixtures do not eliminate the capillary porosity, but reduce it by significantly lowering the volume fraction of CH and at the same time increasing the total amount of C-S-H (Bentz and Edward, 1991). Mineral admixtures with very fine particle sizes are known to increase the water requirement in almost direct proportion to their amount present (Mehta, 1984).

2.5.1 Fly ash:

Fly ashes are by-products manufactured during combustion of powdered coal in power plants. A summary of the properties and chemical composition of different fly ashes was presented by Helmuth, 1987. In general, depending on the amount of chemical composition, fly ash can be classified as Class F or Class C. Class F fly ash is mostly composed of silicate glass containing aluminum, iron, and alkalis, with at least 70% of the chemical composition is made up of SiO₂, Al₂O₃ and Fe₂O₃ (Klieger el al., 1994). Class C fly ash has higher amount of CaO so it possesses more cementing characteristics and is less pozzolanic than Class F. The particles are in the form of solid spheres with sizes ranging from less than 1 μ m to 100 μ m, and an average diameter of 20 μ m (Mehta 1993) (see figure 2.8).





The benefits for using fly ash in concrete include the following characteristics (Klieger el al. 1994):

- > Improve workability.
- Lower heat of hydration.
- ➢ Lower cost concrete.
- > Improve resistance to alkali-silica reaction.
- ▶ Higher long-term strength.
- > Opportunity for higher strength concrete.
- Lower shrinkage characteristics.
- Lower porosity and reduce permeability.

2.5.2 Rice husk ash:

Rice husk ash is achieved from burning rice husks in power plants. Rice husk ash contains high amount silica, highly porous and lightweight, with extremely high surface area. Ordinary Portland cement is expensive and unaffordable to a large portion of the world's population. Since ordinary Portland cement is typically the most expensive constituent of concrete, the replacement of a proportion of it with rice husk ash offers improved concrete affordability. Figure 2.9 illustrates the particle shape of rice husk ash.

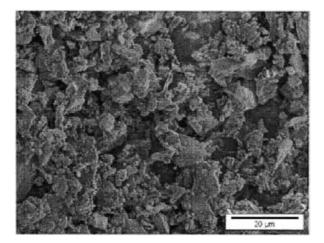


Figure 2.9 The particle shape of rice husk ash (http://www.waterpowermagazine.com)

When used in concrete, rice husk ash provides the following benefits:

- Increase cohesion and reduce segregation.
- Lower cost concrete.
- Speed up setting time.
- Improve compressive strength.
- Improve resistance to acid attack.
- > Improved chloride penetration resistance.
- Decrease porosity.

2.6 Chloride diffusion coefficient:

Besides the performance assessment methods in simulated conditions as described earlier, there are numerous instant and ready to use expressions for determining the chloride diffusion coefficient. However, each method produces a slightly different numerical result. Some of available models investigated in the current theoretical background can be seen as follows:

- 1. K. Takewaka & S. Mastumoto et al 1988.
- 2. Mangat P. & Molly B. et al 1994.
- 3. Gjorv O. E. & Sakai K. et al 1998.
- 4. Webster et al 1999.
- 5. Andrea Bobby & Evan Bentz et al 1999.
- 6. Gehlen et al 2000.
- 7. M. D. A. Thomas & E. C. Bentz et al 2000.
- 8. Palle Thoft & Christensen et al 2002.
- 9. Kyle Stanish & Michael Thomas et al 2003.
- 10. Gowripalan N. & Sirivivatnanon V. et al 2004.

2.6.1 K. Takewaka and S. Mastumoto et al 1988:

Based on the results from existing reinforced concrete structures in Japan, K. Takewaka proposed an expression of chloride diffusion coefficient as a power function of time:

$$D = D_{w/b} \times D_1 \times t^{-0.1}$$
(2.8)

Where:

 $D_{w/b}$ = Coefficient that takes into account the influence of water binder ratio. D_1 = Coefficient that takes into account the type of cement.

t = exposure period.

2.6.2 Mangat P. and Molly B., et al 1994:

In their research proposed another equation for corrosion due to chloride contamination as a function of time t and an empirical coefficient m which is based on the water binder ratio:

$$\mathsf{D} = \mathsf{D}_{\mathsf{i}} \times \mathsf{t}^{\mathsf{m}} \tag{2.9}$$

Where:

D = the chloride diffusion coefficient.

 D_i = the time-dependent diffusion coefficient.

m = an empirical coefficient based on the concrete water binder ratio (w/b) = $2.5 \times (w/b) - 0.6$

2.6.3 Gjorv O. E. and Sakai K. et al 1998:

Based on the data collected from other researches, they proposed an empirical equation for determination of diffusion coefficient as a function of water binder ratio as follows:

$$LogD = -3.0 \times (w/b)^{2} + 5.4 \times (w/b) - 13.7$$
(2.10)

Where:

 $D = diffusion \ coefficient.$ w/b = the water binder ratio.

The above equation applies to concrete mixtures that contain blast furnace slag and silica fume.

2.6.4 Webster et al 1999:

Examine data on measured chloride profiles from a number of researchers to determine appropriate values for an effective diffusion constant, D_{ce} , Webster el al. 1999 found the main parameters to be water binder ratio and type of exposure of concrete

structures. Webster el al. 1999 proposed the following equation for chloride contamination in marine environment, based on data collected around the world, but normalized to an average United Kingdom ambient temperature using the Arrhenius function:

$$D = 0.04 \times (1166^{w/b}) \times 10^{-12}$$
(2.11)

Where:

 $D = diffusion \ coefficient.$ w/b = the water binder ratio.

2.6.5 Andrea Bobby and Evan Bentz et al 1999:

Propose an expression as the same as M. D. A. Thomas and E. C. Bentz et al 2000 but took into account the temperature factor, as follows:

$$D = D_{ref} \left(\frac{t_{ref}}{t}\right)^{m} \times exp\left[\frac{U}{R} \times \left(\frac{1}{T_{ref}} - \frac{1}{T}\right)\right]$$
(2.12)

Where:

D = diffusion coefficient at time t and temperature T

 D_{ref} = diffusion coefficient at some referenced time t_{ref} and referenced temperature T_{ref}

m = constant.

U = activation energy of the diffusion process = 35,000 Joule/mol

R = gas constant

 $T = absolute temperature (^{0}K)$

2.6.6 Gehlen et al 2000:

Gehlen et al 2000 performs Rapid Chloride Migration tests regularly and a database with Rapid Chloride Migration results for a variety of concrete mixtures. In order to compare these diffusion coefficients with diffusion coefficients of concrete from real structures, Gehlen suggests an environmental correction factor and the expression of chloride diffusion coefficient is in form as follows:

$$D = D_{ref} \left(\frac{t_{ref}}{t}\right)^m \times exp\left[b_e \times \left(\frac{1}{T_{ref}} - \frac{1}{T}\right)\right]$$
(2.13)

Where:

D = diffusion coefficient at time t and temperature T

 D_{ref} = diffusion coefficient at some referenced time t_{ref} and referenced temperature T_{ref}

m = constant.

 $T = absolute temperature (^{0}K)$

2.6.7 M. D. A. Thomas and E. C. Bentz et al 2000:

By using the results from bulk experiment proposed the other expression of chloride diffusion coefficient in Life-365 computer program for predicting the service life and life – cycle costs of reinforced concrete exposed to chlorides:

$$D=D_{ref}\left(\frac{t_{ref}}{t}\right)^{m}$$
(2.14)

Where:

 D_{ref} = Coefficient at some reference time t_{ref} = 28 days. m = constant.

2.6.8 Palle Thoft and Christensen et al 2002:

Found that the diffusion coefficient D as a function of the water binder ratio w/b and the temperature T (°C) for cement pastes without of replacement by silica fume. However, they did not mention the time dependence of diffusion coefficient.

$$D = \begin{bmatrix} 11.146-31.015 \times (w/b) - 1.941 \times T + 38.212 \times (w/b)^{2} \\ +4.48 \times (w/b) \times T + 0.024 \times T^{2} \end{bmatrix} \times 10^{-14}$$
(2.15)

Where:

w/b = water binder ratio. T = temperature ⁰C.

2.6.9 Kyle Stanish and Michael Thomas et al 2003:

For ordinary Portland cement concrete with no special corrosion protection applied, the chloride diffusion:

 $D_{28} = 1 \times 10^{(-12.06+2.40 \times W/B)} = Coefficient at some reference time t_{ref} = 28 days (2.16)$ m = constant = 0.20

For Portland cement concrete with silica fume, a reduction factor is applied to the value calculated for Portland cement, D_{OPC} based on the level of silica fume (% SF) in concrete. In addition, the relationship is only valid up to replacement levels of 15 percent of silica fume. The silica fume is assumed that has no effect on m.

$$D_{SF} = D_{OPC} \times e^{-0.165 \times \% SF}$$
 (2.17)
m = 0.20

For Portland cement concrete with Fly Ash and Slag, neither fly ash nor slag are assumed to affect D_{28} , however, both of them impact the rate of reduction in diffusivity and the value of m. In addition, the relation is only valid up to replacement levels of 50 percent of fly ash or 70 percent of slag:

$$m = 0.20 + 0.4 \times (\% FA/50 + \% SG/70)$$
(2.18)

2.6.10 Gowripalan N. and Sirivivatnanon V. et al 2004:

Based on the same source of collected data, proposed another the relationship between the diffusion coefficient and the water binder ratio of concrete as following. However, this equation only pertains to concrete with no additives and/or concrete with fly ash but without blast furnace slag and silica fume:

$$LogD = -3.9 \times (w/b)^{2} + 7.2 \times (w/b) - 14.0$$
(2.19)

Where:

 $D = diffusion \ coefficient.$ w/b = the water binder ratio.

2.7 The propagation phase:

The mechanism of the propagation phase is described in figure 2.10. Based on this mechanism, there are many kinds of models for the corrosion to cracking phrase. The current literature review will investigate three models and the list is according to the chronicle order as follows:

- 1. Bazant's mathematical model.
- 2. Morinaga's empirical equation.
- 3. Youping Liu's model.

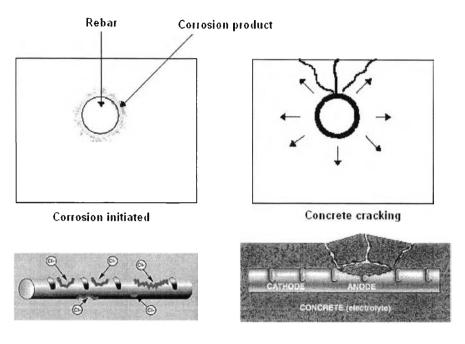


Figure 2.10 Corrosion to cracking diagram (http://www.mbtaus.com.au/admix)

2.7.1 Bazant's mathematical model:

In Bazant's models, the time to cracking is a function of corrosion rate, cover depth, spacing, and certain mechanical properties of concrete such as tensile strength, modulus of elasticity, Poisson's ratio and creep coefficient. A sensitivity analysis of Bazant's theoretical equations demonstrates that for these parameters, corrosion rate is the most significant parameter in determining the time to cracking of the cover concrete. Unfortunately, Bazant's model has never been validated experimentally. The basic assumptions of Bazant's models are as follows:

1. Oxygen and chloride ion transport through concrete cover are quasi-stationary and one-dimensional.

2. A steady state of corrosion producing expansive rust layer begins at depassivation time.

3. The model is based on red rust that is more dangerous for cracking concrete and assumes $\rho_r = \frac{\rho_{\pi}}{4}$, where ρ_r and ρ_{π} are the density of rust products and steel, respectively.

$$t = \rho_{cro} \frac{D \times \Delta D}{S \times j_r}$$
(2.20)

Where:

S = the bar spacing.

D = the diameter of the bar.

 j_r = the rate of rust production.

$$\rho_{cro} = a$$
 function of the mass densities of steel and rust $= \left[\frac{1}{\rho_r} - \frac{0.523}{\rho_{rt}}\right]^{-1} \times \frac{\pi}{2}$ (2.21)
 $\Delta D =$ the change in diameter of the bar

$$= 2 \times f_{t} \times \frac{L}{D} \times \delta_{pp} \text{ (for } S < 6D\text{) and } = f_{t} \times \left(\frac{S}{D} - 1\right) \times \delta_{pp} \text{ (for } L > \frac{S - D}{2}\text{)}$$
(2.22)

 f_t = tensile strength of concrete

L = concrete cover depth

 δ_{pp} = bar hole flexibility

$$\delta_{pp} = \left[\frac{D \times (1+j_{cr})}{E}\right] \times \left[(1+\nu) + D^2 \left(\frac{2}{S^2} + \frac{1}{4L(L+D)}\right)\right]$$
(2.23)

2.7.2 Morinaga's empirical equation:

According to Morinaga's equations, the time to cracking is a function of the corrosion rate, concrete cover depth and reinforcing size. Therefore, the time to cracking can be easily predicted.

$$t = \frac{\frac{0.602 \times d \times (1 + \frac{2c}{d})^{0.85}}{i_{cor}}}{i_{cor}}$$
(2.24)

Where:

t = the time to cracking in days

c = the cover to the reinforcement (mm)

d = the diameter of reinforcing bars (mm)

 i_{cor} = the corrosion rate in gram per day

$$i_{cor} = \left[-0.51 - 7.6 \times N + 44.97 \times (w/b)^2 + 67.95 \times N \times (w/b)^2 \right] \times d/c^2$$
(2.25)

Where:

N = chloride concentration (% on cement weight)

w/b = water binder ratio

c = the cover to the reinforcement (mm)

d = the diameter of reinforcing bars (mm)

2.7.3 Youping Liu's model:

Youping Liu's model considers three phases for corrosion to cracking:

a. Free Expansion: As the passive film is broken by chloride ions, the metallic Fe at the anode is oxidized to form ferrous ions, which can react with hydroxyl ions to

21

produce ferrous hydroxide and then can be further converted to hydrated ferric oxide. It has been assumed that there exists a porous zone around the steel/concrete interface caused by the transition from cement paste to steel, entrapped/entrained air voids and corrosion products diffusing into the cement paste capillary voids. The volume of this porous zone is directly related to the surface area of reinforcement, water binder ratio, degree of hydration and degree of consolidation. As the corrosion takes place on the surface of the steel, the porous zone will gradually fill with the corrosion products. When the total amount of corrosion products W_T is less than the amount of corrosion products required to fill the porous zone around the steel/concrete interface W_P the formation of corrosion products at this stage will not create any stress on the surrounding concrete.

b. Stress Initiation: As the total amount of corrosion products W_T exceeds the amount of corrosion products needed to fill the porous zone around the steel/concrete interface W_P the formation of corrosion products starts to create expansive pressure on the surrounding concrete, and this pressure increases with an increase in corrosion products.

c. Cracking: When the total amount of corrosion products W_T reaches the critical amount of corrosion products W_{crit} the internal stress from the volume increase of rust products will exceed the tensile strength of concrete and crack the cover concrete. It is obvious that W_{crit} is mainly dependent on quality of concrete and cover depth.

2.8 Summary:

Based on the literature described earlier, the service life model of Cady and Weyers 1984 containing the first two phases is considered because the last stage, deterioration phase, can not be modeled by mathematical mean up to date. Moreover, by skipping the deterioration stage, we are one the safe side. In addition, in practice, the end of service life is defined as the time for maintaining or repairing the concrete structure, not the time that the concrete structure collapsed completely.

According to the performance assessment methods, the rapid migration method with the Nordtest NT Build 492 standard:" Chloride migration coefficient from nonsteady state migration experiments" is chosen. The advantage of the rapid migration method is short term test and it considers the movement of chloride ions into concrete specimen. In compared with the other short term methods such as electrical migration and pressure penetration, the test set up of rapid migration method is simpler. Therefore, rapid migration method is the best option.

As it can be seen from the above literature review, most of the expressions of chloride diffusion coefficient are proposed in term of water binder ratio which can be considered as the main parameter. Among these above models of chloride diffusion coefficient, Kyle Stanish and Michael Thomas el al 2003 fashion, particularly the equation 2.16 is investigated for the current study because it takes into account and can express the influence of pozzolanic effect on resistance of cement paste to chloride ingress. In addition, by this fashion, the impact of pozzolan to chloride diffusion

coefficient can be examined in term of the percent of partial replacement of Portland cement by pozzolan which is the more visual than the other model, for example Gowripalan N. and Sirivivatnanon V. el al 2004.

Finally, regarding the propagation phase, the Morinaga's empirical equation is employed. The disadvantage of Bazant's mathematical model as compared with Morinaga's empirical equation is that it has never been validated experimentally in practice. On the other hand, Youping Liu's model is quite complicated because it considers many kinds of rust products in its approach. Practical speaking, it is unnecessary since the propagation phase is very short, in compared with the initiate phase, which in turn, do not change the total service life significantly at all.