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A Durability Model for Chloride and Carbonation Induced Steel Corrosion in Reinforced Concrete Members

by

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A thesis submitted to the Faculty of Graduate Studies and Research
in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

Department of Civil and Environmental Engineering
Carleton University
Ottawa, Ontario, Canada
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Ottawa, administered by the Ottawa-Carleton Institute for Civil Engineering

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**A Durability Model for Chloride and Carbonation Induced Steel Corrosion in
Reinforced Concrete Members**

submitted by

Osman Burkan Isgor

In partial fulfillment of the requirements
for the degree of Doctor of Philosophy

(Department Chair)

(Thesis Supervisor)

(External Examiner)

ABSTRACT

A systematic and robust method for predicting chloride and carbonation-induced steel corrosion in reinforced concrete structures under prescribed exposure conditions is developed. The significant phenomena that contribute to the rate and amount of corrosion of reinforcement; i.e. heat and moisture transfer, chloride, CO_2 and O_2 transport, are modeled by the two-dimensional time-dependent nonlinear finite element method. The governing equations of the various transport phenomena are solved numerically in the time and the space domains. Where appropriate, the coupling effects among the different transport phenomena and the chloride binding/release mechanisms as well as the carbonation process are modeled in order to simulate the field conditions reasonably closely. The proposed finite element model and its associated computer program, CONDUR, are capable of handling any geometry (including cracks), prescribed initial and boundary conditions and pertinent material nonlinearities. Since mass transport in concrete is the subject of on-going research, the computer program is designed to be flexible enough to accommodate improvements and modifications to the adopted models. By using a two-dimensional time-dependent nonlinear finite element method, the corrosion of the reinforcement is treated as an electrochemical process and is modeled as a spatial and temporal function of temperature, moisture, and ionic or molar concentration of various chemicals within the pore solution. The corrosion analysis provides the rate and amount of reinforcement corrosion in a reinforced concrete structure operating within a prescribed environment. To verify the finite element model and its associated computer program, the numerical results are compared with available

experimental data, with reasonable agreement between them. Further numerical simulations have been carried out to demonstrate the capabilities of the developed methodology and the computer program.

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LIST OF SYMBOLS

ρ = density

α = absorbitivity of concrete

φ = degree of carbonation in concrete

ε = emissivity of gray concrete surface

μ = porosity of concrete

σ = Stefan-Boltzman constant

α_l = coefficient for flux boundary conditions

$\Delta\mu_c$ = change in porosity due to carbonation

α_0 = parameter representing the ratio of the maximum and minimum values of the moisture diffusion coefficient

η_a = anodic polarization

ρ_a = density of aggregates

η_c = cathodic polarization

ρ_c = density of cement

α_E = diffusion modification factor due to age of concrete

ΔG° = Gibbs free energy

α_H = diffusion modification factor due to relative humidity

ρ_L = density of the liquid water,

μ_o = initial porosity of concrete

α_T = diffusion modification factor due to temperature

ρ_w = density of water
 a = FHH isotherm coefficient
 A_I = H&J isotherm coefficient
 a/c = aggregate-cement-ratio
 b = FHH isotherm coefficient
 B_I = H&J isotherm coefficient
 c = specific heat of concrete
 C_a = volumetric heat capacity of the air
 C_b = bound chloride concentration
 C_c = carbon dioxide concentration
 C_f = free chloride content
 C_f = free chloride concentration
 C_N = clearness number
 C_o = concentration of the oxygen permeating into concrete
 CPR = corrosion penetration rate
 D' = apparent diffusion coefficient
 D_a = diffusion coefficients of the anions
 D_c = carbon dioxide diffusion coefficient
 D_c = diffusion coefficients of the cations
 D_{Cl} = effective chloride diffusion coefficient
 D_h = isothermal moisture diffusion coefficient
 $D_{h,ref}$ = humidity diffusion coefficients determined at reference conditions
 D_{inf} = chloride diffusion coefficient in an infinite solution

D_L = liquid water diffusion coefficient
 D_O = effective oxygen diffusion coefficient
 D_T = thermal moisture diffusion coefficient
 D_V = vapour diffusion coefficient
 D_w = total moisture diffusion coefficient
 $D_{w,ref}$ = water diffusion coefficients determined at reference conditions
 E_a = electrode potential of the reaction
 E_{corr} = corrosion potential
 E^o = potential of typical electrode reaction
 E_r = electrode potential of the reduction reaction
 F = Faraday's constant
 f_w = volume fraction of the aqueous film at the walls of the pores
 f_w = flux boundary condition
 f_w = fixed boundary condition
 h = relative humidity
 h_c = convection coefficient
 h_c = humidity at which D_h drops halfway between its maximum and minimum values
 h_r = radiation heat transfer coefficient
 i_a = anodic current
 I_c = cathodic current
 i_{corr} = corrosion current
 i_{La} = anodic diffusion limited current densities
 i_{Lc} = cathodic diffusion limited current densities

I_n = direct solar radiation intensity
 i_o = exchange current density
 i_p = external polarization current entering or exiting the system
 J_{fh} = rate of $\text{Fe}(\text{OH})_2$ production at the anode
 J_o^a = rate of O_2 consumption at the anode
 J_o^c = rate of O_2 consumption at the cathode
 J_r = rate of $\text{Fe}(\text{OH})_3$ production at the anode
 k = conductivity of concrete
 K = absolute surface temperature
 K^* = absolute average air temperature
 k_o = reaction rate constant
 k_s = mass diffusion coefficient for the dissolution of $\text{Ca}(\text{OH})_2$
 K_s = absolute shade temperature.
 m = age reduction factor
 n = parameter describing the distribution of moisture diffusion coefficient
 N = shape function
 n_x = direction cosine with respect to x
 n_y = direction cosine with respect to y
 P_o = saturated vapour pressure
 q = flux
 q_a = airflow rate
 q_c = heat loss by convection
 Q_c = sink for carbon dioxide due to the carbonation reaction

Q_{Cl} = sink representing chloride binding mechanism

$Q_{Cl, released}$ = source term representing the released chloride ions

Q_h = source term, more specifically in the present context

q_r = re-radiation by concrete

q_s = total radiation absorbed

Q_w = sink/source term which represents the water generated

q_y = heat conducted into the concrete body

r = electrical resistance

R = universal gas constant

r_D = rate of dissolution of $Ca(OH)_2$ in concrete pore water

r_N = rate of the neutralization reaction

S = degree of saturation

S_c = degree of saturation of the non-wetting phase

S_l = surface on which a flux boundary condition is defined

S_2 = surface on which a fixed boundary condition is defined

t = time

T = temperature

T_l = body surface temperature

t_r = time of exposure at which the relative diffusivity is measured

T_{ref} = reference temperature at which reference chloride diffusivity is measured

T_s = shade air temperature

U = activation energy

v = average wind speed

V = volume of the gas adsorbed at vapour pressure P

V_m = monolayer capacity

W = weight loss after time t

w/c = water-cement-ratio

w_L = liquid water content

x = x-coordinate

y = y-coordinate

z = ionic valance of the ion

1. Introduction

1.1. General

Reinforced concrete is the most prevalent construction material. Concrete is used to construct highways, bridges, buildings, canals, dams, airports, electric poles, pipelines, sewer lines, storage tanks and many other types of structures which constitute the infrastructure of a modern society. In fact, no modern society can build an adequate infrastructure for human habitat without concrete.

The ready availability of the raw materials for manufacturing Portland cement, the principal ingredient of concrete, and of sand and coarse aggregates, its other important constituents, makes concrete a universal construction material. Although average quality concrete can be produced without extensive experience or knowledge, production of high quality concrete, or high performance concrete, requires technological and scientific know-how. Inadequate care and/or know-how will lead to poorly designed concrete structures which may suffer severe serviceability and safety problems.

When mass production of concrete first began in the early part of the 20th century, it was generally believed that concrete was immune from attack by chemical and environmental effects. However, experience has since shown that while good quality concrete is resistant to attack by many chemical and environmental agents, it is not entirely immune to any chemical and environmental hazard. However, the process of deterioration is normally slow and that is the reason for the early optimism with respect to the immunity of concrete.

Today many of the concrete structures that were built more than forty years ago, and which were exposed to aggressive environments, suffer from durability problems. The problem is particularly serious in reinforced concrete structures wherein the corrosion of reinforcing steel has brought into question the safety of these structures.

Today the mitigation of durability problems in reinforced concrete is more of an art than a science. The methodologies that are employed to repair deteriorated structures are not always effective in the long term due to the mechanical and chemical incompatibility between the substrate and the new overlay. While designing reinforced concrete structures for resisting applied loads is strictly governed by well-established and detailed design codes provisions based on laws of mechanics and constitutive laws of materials, there is no code available for designing for durability. Accordingly, designers are unable to design reinforced concrete structures for durability with the same scientific rigour as they do for loads.

There are several reasons for the apparent lack of durability-based design. Principally, it is the lack of adequate knowledge and experience with respect to durability. This is poor due to the historic belief that concrete is inherently durable irrespective of its quality and environment in which it is located. Another reason is the inherent complexity of the phenomenon of durability and the mechanisms of deterioration of concrete, the steel reinforcement and the reinforced concrete composite.

The thermodynamic principles that govern the deterioration processes in reinforced concrete are rather complex and are currently being investigated by many researchers. It is now established that humidity, temperature, freeze-thaw action, the presence of chemicals such as acids, oxygen, carbon dioxide and other gases, the

mechanical and transport properties of concrete, the chemical composition of the steel reinforcement and the interaction of the mechanical and environmental stresses and deformations are some of the factors that affect the durability of concrete.

Notwithstanding the preceding complexities, based on available phenomenological and mechanistic models of concrete and reinforcement, one can begin to formulate detailed methods for predicting the durability of reinforced concrete structures. These models can be used to determine the service life maintenance of reinforced concrete structures, and further development and application of these methods may in due course lead to the development of design codes for durability akin to the current design codes for mechanical strength and deformations.

In the current investigation, available models of concrete and reinforcement deterioration will be combined with advanced numerical techniques to develop a finite element program that can be used to predict the durability of reinforced concrete structures in a given environment. As stated earlier, the deterioration phenomenon is complex, therefore the scope of this study will be limited. Furthermore, the computer program will use available deterioration models, but it will trace the deterioration process in a detailed and systematic fashion. The program will be designed to trace both the initiation and propagation of deterioration in a reinforced concrete structure. However, no attempt will be made to couple mechanical deterioration with chemical and environmental processes.

To further fix ideas, in the following, some basic concepts and definitions related to the durability of concrete will be discussed.

1.2. Durability of Concrete Structures – Basic Concepts

Durability of concrete can simply be defined as the resistance of concrete to physical and chemical attack resulting from either interaction with the environment (external agents) and/or interaction among its constituents (internal agents).

As indicated in Figure 1.1, the deterioration of reinforced concrete structures can be divided into three main types:

1. Physical deterioration (due to frost, fire, abrasion, cracking)
2. Chemical deterioration (due to sulfate and acid attack, leaching, alkali-aggregate reaction)
3. Reinforcement corrosion (due to carbonation, chloride attack)

Cracking occurs in concrete for a variety of reasons. Load induced cracks often occur but are generally harmless. Heat of hydration and drying shrinkage during setting can result in large cracks in massive concrete structures such as dams. Restraint of movement in concrete structures or lack of adequate expansion joints will cause and/or exacerbate cracking in concrete structures. The expansion of corroding steel can also lead to delaminating cracks that are rather serious.

Fresh concrete cannot hydrate if the mix freezes, although it can re-hydrate after subsequent warming and re-vibration, but its ultimate strength will be affected if it experiences frost before setting and proper curing. Hardened concrete can be affected by freeze-thaw action, leading to large cracks and spalling. This occurs due to the expansive stresses caused by the freezing of the pore water in damp concrete.

Effect of fire is another process which can be classified under physical deterioration. Concrete's heterogeneous nature, as the various components have different

coefficients of expansion, creates serious problems at high temperatures (above 300°C). At these temperatures, cracking and explosive spalling may result, which could lead to a significant loss of cross sectional area and carrying capacity. Reinforcing steel may also lose its carrying capacity and cause large deflections at high temperatures.

Figure 1.1: Deterioration of reinforced concrete structures

Figure 1.2: Initiation of corrosion in steel reinforcement

Figure 1.3: Continuation of corrosion in steel reinforcement

As shown in Figure 1.1, sulphate attack is one of the main reasons of chemical deterioration in concrete structures exposed to sulphate bearing water. Sulphates react with the calcium aluminates in the concrete creating a substance called “ettringite”. Ettringite is an expansive material and causes large stresses and cracks in the concrete.

Another common deterioration mechanism is alkali-aggregate reactivity. The most common form of alkali-aggregate reaction (AAR) is the alkali-silica reaction (ASR), which is associated with rocks containing silica in its active form. Chert, limestone and certain volcanic rocks may contain the reactive ingredients that form an alkali-silicate gel at over 75% relative humidity. The reaction produces expansive stresses and may cause cracking. If the concrete is excessively permeable, due to its solubility in water, calcium hydroxide leaches out of concrete, resulting in the deterioration of the structural member. Leaching is more common in structures that are exposed to repetitive wetting and drying cycles such as offshore structures.

In a reinforced concrete member, corrosion of steel can take place as a result of electro-chemical or galvanic reactions. Galvanic action is a consequence of the electron transfer between dissimilar metals. In the absence of dissimilar metals, which is generally the case for reinforced concrete, the corrosion is initiated by local imperfections along the steel or local differences in the concentrations of the electrolyte as shown in Figure 1.2. Once the rust has formed, the steel surface beneath it becomes deficient in oxygen and becomes the anode. Therefore, corrosion continues beneath the rust cover as shown in Figure 1.3. Eventually, this will result in the failure of the reinforcement and possibly of the structure.

The presence of chloride around the reinforcement creates imperfections or exacerbates the effects of the existing imperfections. It acts as a starter for the electrochemical reaction, which results in the corrosion of the steel. Carbonation acts as a catalyzing agent to the corrosion process by degrading the concrete and making it less alkali, leaving the steel reinforcement unprotected. The details of these two processes (chloride attack and carbonation) will be presented later in this study.

1.3. Problem Definition

In general, in order for the corrosion reaction to start, the main ingredients of the corrosion reaction; i.e., oxygen, water and dissolved ions, must be present around the reinforcement. Initially, the reinforcing steel inside the concrete is generally covered by a passivating layer, which is basically a form of iron oxide. The passivating layer acts as a protective coat on the steel. As long as this protection is present around the steel, corrosion cannot start.

The environment in which the structure operates may weaken or eliminate the passivating layer around the reinforcement. Some chemicals (such as chlorides) have the potential to react with the passivating layer and diminish its thickness (depasivation). As a result, some parts (pitting corrosion) or the entire length of the steel reinforcement (general corrosion) may destroy the passivating layer. If at these locations the steel is exposed to oxygen and dissolved ions that transfer electrons, the corrosion of the reinforcement will commence.

Depasivation of the protective coat can occur if a certain amount of specific chemicals (e.g. chlorides) accumulate around the reinforcement. This amount is called

the depassivation threshold level. In the case of a highway or a road bridge, de-icing salts may be the reason for the chloride ingress; for an offshore structure the salt in the sea may be the source. Regardless of the source of the salt, the aggressive ions must be transferred to the steel by passing through the surrounding concrete.

Modeling chloride ingress into concrete is a complex time-dependent problem and is affected by many factors such as temperature, moisture, concrete properties, presence of carbonation (disintegration of concrete due to CO_2 penetration into concrete), etc. A chloride ingress model must track all the variables and their coupling effects carefully in order to simulate the real conditions. In addition to this, since the depassivation threshold is a function of chloride to hydroxide ions ratio, the amount of hydroxide produced by the electrochemical reactions inside the concrete must also be checked during the analysis.

As mentioned before, in order for the corrosion, which is basically an electrochemical reaction, to proceed, the presence of oxygen, water and dissolved ions is essential. Since the concentration of these constituents determines the rate of corrosion, the calculation of the concentration of each agent must also be carried out during analysis. Once corrosion starts, the chemical composition of the concrete pore solution changes. This affects the electrical resistance of the concrete which plays a major role in the rate of ion diffusion necessary to complete the corrosion reaction. As corrosion proceeds, the amount of corrosion products can rise to such levels that it can cause cracks in the concrete. These cracks may increase the rate of ingress of the corrosive agents in concrete, resulting in an increase in the rate of corrosion. The process ends with the failure of the structure due to one of the several possible reasons such as loss of carrying

capacity, excessive deflection, unacceptable amount of cracking and spalling, bond failure, etc.

The problems associated with the modeling of the process of corrosion in reinforced concrete structures, as described above, can be summarized as follows:

1. Material (e.g. chloride, H_2O , O_2 , CO_2 , etc.) ingress in concrete is a complex phenomenon, involving many factors such as ionic diffusion, convection, adsorption, electrical conductivity, temperature, moisture content, pore size distribution, the chemistry of the concrete matrix, etc. It has to be noted that most of these factors are coupled, which makes the problem even more complex.
2. In the case of chloride ingress, the binding characteristic of the concrete matrix with chloride ions is an important property. The amount of free chloride that can reach the reinforcement is not equal to the amount of chloride that enters the system.
3. If the pH of concrete pore solution drops below a certain value, some of the bound chlorides may be released and may contribute to the corrosion process.
4. The moisture content of the structure is one of the determining factors in how the ions move in concrete. If the concrete is fully saturated (underwater structures), ionic diffusion plays a very important role. If the concrete is partially saturated (splash zones of off-shore structures), convection, which is a much faster mode of ion transfer than ionic diffusion, becomes the predominant mechanism.

5. The existence of cracks in the concrete changes the mass transfer parameters of the concrete significantly. Smeared crack models, which are intended to modify the mass transfer coefficients, do not necessarily represent the real situation.
6. Most of the existing models approach the problem of mass transfer in concrete (in this particular case, the transfer of chloride, CO_2 as well as moisture and oxygen gas) as a one-dimensional problem. This restricts the applicability of the existing methods to idealized conditions.
7. Corrosion of steel in concrete is an electrochemical process which is not fully understood. Current research shows that the following factors are important in this process: type of concrete and reinforcement, formation of cathode, anode and passivating layer, depassivation due to chlorides and carbonation, the pore size and its distribution around the reinforcement, chemistry of the pore solution around reinforcement, oxygen and water content at the cathodic sites, electrical resistivity of concrete, polarization, etc. It can be noticed from this list that the model for simulating corrosion of steel in concrete can be very complicated.
8. There are several possibilities of failure due to corrosion in concrete. A decrease in cross sectional area of the reinforcement may reduce the load carrying capacity of the structure. The bond between steel/concrete interface may be lost resulting in slippage of the reinforcement which causes excessive deformations or complete loss of capacity. The concrete surrounding the steel may crack or experience spalling as a result of the stresses created by the corrosion products.

In the light of the above complexities, a major task is to simulate the interactions and coupling effects among the various pertinent phenomena as realistically as possible.

1.4. Objectives and Scope of the Research

The main objective of this study is to develop a systematic and robust method for predicting the corrosion-induced deterioration processes that a reinforced concrete structure may experience during its service life. In particular, the model will focus on chloride and carbonation induced corrosion of reinforcement under prescribed exposure conditions.

The significant phenomena that contribute to the rate and amount of corrosion of reinforcement (chloride, moisture, temperature, etc.) will be modeled by the two-dimensional time-dependent nonlinear finite element technique. The governing equations of the various transport phenomena will be solved numerically in the time and the space domains. The finite element model and its associated computer program will be capable of handling any geometry (including cracks), prescribed initial and boundary conditions and pertinent material nonlinearities. Where appropriate, the coupling effects among the different transport phenomena and the chloride binding / release mechanisms as well as the carbonation process will be modeled in order to simulate the field conditions reasonably closely. Since mass transport in concrete is the subject of on-going research, the computer program will be flexible enough to accommodate improvements and modifications to the current models.

The corrosion of the reinforcement will be treated as an electrochemical process and will be modeled as a two-dimensional time-dependent nonlinear phenomenon using

the finite element method. The corrosion process will be modeled as a spatial and temporal function of temperature, moisture, and ionic or molar concentration of various chemicals within the pore solution. The corrosion analysis will provide the rate and amount of reinforcement corrosion in a reinforced concrete structure operating within a prescribed environment.

To verify the finite element simulation results, they will be compared with available experimental data and further numerical simulations will be carried out to demonstrate the capabilities of the developed methodology and its associated computer program. However, experimental work to verify the model, development of new material models and the coupling of environmental and mechanical stresses are not within the scope of this study.

2. Literature Review

2.1. General

The concepts of durability of concrete and the modeling of the service life of a structure have been the subject of research for some time. The early models were focused on establishing governing equations and qualitative approaches for their application (Halstead, 1976; Bazant (1979a, b). Tuutti (1982) was among the early researchers who established the main principles of this process by dividing the reinforced concrete deterioration process into two stages: initiation and propagation. In the initiation period, the steel reinforcement remains passive; i.e. no loss of cross sectional area of the steel occurs but the corrosive agents are transported and even a protective layer of oxide film is formed around the steel (passivation). In the propagation period, the structure deteriorates as a result of the loss of reinforcing steel area and accumulation of corrosion products around the bar surface causing cracks in the structure.

The purpose of this thesis is to model the chloride and carbonation induced corrosion of steel reinforcement in concrete structures. As it was briefly mentioned before and will be discussed in further detail in the following chapters, reinforcement corrosion depends on several factors such as temperature, moisture content, chloride, CO₂ and O₂ concentrations, the mix properties, the composition of cement, the presence of cracks as well as the electrical resistivity of concrete. The initiation stage of such a model involves the analysis of heat, moisture, chloride, CO₂ and O₂ transfer, while the propagation (corrosion) stage entails the determination of the amount of rust produced on

the steel surface through the current densities which can be calculated by solving the electric potential distribution in concrete.

It will be demonstrated in this literature review that although a large number of analytical and experimental studies have been carried out on the service life modeling of reinforced concrete structures, most of the previous work has focused on the initiation stage modeling with special attention to the effects of either the chlorides or the carbonation, but generally not both. Most of these initiation stage models were based on Fick's second law in one-dimensional space. In the majority of cases, the propagation stage has been considered as an isolated problem independent from the initiation stage, which may not simulate the actual reinforcement corrosion problem realistically because the two stages cannot be separated from each other. Most of the proposed corrosion models do not fully utilize the basic principles of corrosion theory, which requires a full-integration with the initiation stage causing complex boundary conditions and severe nonlinearities. Although some attempts have been made to simulate the reinforcement corrosion as an electrochemical process by using the finite element and difference methods, due to the simplifications and assumptions used in these models, they remain rather elementary. A recent paper from Li et al. (2001) also underlines this point by stating, "...combined effect on the initiation and propagation of reinforcement corrosion has not been fully investigated as confirmed in the most recent literature..."

This chapter will review the literature developed in the field of chloride and carbonation induced steel corrosion in concrete structures, with special attention to both initiation and propagation stages. It will demonstrate the reasons for the necessity of the current research by pointing out the achievements to date and gaps in knowledge that still

exist. It will cover the published experimental and analytical work on the topics of moisture, chloride, carbon dioxide, and oxygen transfer in concrete as well as the corrosion of reinforcement. It has to be noted that since the literature on this topic is significantly large and sometimes repetitious, the focus will be on the more prominent studies. A more comprehensive history of the general topic of durability of concrete structures can be obtained from the literature reviews provided by Kropp (1995, 1996) and Johanneson (1998). In addition to this, the literature review of heat transfer problem will not be presented here since this topic is very well established. A comprehensive review of the literature can be obtained from other resources (Sucec, 1985).

2.2. Moisture Transport in Concrete

After the heat transfer problem, probably one of the most widely studied topics in field problems is the modeling of moisture transport in porous materials. The mathematical formulation of mass transfer in concrete at the macroscopic level is usually based on diffusion equations which were first established by Philip and de Vries (1957) and improved by Whiteker (1977) and Bear and Bachmat (1990). Bear and Bachmat (1990) used mathematical techniques to average the moisture diffusion due to vapour and liquid water movement and represented the moisture diffusion coefficient as a homogenized version of the two processes. More information on the homogenization technique for the determination of moisture transport in porous materials can be found in Samson et al. (1999). A similar approach has been used by Gawin et al. (1995) to model the coupled heat, water and gas flow in porous media. The moisture diffusion coefficients required to solve these diffusion models have been provided by various

researchers (Bazant and Najjar, 1971, 1972; Bazant and Thonguthai, 1978; Saetta et al., 1993; Gawin et al., 1995; Pel, 1995; Kunzel, 1995; Sander et al., 1998; Kim and Lee, 1999; Martys, 1999).

Hall (1989) studied the water sorptivity and the effect of capillary action in the moisture diffusion process of mortars and concretes. The adsorption isotherms, which provide the mathematical model for the equilibrium of the liquid and vapour phases of water in the porous materials, have been studied by Langmuir (1918), Brauner et al. (1938), Frinkel (1946), Hill (1952), Halsey (1952), Harkins and Jura (1943, 1944) and Xi et al. (1994) and a well-established methodology has been developed.

Other topics on the moisture transport in concrete including the effect of self-dessication (Bazant and Najjar, 1971), the moisture movement due to high thermal gradients, which may be encountered when there is high and sudden temperature changes in the environment as in the case of nuclear power plants or fires (Dinulescu, 1980), the effect of curing and aging (Mangat, 1994) have also been studied. More information and literature reviews of the moisture transport in porous building materials, with specific attention to concrete, can be found in other resources such as Garboczi (1990), Dullien (1992), Xi et al. (1994), Neville (1996), Nilsson and Tang (1996), Pel (1996), Bentz et al. (1999).

Summarizing, the moisture transfer problem in porous concrete has been widely studied and a significant number of computer models have been developed over the years, which can solve the transient and/or nonlinear and/or coupled moisture transport phenomenon in porous materials. A detailed list of these programs and their capabilities can be found in the literature review provided by Ojanen et al. (1999). However, the

main purpose of the current study is not to model the moisture transport in concrete, but to model the chloride and carbonation induced reinforcement corrosion in concrete structures. In other words, the modeling of moisture transport constitutes a small but important part of the proposed model. Therefore, the transient nonlinear moisture transfer model proposed in the current study has been designed to be robust and as accurate as the existing computer models.

2.3. Chloride Transport in Concrete

The effect of chloride ions on concrete structures has been best described by Verbeck (1975) as “a specific and unique destroyer.” Numerous experimental and analytical studies have been carried out on the topic. In the analytical part, most of the studies have focused on modeling the chloride ingress as a diffusion problem; i.e. by using Fick’s first and second laws (Crank, 1975; Sergi et al., 1992, Seatta et al., 1993; Frey et al., 1994, Nilsson et al., 1993, 1994). There have also been attempts to model the process by using electrochemistry, particularly the Nemst-Plank equation (Andrade, 1993; Chatterji, 1993).

The chloride ions in concrete can be found in three different forms: dissolved in pore solution as mentioned above (free chloride), physically adsorbed into the pore walls and chemically bound to the hydration products of concrete (Neville, 1995). The early models did not consider the effects of chloride binding and adsorption of chloride ions by the pore walls (Crank, 1975) and remained rather elementary. Although it is possible to obtain a closed-form solution of Fick’s second law if one reduces the diffusion problem to a simple one-dimensional semi-infinite medium, without chloride binding and

adsorption (Crank, 1975), this is only valid when both the diffusion coefficient and the surface concentration are assumed to be constant in space and time. The heterogeneous nature of concrete and the presence of more complex boundary conditions in real situations make this closed-form solution inapplicable in most cases. However, it is possible to find examples where this solution can be used (negligible binding and no adsorption) and to obtain a crude initial estimate. Nilsson et al. (1996) suggested that the assumption for constant diffusion coefficient can be valid for structures that have been in service for a long time. Constant surface chloride concentration can be obtained if the concrete is totally submerged in salt water (Amey et al., 1998). However, this would be an over-simplification of the problem since the diffusion coefficient is a function of several factors such as temperature, humidity, etc. and a constant surface concentration does not simulate most real life situations.

By using the simplified closed-form solution proposed by Crank, Browne (1982) developed a method for designing reinforced concrete structures against chloride-induced corrosion. He used the conceptual model developed by Tuutti (1982), which suggested that the design life of reinforced concrete structures could be assumed to be the time for the concrete chloride content around the reinforcing bar to exceed a critical value of 0.4% by weight of cement. He developed a nomogram illustrating a family of curves representing the variation in chloride content with depth and the time for the given values of diffusion coefficient and surface concentration. Similar aids were been developed by others using Browne's methodology. Generally, apparent values of diffusion coefficient and surface concentration are calculated by fitting the solution proposed by Crank (1975), using least-squares methods, to chloride profiles obtained from either core samples of

real structures or specimens tested in the laboratory. Maage et al. (1995) showed that using apparent diffusion coefficient gives only the average impact of all the chloride ingress mechanisms and does not reflect the intrinsic material properties. Funahashi (1990) and Sergi et al. (1992) applied the finite difference scheme to solve for chloride diffusion according to Fick's second law. They also used the least-square methods to calculate the apparent diffusion coefficient and surface concentration. It has to be noted that although finite difference method provides a practical way of solving differential equations, its applicability is severely restricted when the initial and boundary conditions become complicated and nonlinearity and coupling effects come into the picture. Finite element method, on the other hand, is a very powerful tool which can be used to solve nonlinear, time-dependent, coupled differential equations with complex initial and boundary conditions; therefore, it will be used in the current study to model the chloride and carbonation induced steel corrosion process in concrete.

One of the most detailed studies on modeling chloride ingress in concrete was performed by Seatta et al. (1993). Saetta et al. (1993) approached this problem by coupling heat transfer within concrete to chloride ingress without any consideration to the propagation stage modeling. She considered a sinusoidal seasonal temperature variation and solved this coupled problem using a simple finite element methodology. A similar approach was also adopted by Martín-Pérez (1999) in her service life model. Martín-Pérez (1999) also incorporated an elementary corrosion model which was based on the Butler-Volmer kinetics across a cross sectional area of a steel bar and did not solve the continuity equation to obtain the electric potential distribution and longitudinal current densities along the length of the reinforcement. Therefore, although both methods

provided a finite element approach to the chloride diffusion problem, they did not rigorously model the propagation stage, and its effects on the service life prediction of concrete structures.

Saetta et al. (1993) expressed the diffusion coefficient as a function of time, degree of cement hydration and relative humidity of the pores by correcting a reference value of diffusion coefficient evaluated at standard conditions (23°C, 28 days concrete and 100% relative humidity). Tang and Nilsson (1996 a, b) followed a similar approach by defining the diffusion coefficient as a function of temperature, age and concrete depth. Berke and Hicks (1994) and Amey et al. (1998) also related the diffusion coefficient to temperature by using an Arrhenius-type equation. Amey et al. (1998) suggested taking a weighted average temperature based on the number of months and average seasonal temperatures to account for the variation in temperature. Based on seasonal records, other researchers adopted sinusoidal variability of the temperature over the period of one year (Tang and Nilsson, 1996).

Experimental studies have shown that the chloride diffusion coefficient decreases with time due to increased maturity of the exposed concrete (Nilsson et al., 1996). Using experimental data, various researchers have proposed similar mathematical descriptions of the decay of the diffusion coefficient with time (Mangat and Moloy, 1994; Maage et al., 1995). It has been observed that this decay is a function of the mix proportions and type of curing applied to the concrete. Other studies have proved that the water-cement-ratio also has a significant impact on the decay (Maage et al., 1996; Bamforth, 1998). Therefore, any robust model must take into account the effect of the age of concrete on diffusion.

The presence of water in pore space of the concrete is an essential element of diffusion of chloride ions in concrete. A decrease in moisture content also decreases the diffusion of the ions. Sætta et al. (1993) and Martín-Pérez (1999) suggested an empirical equation for this relationship based on the studies conducted by Bazant and Najjar (1971).

Tang and Nilsson (1996) observed that the chloride diffusivity is usually lower in the outer parts of the concrete cover. As a consequence of this observation, they came up with an expression, which expresses the diffusion coefficient as a function of concrete depth. This “skin effect” was also modeled by Andrade et al. (1995) by assuming that the chloride diffusivity in concrete takes different values in the outer and inner parts of the concrete cover. They obtained a closed-form solution to Fick’s second law by assuming a two-layered medium (skin and bulk).

As mentioned previously, chloride in concrete may be in bound form, which is a result of the chemical reaction of chloride ions with the hydration products of concrete. Beaudoin et al. (1990) demonstrated the interaction of the chloride ions with the calcium-silicate-hydrate (C-S-H). Many researchers (Sergi et al., 1992; Sandberg, 1993, 1998; Papadakis et al., 1996; Glass, 1995, 1999, 2000) have showed that there exists a state of equilibrium between the free and the bound chlorides; therefore, there are always free chlorides in the liquid phase. After these observations, most of the models included the chloride binding mechanisms in their formulations. Generally, they have considered chloride binding indirectly by modifying the effective chloride diffusion coefficient (Sergi et al., 1992; Tang and Nilsson, 1993; Nilsson et al., 1994; Papadakis, 1996).

Some of the chloride binding models are linear models (Tuuti, 1982; Seatta, et al., 1993), the Langmuir isotherm (Sergi et al., 1992), and the Freundlich isotherm (Nilsson et al., 1994). One of the latest models on chloride binding was developed by Tang and Nilsson (1998) which combined the effect of temperature on the chloride binding mechanism. Castellote et al. (1999) also suggested the use of BET adsorption isotherm, which is generally used for modeling the adsorption of the vapour by the solid walls of a porous medium.

Neville (1995) pointed out that the presence of sulphate ions might result in the release of the bound chloride ions due to the preferential formation of calcium-sulpho-aluminate-hydrates. Likewise, carbonation of the concrete cover has a similar effect in releasing bound chlorides in the system (Andersen, 1997; Glass, 2000).

Several researchers have also approached some of the different aspects of the chloride ingress problem. Johansson (1997) pointed out the nonlinear nature of the problem. The effect of chloride penetration due to wetting and drying cycles; i.e. due to the convective movement of water, has been included in some of the models (Seatta, 1993; Martín-Pérez, 1999). The influence of the electrostatic fields generated by the ionic concentration gradient was investigated by Nagesh and Bhattacharje (1998). Hobbs (1999) showed the influence of the aggregates on the chloride ion diffusion into concrete. The effect of cracking on the water and chloride ingress into concrete was studied by Frangopol et al., 1997 and Aldea et al., 1999. Effect of the cyclic chloride exposure on chloride ingress was studied by Hang and Hooton (1999). Englund et al. (1998) used a probabilistic approach to model the chloride ingress problem.

Summarizing, many chloride ingress models have been developed by using similar approaches and many more could be added to the list above (Masi et al.; 1997; Wee et al., 1997; Dhir et al., 1998; Weyers, 1998; Costa and Appleton; 1999a, b; Xi et al., 1999; Onyejekwe and Reddy, 2000, etc.). The important observations that can be made are: (1) many mechanical, chemical and environmental factors affect chloride diffusion in concrete, (2) extensive experimental studies have been performed to quantify the effects of many of the important factors, (3) the experiments have mostly concentrated on the effect of each factor in isolation, and have not always considered the interaction of the various factors and its impact on the diffusion of chlorides, (4) analytical and numerical, primarily one-dimensional, models based on Fick's laws, have been developed by a number of investigators for chloride diffusion, (5) more experimental work is needed to further investigate and elucidate the interaction phenomena and their significance.

In the current study, some of these interactions will be included in the finite element formulation. The choice of which interactions to include is made based on the availability of adequate and sufficiently verified information in the literature.

2.4. CO₂ Transport and Carbonation in Concrete

Carbonation in concrete has also been studied widely. A good understanding of the general principles governing the carbonation process can be obtained from Sickert (1997). It has to be noted that carbonation itself does not cause deterioration of concrete but it has significant effect on the corrosion of reinforcement. Another effect is the carbonation shrinkage (Sadegzadeh and Kettle, 1986; Laplante et al., 1991). However,

the major effect on durability stems from the fact that carbonation reduces the pH level of concrete. In reality, air contains CO_2 , which in the presence of moisture, becomes carbonic acid and reacts with hydrated cement (Neville 1996). Papadakis (1991) showed that the pH of the pore water in the hardened cement paste drops from the range of 12.6-13.5 to a value around 9. It has been shown (Neville 1996) that the carbonation reaction can take place even at small concentrations such as 0.03 % by volume, which is the average concentration in the rural air. In large cities this level can rise up to 0.1% by volume. Schubert et al. (1974) demonstrated that the rate of carbonation increases with increasing levels of CO_2 concentration. Maintenance of the passivating layer around the steel significantly depends on the pH (alkalinity) of the pore water in the concrete covering the reinforcement. Therefore, it is crucial to determine whether carbonation has reached the steel level.

Parrot (1991) suggested that under normal conditions, carbonation is controlled by carbon dioxide diffusion in the empty pores of the exposed surface layer of concrete which results in a carbonation front that moves from the exposed surface to the inside of concrete (Neville, 1996). Due to this reason, many researchers have proposed a correlation between the carbonation depths with air permeability and water sorptivity of concrete (Dhir et al., 1989; Bentur, 1990; Basheer et al., 1994; Ballim, 1994; Parrott, 1992; Balayssac et al., 1993, 1998).

Currie (1986) proposed an equation for the determination of the depth of carbonation. According to this formulation, under steady hygrometric conditions, the depth of carbonation increases in proportion to the square root of time, which is characteristic of sorption rather than diffusion. The square root of time and the depth of

carbonation are related to each other by carbonation coefficient. According to Currie (1986) the carbonation coefficient can be taken as 3 or 4 mm/year^{0.5} for low strength concrete. Wierig (1984) also gave estimations of carbonation profiles for several concrete types over a period of 16 years.

Dhir et al. (1989) investigated the relationship between air permeability and carbonation depth after 20 weeks of accelerated carbonation and proposed a relationship between carbonation depth and the intrinsic permeability of concrete. Parrott (1992) developed a relationship between the carbonation depth and the oxygen permeability. Ballim (1994) correlated ten-month carbonation depths with 28-day oxygen permeability and water sorptivity, both resulting in correlation coefficients around 0.95.

Correlating the carbonation depth with the intrinsic or gas permeabilities has provided a good understanding of the one-dimensional carbonation problem with steady-state boundary conditions (relative humidities, temperatures, carbon dioxide profiles, etc). However when kinetic boundary conditions are considered and the two-dimensional case is investigated, the correlation equations developed could not predict the carbonation process accurately (Papadakis et al., 1991).

Papadakis et al. (1991) proposed a comprehensive carbonation model which used the basic chemical principles governing the process. They proposed that simple diffusion theory could be used to model the carbon dioxide diffusion in concrete and they proposed a diffusion coefficient for carbon dioxide to be used in the solution. Their model was robust and included the effects of composition of the cement, the rates of reactions taking place during carbonation, the aggregate content in the hardened cement paste and the porosity of the concrete. They have shown good agreement between their model and the

experimental studies that they have conducted with variable boundary conditions. However, their model is not implemented a numerical scheme which could be applied to different geometries, variable boundary conditions, or non-homogeneous materials.

Seatte et al. (1993) also followed a similar approach but used a different material model for the carbon dioxide diffusion in concrete. They considered the coupling effects among heat, moisture and carbonation and offered a finite element technique, although it was rather simplistic, for the solution of the governing phenomena. However, no attempt was made to combine the propagation stage to their initiation stage model.

Many researchers (Ho and Lewis, 1987; Lo et al., 1994; Jones et al., 1999) carried out experiments with variable boundary conditions. Castellote et al. (1999) investigated the effect of loading and associated cracking on carbonation penetration in concrete structures. A similar experimental study has been carried out by Schutter (1999), which attempted to quantify the influence of cracks on the carbonation of concrete structures.

A general observation about carbonation literature is that the phenomenon has been extensively studied in isolation. The fundamental chemistry and physics of the carbonation process are well established and various semi-empirical models have been proposed. In this study, a robust model based on available literature will be implemented in the finite element formulation. A unique feature of this model will be the coupling of the carbonation and chloride diffusion, something that has not been previously modeled in detail.

2.5. Corrosion of Reinforcement in Concrete

So far, studies dealing with the initiation stage of corrosion have been discussed. Corrosion of steel, on the other hand, takes place in the propagation stage after the

depassivation of the reinforcing steel. Depassivation of reinforcing steel, which results in corrosion of reinforcement in concrete, can occur because of carbonation and associated loss of alkalinity in concrete cover (Papadakis, 1991) or localized breakdown of the passive layer when sufficient amount of chloride ions reach the steel (Neville, 1996).

The “sufficient amount” of chloride ions is described as the “chloride threshold concentration” and this value has to be reached around steel in order to start the corrosion reaction. Several researchers (Haussman, 1967; Gouda, 1970; Diamond, 1986; Glass and Beunfeld, 1995; Nilsson, 1996; Tang and Nilsson, 1996; Hussain et al., 1996) and concrete building codes (CSA A.23, ACI 318, ACI 222, etc.) propose different methods to determine this threshold concentration. For example, the Canadian Concrete Code, CSA A23.3, and the American Concrete Code, ACI 318, recommend a maximum permissible chloride ion concentration coming from the mixing ingredients of 0.06% by mass of the cement for prestressed concrete and 0.15% by mass of the cement for reinforced concrete. The reason for recommending lower maximum values for the prestressed concrete is that prestressed steel is more vulnerable to pitting corrosion and the accompanying failure mechanism (Martin-Perez, 1999). Haussman (1967) proposed that the free chloride threshold concentration is about 60% of the $(OH)^-$ ion concentration. This suggestion is made based on laboratory experiments on steel immersed in calcium hydroxide solution ($Ca(OH)_2$). Gouda (1970) conducted similar experiments with potassium and sodium hydroxide solutions and suggested a logarithmic relationship between the chloride ion concentration and the pH of the pore solution. Diamond (1986) analyzed Gouda’s experimental data and found the threshold value to be 30% of the hydroxyl ion concentration versus the 60% reported by Haussman. Glass and Buenfeld

(1995) recommended a range between 26% to 40%, but suggested that representing the chloride threshold as a fraction of the hydroxyl concentration is difficult to model. Therefore, they proposed the threshold level in terms of the total chlorides by mass of cementing material used in the concrete. Typical threshold values in this form for different types of concretes ranged from 0.17 to 2.5% (Glass and Buenfeld, 1995).

Another important factor in the corrosion process is the presence of dissolved oxygen in the pores around the steel reinforcement. In the beginning of the corrosion, the oxygen already available in the pores, which is generally in the range of 0.05 kg/m^3 of the pore solution (Bazant, 1979a), is used and quickly exhausted. Therefore, a continuous ingress of oxygen from the atmosphere is necessary for the corrosion reactions to continue. Assuming that oxygen does not react with any of the constituents of concrete (Neville, 1996), the dissolved oxygen penetration in concrete can be modeled by simple diffusion (Martin-Perez, 1999). Harker et al. (1987) proposed a model to predict the oxygen diffusivity in terms of the degree of pore saturation. This model was based on the linear regression analysis of oxygen diffusivities reported in the literature for different moisture contents. Papadakis (1991) also suggested a diffusivity model, which included the effects of relative humidity and the porosity of the concrete.

The general theory of corrosion, which is a very well-established field, has been studied for a long time and a significant number of publications on the topic can be found in the literature (Uhlig, 1967; Evans, 1960; Pourbaix, 1970; Oudar, 1975; Atkins, 1988; Scully, 1990). The modeling of corrosion of reinforcing steel in concrete, on the other hand, is a relatively new field. Some attempts have been made to model the reinforcement corrosion as an electrochemical reaction (Harker et al., 1987; Walton and

Sagar, 1987; Walton et al., 1990; Krank and Sagues, 1994; Balabanic et al., 1996; Matsushima et al., 1996; Yalcin and Ergun, 1996; Yokozeki et al., 1997, Martin-Perez, 1999). Among these studies, although extensive simplifications have been made, the one conducted by Krank and Sagues (1994) is important since it used a numerical method (the finite difference method) to solve the governing equations for reinforcement corrosion in concrete in two-dimensional space. Unfortunately, these studies were focused on the corrosion (i.e. propagation stage) only, and did not consider the dynamic relation with the transport of the corrosive agents in concrete (i.e. initiation stage). In addition to this, they made some assumptions, particularly in the polarization and passivation behaviour of the reinforcement, which resulted in oversimplification of the phenomenon.

2.6. Summary

It can be concluded from the literature review presented here that a significant amount of work has been carried out on modeling of the initiation stage of the reinforced concrete durability problem. Some of these studies have focused on chloride penetration, and others on the carbonation; however not on both. Although some studies exist (Seatta et al., 1993; Martín-Pérez, 1999), which used the finite element method to solve the equations governing the mass transport phenomena in concrete, they were not powerful enough to model any geometry (including cracks) and variable boundary conditions that may exist in an actual structure.

Unlike the initiation stage, modeling of the propagation stage; i.e. reinforcement corrosion, has not been performed extensively. Most of the existing models are based on rather simple methodologies such as ring models and do not simulate the corrosion

process realistically (Martín-Pérez, 1999). Some attempts have been made to utilize the numerical methods (Kranc and Sauges, 1994) to model the reinforcement corrosion; but the problem has been approached as a stand-alone phenomenon without considering the initiation stage. Even in the stand-alone solution, a large number of assumptions have been made, some being very critical, which resulted in the oversimplification of the corrosion phenomenon modeling.

The foregoing literature review reveals that substantial progress has been made in understanding the fundamental characteristics of the chloride diffusion and carbonation through empirical observations. Furthermore, the available phenomenological models consider the important parameters that affect the preceding two processes. Similarly, the chemistry of reinforcement corrosion is sufficiently studied and the process is adequately understood. Using the finite difference or finite element methods, the phenomenological models have been used by other investigators to develop numerical simulations, which agree reasonably with available experimental data. However, a general and robust simulation tool to model both the initiation and propagation stages of corrosion in a robust and holistic manner is lacking. Accordingly, in this thesis a more general simulation tool will be developed, using the latest theoretical and empirical models, including detailed coupled and nonlinear effects.

3. Heat, Moisture, CO₂, Chloride and O₂ Transport in Concrete

3.1. General

Modeling durability begins with the investigation of the deleterious materials ingress and transport into concrete. This comprises the so-called “initiation stage” of the durability model which determines the profiles of the deteriorative agents in the concrete at a given point in space and time.

Materials in liquid and gas phases can enter concrete and can affect its durability: e.g. water, in pure form or in dissociative form carrying aggressive ions or compounds like chlorides or sulfates; or gases such as carbon dioxide, oxygen or water vapour. The main attributes of any model developed for material ingress in porous media are the characteristics of the solute (e.g. chloride, CO₂), the solvent (e.g. pore water), and the solid phase (e.g. hydrated cement paste and aggregates). In addition to these, the gaseous (air and water vapour) phase, which exists in the pore space of the unsaturated concrete, may also be considered. The chemical composition of the diffusing agents is also very important since it significantly affects the chemical reactions (e.g. carbonation and acid attack) or physical bindings (e.g. chloride binding) during the transport process.

As will be shown in the following sections, the ingress and transport of chloride ions and CO₂ gas are dependent on the temperature and moisture distribution in concrete.

In addition, it is a well-known fact that heat and moisture transport phenomena are also coupled with each other. Also, the carbonation reaction and the chloride binding mechanism affect the chemistry and physical characteristics of the medium, which in turn lead to modified ingress rates. Due to the aforementioned coupling effects and material nonlinearities associated with some of these parameters, the modeling of the chloride and CO₂ transport phenomena in concrete is a very challenging task.

This chapter will demonstrate the principles outlining this complex process and mathematical relationships that are used in the proposed finite element model. First of all, the heat and moisture transport mechanisms, which are prerequisites for the analysis of chloride and CO₂ diffusion in concrete, will be presented. Then the chloride and CO₂ ingress and their transport mechanisms, including the coupling effects and the associated nonlinearities, will be discussed.

3.2. Heat Transfer in Concrete

Thermal conduction inside concrete for a two-dimensional problem is governed by Fourier's law, which is represented by a two-dimensional equation:

$$-\frac{\partial}{\partial x}(-k\frac{\partial T}{\partial x} + q_a C_a T) - \frac{\partial}{\partial y}(-k\frac{\partial T}{\partial y} + q_a C_a T) = \rho c \frac{\partial T}{\partial t} \quad (3.1)$$

where k is the conductivity of concrete [W / m °C], T is the temperature [°C], ρ is the density of concrete [kg / m³], c is the specific heat of concrete [J / kg °C], t is the time [s], C_a is the volumetric heat capacity of the air [J/m³ K] and x and y are two orthogonal directions of the heat flow. The airflow rate is denoted by q_a and can be neglected for concrete structures. Therefore, Eq.3.1 can be simplified as:

$$-\frac{\partial}{\partial x}\left(-k\frac{\partial T}{\partial x}\right)-\frac{\partial}{\partial y}\left(-k\frac{\partial T}{\partial y}\right)=\rho c\frac{\partial T}{\partial t} \quad (3.2)$$

Table 3.1 gives the typical values of the thermal conductivity, k , recommended by Loudon and Stacey (1966). The conductivity of concrete depends on the density, moisture content and the type of aggregate used. For normal weight concrete, density may not be a significant factor, but due to the low thermal conductivity of air, in lightweight concrete, a slight change in density may affect the conductivity considerably. Since the conductivity of the water is higher than the conductivity of air, the moisture content affects the overall conductivity of the concrete. The mineralogical characteristics of the aggregates used in the concrete also have an important effect on the concrete conductivity. For example, concrete produced by quartzite has a conductivity of 3.5 W/m°C, while concrete produced by basalt has a conductivity of 2.0 W/m°C (Scanlon and McDonald, 1994). Although, in theory, thermal conductivity is also a function of the temperature, it can be assumed that, at the temperatures ranges in which concrete structures are considered (-40°C to +40°C), it remains constant (Neville, 1996).

Specific heat, c , has a range of 840 to 1170 J/kg°C in ordinary Portland cement concrete and represents the heat capacity of the material. Although the type of the aggregate used does not significantly affect specific heat, its value increases with an increase in the moisture content of the concrete (Neville, 1996). It has been shown that (Basha and Salveduria, 1998) the effect of the moisture content on the specific heat, c , and the conductivity, k , is relatively small for the normal range of temperatures to which most structures are subjected; therefore, it can be ignored.

Although the heat transfer inside the concrete is governed by Eq.3.2, the boundary conditions at the concrete surface, such as the presence of wind and solar radiation, affect

the temperature profile significantly and must be considered. The net heat flux through a concrete surface can be written as:

$$q_s - q_c - q_r - q_y = 0 \quad (3.3)$$

Table 3.1: Values of thermal conductivity (W / m °C) by Loudon and Stacey (1966)

	Aerated Concrete		Lightweight concrete ⁽¹⁾		Lightweight concrete ⁽²⁾		Normal weight concrete ⁽³⁾	
Density Kg/m ³	Moisture Content (% by volume)							
	5	8	5	8	5	8	2.5	5
320	0.109	0.123	0.087	0.100	0.130	0.145		
480	0.145	0.166	0.116	0.130	0.173	0.187		
640	0.203	0.223	0.159	0.173	0.230	0.260		
800	0.260	0.273	0.203	0.230	0.303	0.332		
960	0.315	0.360	0.260	0.289	0.376	0.433		
1120	0.389	0.433	0.315	0.360	0.462	0.519		
1280	0.476	0.533	0.389	0.433	0.562	0.635		
1440			0.462	0.500	0.678	0.748		
1600							0.706	0.808
1760							0.838	0.952
1920							1.056	1.194
2080							1.15	1.488
2240							1.696	1.904
2400							2.267	2.561

(1) Produced by using expanded slag as the aggregate

(2) Produced by using expanded clay or sintered fly ash as the aggregate

(3) Produced by using normal weight aggregate such as quartzite or dolomite

where q_s is the total radiation absorbed, q_r is the re-radiation by concrete, q_c is the heat loss by convection due to the air in contact with the surface of the structure and q_y is the

heat conducted into the concrete body. Assuming that the concrete surface is not under permanent shade and the re-radiation from other structures can be ignored, the total radiation absorbed by the concrete surface can be calculated from:

$$q_s = \alpha I_n \quad (3.4)$$

where α is the absorptivity of concrete which varies between 0.5 to 1.0 and depends on the colour and the texture of the surface (Emerson, 1973; Priestley, 1976) and I_n is the direct solar radiation intensity (Threkald, 1970) which can be approximated by using a trigonometric series approach (Clausing, 1976) resulting in:

$$I_n = C_N G_z e^{(-\tau / \cos \beta)} \quad (3.5)$$

where C_N is the clearness number which depends on the location of the structure within the world and can be obtained from meteorological maps (Threkald, 1970). For example, for Nevada, $C_N = 1.15$ and in Gulf of Mexico, $C_N = 0.9$, β is the solar zenith angle which can be defined as the angle between solar radiation and the normal to the horizontal plane at location of the structure and is a function of the time of the day, G_z and τ are given by the following trigonometric series:

$$G_z = 1162.4 + 77.4 \cos(C) - 3.6 \cos(2C) - 3.4 \cos(3C) \\ + 1.8 \sin(C) - 0.6 \sin(2C) + 0.9 \sin(3C) \quad (3.6)$$

$$\tau = 0.1717 - 0.0344 \cos(C) + 0.0032 \cos(2C) + 0.0024 \cos(3C) \\ - 0.0043 \sin(C) - 0.0008 \sin(3C) \quad (3.7)$$

where $C = 2\pi n / 366$, n is the day of the year.

Since some of the direct solar radiation diffuses and dissipates in the atmosphere, I_n has to be modified accordingly. The solar radiation after the atmospheric dissipation is

approximated by Calusing (1976) and more information can be obtained from the referred paper.

Heat loss through the concrete surface by convection can be calculated by:

$$q_c = h_c (T_l - T_s) \quad (3.8)$$

where T_s is the shade air temperature, T_l is the body surface temperature and h_c is the convection coefficient [$\text{W/m}^2\text{C}$].

Re-radiation from the concrete surface can be obtained by Stefan-Boltzman law:

$$q_r = \varepsilon \sigma (K^4 - K^{*4}) \quad (3.9)$$

where ε is the emissivity of gray concrete surface, which is equal to the ratio of emission from gray surface to that from perfect radiator at the same temperature and can be taken as 0.9 for most cases, σ is the Stefan-Boltzman constant ($5.669 \times 10^{-8} \text{ W/m}^2\text{K}^4$), K is the absolute surface temperature [K] and K^* is the absolute average sky temperature [K] which can be approximated as 228 K (Potgieter and Gamble, 1983). Re-arranging Eq.3.9, we obtain:

$$\begin{aligned} q_r &= \varepsilon \sigma (K^4 - K_s^4) + \varepsilon \sigma (K_s^4 - K^{*4}) \\ &= \left\{ \varepsilon \sigma (K^2 + K_s^2) (K + K_s) \right\} (T_l - T_s) + \varepsilon \sigma (K_s^4 - K^{*4}) \\ &= h_r (T_l - T_s) + \varepsilon \sigma (K_s^4 - K^{*4}) \end{aligned} \quad (3.10)$$

where h_r is the radiation heat transfer coefficient [$\text{W/m}^2\text{C}$] and K_s is the absolute shade temperature [K]. From Fourier's law, the conduction heat transfer through the surface can be written as:

$$q_y = -k \left(n_x \frac{\partial T}{\partial x} + n_y \frac{\partial T}{\partial y} \right) = k \left(\frac{\partial T}{\partial n} \right) \quad (3.11)$$

where n_x and n_y are direction cosines with respect to x and y directions and n is the direction perpendicular to the surface.

If the convection and radiation heat transfer coefficients are combined ($h = h_c + h_r$) and the heat flux equations given in Equations 3.4, 3.9, 3.10 and 3.11 are brought together, the following boundary condition at the concrete surface needs to be considered:

$$\alpha I_n - \varepsilon \sigma (K_s^4 - K^{*4}) - h(T_i - T_s) + k \left(\frac{\partial T}{\partial n} \right) = 0 \quad (3.12)$$

Several researchers have suggested expressions for h as a function of average wind speed (Thurston, 1978, Priestley and Buckle, 1979). Since most of these expressions give similar results, the following equation, which is suggested by Priestley and Buckle (1979), will be used in the present study to evaluate h :

$$h = 13.5 + 3.88v \quad (3.13)$$

where v is the average wind speed [m/s].

It has to be noted that Eq.3.12 requires a nonlinear solution for Eq.3.2 due to the K^4 term. However, depending on the time of the day some simplifications can be made. Since $K_s \cong K^*$ during the daylight, net solar radiation heat flux reduces to αI_n . Similarly since there is no solar radiation during the evening, the radiation heat flux can be calculated from $-\varepsilon \sigma (K_s^4 - K^{*4})$. All of the material and surface properties explained above and the exposure data such as temperature variations, average wind speed, etc. are input the proposed model as external data. Further information about the heat transfer modeling in concrete structures can be obtained from Potgieter and Gamble (1983).

3.3. Moisture Transfer in Concrete

The total moisture in concrete pore space is composed of liquid water and water vapour. Samson et al. (2001) showed that if the liquid water phase in the concrete pore space is assumed to be continuous, the gravitational effects are neglected, the movement of the total moisture in terms of liquid water content, w_L [m^3 of water per m^3 of concrete], can be described by:

$$\frac{\partial}{\partial x} \left(D_w \frac{\partial w_L}{\partial x} \right) + \frac{\partial}{\partial y} \left(D_w \frac{\partial w_L}{\partial y} \right) + Q_w = \frac{\partial w_L}{\partial t} \quad (3.14)$$

where Q_w [$\text{kg}/\text{m}^3 \cdot \text{s}$] is the sink/source term which represents the water generated or removed from the system (e.g. the case of carbonation in which water is generated), D_w [m^2/s] is the total moisture diffusion coefficient which contains the influence of both liquid and vapour phases as:

$$D_w = \frac{\rho_L D_L + D_V}{\rho_L} \quad (3.15)$$

where ρ_L [kg/m^3] is the density of the liquid water, D_L [m^2/s] is liquid water diffusion coefficient, and D_V [m^2/s] is the vapour diffusion coefficient. Eq.3.14 is called “Richards’ Equation”, which is obtained by using a homogenization technique that requires the derivation of the flow equations for each phase (liquid and gaseous) at the microscopic level and then integrating over a representative elementary volume. Eq.3.14 represents the flow of total moisture flow (i.e. vapour and liquid water together) but uses the liquid water content as its state variable. It has to be noted that Eq.3.14 also assumes that although partial pressures between the liquid and vapour phases at different locations within the concrete body may be different, the total pressure is uniform throughout the pore space of the concrete; i.e. there is no gas or liquid flow due to pressure gradient. A

complete explanation of the homogenization technique and the derivation of Eq.3.14 can be obtained from Samson et al. (1999, 2001). The terminology used here is taken from the literature and it is important to underline the fact that the phenomenon described herein is not a diffusion process.

Eq.3.14 also implies the following assumption: The self-dessication during the hydration process and thermal gradient has no effect on moisture transfer. In fact, in normal strength concrete, the decrease in water content due to self-dessication is very small and can be neglected for practical purposes. This assumption has been shown to be true even when the hydration process is not yet complete (Bazant and Najjar, 1994). For high strength concrete, due to low water-cement-ratio of the concrete mix, self-dessication becomes significantly high and has to be taken into account (Bentz et al., 1997). Since this study is limited to normal strength concrete, the effect of self-dessication can be ignored.

The representation of moisture flow in terms of liquid water content, w_L , is important since it also provides the amount of possible dissolved ions (e.g. chloride ions) transported through advection; i.e., by the movement of liquid water. The advection of dissolved ions can be quite important in structures with wetting-and-drying cycles (Tuutti, 1993) since this process is significantly faster than the transport of ions by ionic diffusion. During wetting, the dissolved ions flow into the concrete with water and during drying they remain there while the water evaporates. In the proposed model, when there is wetting and drying cycles, the moisture flow will be represented by Eq.3.14 in which the liquid water content, w_L , is used as the state variable.

As an alternative approach, the total moisture flow can be represented in terms of relative humidity, h . This representation is also important since most of the material properties in the literature have been developed as a function of relative humidity. In the proposed model, if there is no wetting and drying, the moisture flow will be represented by Eq.3.16 in which the relative humidity, h , is used as the state variable. The moisture flow in concrete in terms of pore relative humidity, h , can be written as:

$$\frac{\partial}{\partial x}(D_h \frac{\partial h}{\partial x}) + \frac{\partial}{\partial y}(D_h \frac{\partial h}{\partial y}) + \frac{\partial}{\partial x}(D_T \frac{\partial T}{\partial x}) + \frac{\partial}{\partial y}(D_T \frac{\partial T}{\partial y}) + Q_h = \frac{\partial w_L}{\partial h} \frac{\partial h}{\partial t} \quad (3.16)$$

where D_h [m²/s] is the isothermal moisture diffusion coefficient, D_T [m²/s] is the thermal moisture diffusion coefficient, Q_h [kg/m³.s] is the source term, more specifically in the present context, the water contribution from the carbonation reaction, $\frac{\partial w_L}{\partial h}$ is the moisture capacity which is basically the relationship between the liquid water and the pore relative humidity and $\frac{\partial h}{\partial t}$ is the change in pore relative humidity with time.

It has to be noted that, in general, the moisture transfer due to humidity gradient is three orders of magnitude faster than moisture transfer due to temperature gradient (Basha and Salvedurai, 1998). On the other hand, if there is a possibility of a sudden and large temperature gradient formation, the temperature-gradient driven moisture transfer becomes significantly important and must be considered.

Although empirical expressions have been suggested for Q_h (or Q_w) (Saetta et al., 1993, 1995), time-dependent nonlinear finite element solution of the governing equation given by Eq.3.16 allows us to utilize the basic principles of chemistry to determine these values at each time step as long as the amount of CO₂ transported into the concrete and

the amount of Ca(OH)_2 in the hydrated cement paste are known (Papadakis, 1993). The calculated Q_h value can be modeled as a source term in the finite element formulation and Eq.3.16 can be solved by using a non-linear solution scheme.

When the moisture transport equation is presented in terms of pore relative humidity, h , as given in Eq.3.16, the different phases of water inside the concrete pores; i.e., free liquid water, adsorbed water and vapour, are assumed to be in thermodynamic equilibrium. This assumption can be justified by considering the fact that the moisture flow in concrete is a very slow process and there is ample time for the phases to reach dynamic equilibrium (Bazant and Najjar, 1972). Therefore, the relationship between the pore relative humidity and the free water, $\frac{\partial w_L}{\partial h}$, can be represented by, the so-called, adsorption isotherms. Different adsorption isotherms have been developed for different purposes over the years and the next section will focus on the basic principles of some of the more important ones.

3.3.1. Adsorption Isotherms

As stated previously, the moisture capacity, $\frac{\partial w_L}{\partial h}$ in Eq.3.16 represents the relationship between the free water and pore water contents and can be determined by using of one of the available adsorption isotherms such as Langmuir isotherm (Langmuir, 1918), BET isotherm (Brauner, Emmett and Teller, 1938), FHH isotherm (Frinkel, 1946; Hill, 1952; Halsey, 1952) or H&J isotherm (Harkins & Jura 1943, 1944).

Adsorption can be defined as the fixation of vapour molecules in the pore space onto a completely dry pore wall or to water molecules already adsorbed on the wall.

Langmuir (1918) suggested that the porous surface has a certain number of sites; some occupied by adsorbed water molecules and some being free. He developed the so-called *Langmuir Equilibrium Adsorption Isotherm* by equating the rate of condensation in the free pore space to the rate of evaporation from the occupied pore space. Langmuir's isotherm has rarely been useful for porous materials such as concrete where the adsorption takes place in multiple layers. To overcome this problem, Brauner et al. (1938) developed a model for gas adsorption on solids. It can be assumed that the model was a generalization of Langmuir's theory of monolayer adsorption.

BET (Brauner-Emmett-Teller) equilibrium isotherm is based on the assumption that adsorption takes place in multiple layers. BET equilibrium isotherm assumes that Langmuir isotherm is valid for each single layer formed during the adsorption; with the exception of the first layer where the energy of adsorption may have a special value. The energy of all other layers is equal to the energy of condensation of the liquid adsorbate. In addition to this, it is assumed that evaporation and condensation can only take place from the exposed surfaces.

A standard two-parameter isotherm based on the simplest BET model can be written in various ways. The isotherm form, which gives the amount of gas adsorbed as a function of relative pressure of the adsorbing gas can be written as (Brauner et al., 1938):

$$\frac{V}{V_m} = \frac{C \left(\frac{P}{P_0} \right)}{\left(1 - \frac{P}{P_0} \right) \left[1 + (C - 1) \left(\frac{P}{P_0} \right) \right]} \quad (3.17)$$

where V is the volume of the gas adsorbed at vapour pressure P , V_m is the volume of the gas which could cover the entire adsorbing surface with a mono-molecular layer, P_0 is the

saturated vapour pressure (the pressure of the vapour in equilibrium with bulk liquid at the temperature of the measurement), P/P_o is the relative pressure and C is a constant for the gas/solid combination which can be expressed as:

$$C = e^{\frac{Q_g - Q_L}{RT}} \quad (3.18)$$

where $(Q_g - Q_L)$ is the net heat of adsorption which can be approximately taken as 7100 J/mol for concrete, R is the gas constant (8.31447 J /mol-K) and T is the temperature (K).

Despite its simplicity and applicability to the indirect calculation of some properties such surface area, porosity and pore space distribution of porous materials, the BET theory has some disadvantages. It suggests that the adsorption will be infinite if the pressure in the surrounding vapour is equal to the saturation pressure. In addition to this, the heterogeneous nature of the porous medium (such as concrete) does not allow the ordered multilayer formation as the BET method assumes. Therefore, its range of application is generally restricted.

The issues associated with the BET isotherm have been improved by the incorporation of the concept of capillary condensation into the theory (Halsey, 1948, 1952; Frenkel, 1946; Hill, 1949). Before going into details of these isotherms, one has to understand the principles of capillary condensation. At the interface between a liquid and a gas, or two immiscible fluids, a film or a special layer seems to form on the liquid, apparently owing to the attraction of liquid molecules below the surface. The formation of this film may be visualized on the basis of surface energy per unit area required to bring the molecules to the surface. The surface tension is then the stretching force required to form a film. For example, the surface tension of water varies between 0.074 N/m at 20 °C to 0.0059 N/m at 100 °C.

When a number of adsorbed layers are formed at the pore surfaces, so that a liquid meniscus can form, another mechanism becomes important in mass transport: *capillary condensation*. As the amount of adsorbed liquid grows such that the ratio between vapour pressure and the saturation pressure at a given temperature exceeds a certain level (generally 25–45 %), the vapour molecules start to condense in the pore space. For water, this ratio can be assumed to be 45%. This process is a consequence of liquid water present in the pores forming curved surfaces. In other words, if the adsorption of vapour molecules forms layers at the surfaces due to a certain relative vapour pressure in the pores, a point will be reached where the adsorbate starts to behave like a normal liquid. This creates a curved boundary surface next to the vapour phase. This curvature is maintained by the surface tension (energy) and the hydrostatic pressure over the same surface. The pressure difference is often referred to as capillary pressure.

Considering the adsorption and capillary condensation of vapour molecules together, some researchers have developed isotherms which have a larger range of applicability. Among these, the following two are deemed to be important as discussed next.

Halsey (1948, 1952) suggested the following equation:

$$\ln\left(\frac{P_0}{P}\right) = \frac{a}{\left(\frac{V}{V_m}\right)^s} \quad (3.19)$$

where a and s are the constants for the gas/solid pair. Frinkel (1946) and Hill (1949, 1952) also derived this equation and related a and s explicitly to molecular forces to produce FHH isotherm. The relationship can be rearranged in the form:

$$V = V_m \left[\frac{a}{\ln\left(\frac{P_0}{P}\right)} \right]^b \quad (3.20)$$

where $b = 1/s$. The constants a and b should be determined for each gas/solid system since they must vary with the net heat of adsorption and the manner in which the latter decays as the first layer fills and multiple layers are adsorbed. To obtain a , b and V_m we plot $\ln(V)$ vs. $\ln(\ln(P_0/P))$ and fit a straight line to data. The slope of this line is $-b$ and the intercept is equal to $\ln(V_m) + b \ln(a)$. Therefore:

$$a = e^{\left[\frac{\text{intercept} - \ln(V_m)}{b} \right]} \quad (3.21)$$

To find the value of the constant a we assume that V_m is equal to the volume of the monolayer of adsorbed vapour determined from the BET equation. The FHH isotherm tends to fit adsorption data over a wider range of relative pressures than the BET isotherm and has been fitted to a number of published adsorption isotherms (Alzamora and Cortes 1976) in which the value of s was found to fall in the range 1.2 to 2.8 (i.e. b in the range 0.4 to 0.8) and a in the range 2.1-3.0.

Harkins and Jura (1943, 1944) developed another isotherm for the adsorption process based on a model of the adsorbed gas behaving like a film on a liquid surface, which had the following form:

$$\log\left(\frac{P}{P_0}\right) = B - \frac{A}{V^2} \times 10^{-6} \quad (3.22)$$

where A and B are constants for the gas/solid pair and V is the volume of gas adsorbed (in mm^3 at STP) per gram of adsorbate at the relative pressure P/P_0 . To find the values of the constants A and B , $\log(P/P_0)$ is plotted as a function of $1/V^2$ and a straight line is fitted

over the linear range, which for nonporous solids often extends over twice the range in P/P_0 compared to the linear range on a BET plot.

Figure 3.1 shows a comparison among three-parameter BET, FHH and H&J isotherms with respect to the experimental data (IBA, 1996). It can be observed from the figure that all of the isotherms can predict the process quite accurately up to 40% relative humidity. A divergence from the experimental results is noticeable beyond 40%. On the other hand the FHH and H&J isotherms are quite accurate up to 80% relative humidity, and give acceptable results up to 90% relative humidity. For fully saturated samples, the adsorption is overestimated by a margin of 40%.

Figure 3.1: Comparison of the three-parameter BET, FHH and H&J isotherms with experimental data

It is important to note that all of the adsorption isotherms discussed above make the assumption that the water is pure. In the case of concrete, the pore water contains high concentrations of ions (e.g. chlorides). It has been shown that (Kotz and Purcell,

1987) the vapour pressure decreases as the ionic concentration of the water increases. On the other hand, Samson et al. (2001) noted that this decrease is rather small and can be omitted for concrete pore water ionized with chlorides.

3.3.2. Moisture Transport Coefficients

The moisture transport coefficients, D_h and D_w , depend on several factors such as temperature, existing relative humidity, age of the concrete, exposure, pore structure, etc. Although several researchers (Bazant and Najjar, 1972; Bazant and Thonguthai, 1978; Saetta et al., 1993; Gawin et al., 1995; Pel, 1995; Kunzel, 1995; Sander et al., 1998; Kim and Lee, 1999; Martys, 1999) have proposed models for the determination of these coefficients, due to the complexity of the problem, further studies on the topic are still in progress. Since it is not the intention of this research to develop material models, one of the existing models will be utilized in this study. The model for the determination of D_h [m^2/s], which was proposed by Bazant and Thonguthai (1978) and given in Eq.3.27a, has been used by several researchers (Saetta et al., 1993; Gawin et al., 1995; Martín-Pérez, 1999) and design specifications (CEB-FIB 1990, 1993) and will therefore be implemented in this study. Similarly, the model proposed by Martys (1999) and given in Eq.3.27b, will be used to model D_w [m^2/s].

$$D_h = D_{h,ref} \left(\alpha_0 + \frac{1 - \alpha_0}{1 + \left(\frac{1 - h}{1 - h_c} \right)^n} \right) \left(e^{\left[\frac{U}{R} \left(\frac{1}{T_{ref}} - \frac{1}{T} \right) \right]} \right) \left(0.3 + \sqrt{\frac{13}{t_e}} \right) \quad (3.27a)$$

$$D_w = D_{w,ref} (1 - S)^{-1.7} \left(\frac{S_c - S}{S_c} \right)^{2.2} \quad (3.27b)$$

where $D_{h,ref}$ [m^2/s] and $D_{w,ref}$ [m^2/s] is the diffusion coefficients determined at reference conditions; α_0 is a parameter representing the ratio of the maximum and minimum values of the moisture diffusion coefficient and it was found to be close to 0.05 for most of the concrete types; h_c is the humidity at which D_h drops halfway between its maximum and minimum values and can be taken as 0.75; n is a parameter describing the distribution of D_h , and experimental studies (Bazant and Najjar, 1971, 1972) have shown that a value between 6 – 16 can be used, depending on the type of the concrete; U [kJ/mol] is the activation energy for the moisture diffusion process in concrete and can vary between 20 to 40 kJ/mol, depending on the type of the concrete; R is the universal gas constant which is equal to 8.314×10^{-3} kJ/K.mol; T_{ref} [K] is the reference temperature at which $D_{h,ref}$ is measured; T [K] is the temperature of the medium; t_e [days] is the equivalent hydration period which represents the degree of hydration of the concrete, S is the degree of saturation and S_c is the degree of saturation of the non-wetting phase needed for the non-wetting blobs to percolate and can be approximately taken as 0.5 (Martys, 1999).

3.3. *CO₂ Diffusion and Carbonation in Concrete*

The reinforcing steel inside the concrete is generally covered by a passivating layer, basically a form of iron oxide, which acts as a protective coat on the steel. Concrete with its high alkalinity serves as a protective medium for the passivating layer and as long as this protection is present around the steel, corrosion does not start. However, the environment in which the structure operates may weaken or even eliminate

the passivating layer around the reinforcement; for instance, CO_2 has the potential to dissolve in concrete pore water and react with the hydration products, causing a reduction in the alkalinity, i.e. a reduction in pH from 13 or 12 to levels below 9. At low alkalinity, concrete loses its protective nature, thereafter, when the embedded steel is exposed to oxygen and ion-bearing solution, the corrosion of the reinforcement commences.

Another important consequence of carbonation is a possible change in the transport properties of concrete induced by volume and pore structure changes due to carbonation. In certain cases the permeability of carbonated concrete may increase, as in the case of concrete made with blended cements such as blast furnace slag (BFS) and fly ash concrete; in others, it may decrease as in ordinary Portland cement (OPC) concrete (Johannesson., 1998). It has to be noted that the effect of carbonation on the pore structure and the permeability properties of concrete is a complex problem for which a satisfactory model is yet to be developed. Nevertheless, the available models are adequate for providing a reasonably satisfactory explanation for the observed behaviour of reinforced concrete structures subjected to carbonation.

Carbonation can simply be defined as the reaction of carbon dioxide with Ca(OH)_2 in the hardened cement paste resulting in the production of CaCO_3 . This reaction can be achieved if Ca(OH)_2 dissolves in concrete pore water following the reaction:

Carbon dioxide also dissolves in concrete pore water and forms carbonic acid before reacting with the dissolved Ca(OH)_2 , viz.:

The following neutralization reaction completes the final stage of carbonation:

The rates of the reactions given in Equations 3.28 and 3.30 play an important role in the carbonation of concrete. Basic chemical principles can be utilized to determine these rates. The rate of dissolution of $Ca(OH)_2$ in concrete pore water given by Eq.3.28, r_D , and the rate of the neutralization reaction given in Eq.3.30, r_N , are given by Eq.3.31 and Eq.3.32, respectively (Papadakis et al., 1991):

$$r_D = 1.685 \times 10^{-5} \mu f_w k_s a_s [Ca(OH)_2(s)] ([OH^-]_{eq} - [OH^-]) \quad (3.31)$$

$$r_N = HRTk_2 [OH^-]_{eq} [CO_2(g)] \quad (3.32)$$

where f_w is the volume fraction of the aqueous film at the walls of the pores, μ is the porosity of concrete, k_s is the mass diffusion coefficient for the dissolution of $Ca(OH)_2(s)$ which can be approximated to be 5.0×10^{-5} m/s, a_s is the pore area per unit concrete volume, $[Ca(OH)_2(s)]$, $[CO_2(g)]$ and $[OH^-]$ are the molar concentrations of $Ca(OH)_2(s)$, $CO_2(g)$, OH^- per unit volume of concrete, $[OH^-]_{eq}$ is the molar concentration of OH^- at equilibrium, which is equal to 43.2 mol/m^3 at 25°C , H is the Henry's constant for the dissolution of $CO_2(g)$ in water, which is equal to $34.2 \text{ mol/m}^3\text{atm}$ at 25°C , R is the universal gas constant, T is the absolute temperature in K, and k_2 is a rate constant given by $8.3 \text{ m}^3/\text{mol}\cdot\text{sec}$. A more detailed explanation of the reaction rates for carbonation can be found in Papadakis et al. (1991).

The carbonation reactions in Equations 3.28 to 3.30 occur ideally when the relative humidity of the concrete is between 50% to 70% (Neville, 1996). If the humidity

is less than 50%, CO_2 ions cannot be dissolved completely due to inadequate water in the pores. If the humidity is larger than 70%, the water inside the pores inhibits the CO_2 diffusion, resulting in slower rates of carbonation. Between 50 to 70% relative humidity, Ca(OH)_2 , which is a hydration product in concrete, reacts with CO_2 in a neutralization reaction which produces CaCO_3 and water. The amount of Ca(OH)_2 in a fully hydrated OPC can easily be determined if the type of cement used and the concrete mix properties are known. The Ca(OH)_2 content in a fully hydrated OPC is around 30% by weight. (Neville, 1996). The final product, CaCO_3 , has a very low solubility and contributes to the clogging of the pore system causing a decrease in the fluid and gas permeability in OPC concrete. Since the Ca(OH)_2 content in BFS or fly ash concrete is very low, the C-S-H phase goes into the carbonation reaction. Although this reaction occurs at a much slower rate than the carbonation of Ca(OH)_2 , the resulting product will cause an increase in the fluid and gas permeability of concrete (Taylor, 1990). It has to be pointed out that the investigation of the blended cement concrete structures (e.g. BFS or fly ash concrete) is not within the scope of this study.

In order to model the carbonation process in OPC concrete structures, it is imperative to determine the amount of CO_2 diffusing into them. Since the CO_2 transport in concrete is a function of temperature and moisture content, it is necessary to consider these processes while dealing with carbonation.

It can be observed in Eq.30 that H_2O is produced as a result of the carbonation reactions. Therefore, when the moisture transfer analysis is carried out in the presence of carbonation, the effect of the additional water produced during the neutralization reaction has to be included in the analysis.

As mentioned before, the carbonation process changes the transport properties of the concrete. In other words, in OPC concrete, a reduction in D_h and D_c can be observed as the carbonation reaction proceeds. Although modeling of this change is a very a complex problem and requires extensive experimental studies, decay functions for moisture diffusion and the carbon dioxide diffusion coefficients, which are functions of the degree of carbonation, can be suggested based on available data and the nature of the problem. It has to be noted that moisture transport through wetting and drying cycles may also change the pore structure of concrete (Beaudoin, 2001); however this change will not be incorporated to the current model. A decay function, $f_d(t, \varphi)$, can be used to determine the change in porosity in the concrete due to the carbonation process:

$$\Delta\eta_c = (1 - f_d(t, \varphi))\mu_o \quad (3.33)$$

where t is the time, φ is the degree of carbonation in concrete which was defined by Matsushita (2000), μ_o is the initial porosity of concrete and $\Delta\mu_c$ is the change in porosity due to carbonation. A bi-linear decay function as shown in Figure 3.2 can be used to simulate the effect of carbonation on the diffusion properties of moisture and CO_2 transport processes. The parameters a and b in Figure 3.2 can be determined based on the change in porosity of concrete due to carbonation. The relationship between the carbonation and the reduction in porosity has been studied by Papadakis et al. (1991), and for a fully hydrated concrete, is given as:

$$\eta(t) = \mu_o - \Delta\mu_c \quad (3.34)$$

where $\mu(t)$ is the porosity of concrete at time t , μ_o is the initial porosity of concrete and $\Delta\mu_c$ is the change in porosity due to carbonation. $\Delta\mu_c$ can be calculated based on the amount of $\text{Ca}(\text{OH})_2$ consumed during the carbonation or from Eq.3.33.

Figure 3.2: Decay function as a function of the degree of carbonation

Although carbonation reactions given by Equations 3.28 to 3.30 may affect the heat balance equilibrium of the system, its contribution to the overall temperature distribution in concrete is rather small. Therefore, the effect of carbonation to the temperature distribution in concrete can be ignored.

The transport of carbon dioxide inside concrete is governed by the following equation:

$$\frac{\partial}{\partial x} \left(D_c \frac{\partial C_c}{\partial x} \right) + \frac{\partial}{\partial y} \left(D_c \frac{\partial C_c}{\partial y} \right) + Q_c = \frac{\partial C_c}{\partial t} \quad (3.35)$$

where D_c [m^2/s] is the carbon dioxide diffusion coefficient, C_c [kg/m^3 pore solution] is the carbon dioxide concentration and Q_c [$\text{kg}/\text{m}^3 \cdot \text{s}$] is the sink term representing the reduction of carbon dioxide due to the carbonation reaction and can be determined using the basic principles of chemistry.

D_c depends on several factors such as temperature, existing relative humidity, age of the concrete, exposure, etc. Different models for the determination of D_c can be found

in the literature (Papadakis et. al, 1991, 1993; Saetta et al., 1993; Sickert, 1997). For the current study, the following model proposed by Papadakis et al.. (1993) will be used:

$$D_c = 1.64 \times 10^{-6} \mu_p(t) (1 - h)^{2.2} \quad (3.36)$$

where h is the relative humidity at time t and $\mu_p(t)$ is the porosity of the hardened cement paste given as:

$$\mu_p = \mu(t) \left(1 + \frac{\frac{a}{c} \frac{\rho_c}{\rho_a}}{\frac{a}{c} \frac{\rho_c}{\rho_w}} \right) \quad (3.37)$$

where a/c is the aggregate-cement-ratio, w/c is the water-cement-ratio, ρ_c , ρ_a and ρ_w are the densities of cement, aggregates and water, respectively.

3.4. Chloride Diffusion in Concrete

Chloride ions in concrete could be found in three forms: bound to hydration products of the cement, adsorbed on the surfaces of the pore walls, and dissolved in the pore solution (free chloride). These ions can enter concrete either during mixing (from mixing water, aggregates, etc.) or from the environment after the setting. For the former, concrete building codes give certain guidelines for the maximum allowable chloride concentration that can be inherited during mixing (CSA A23.1; ACI 318; ACI 222; BA 8110).

The chloride transport in concrete can occur in two ways: by the movement of liquid water; i.e., through convection, and by diffusion due to the concentration difference between two points in the pore solution.

If the concrete is not subjected to wetting-and-drying cycles, the chloride ingress into concrete can simply be modeled by the following quasi-harmonic equation as long as appropriate diffusion coefficients for the chloride movement in concrete are selected:

$$\frac{\partial}{\partial x}(D_{cl} \frac{\partial C_f}{\partial x}) + \frac{\partial}{\partial y}(D_{cl} \frac{\partial C_f}{\partial y}) + Q_{cl} = \frac{\partial C_f}{\partial t} \quad (3.38)$$

where D_{cl} [m^2/s] is the effective chloride diffusion coefficient, C_f [kg/m^3 of pore solution] is the free chloride content, and Q_{cl} [$\text{kg}/\text{m}^3.\text{s}$] is the sink term representing chloride release mechanism which will be explained later in detail.

If the concrete is subjected to wetting-and-drying cycles, Eq.3.38 has to be modified to contain a term representing the chloride transport through convection. Although the solution of this modified equation is possible, a simplified approach is used in the proposed model to determine the chloride ingress when there is wetting and drying cycles. First of all, the amount of chloride ions carried into the concrete through convection is determined. This can be achieved by solving Eq.3.14 and determining the liquid water profile, w_L , in concrete during the wetting-and-drying cycles. The chloride ions carried through convection can then be calculated since the chloride concentration of the liquid water is known. The chloride ions, which have entered the structure through convection, diffuse into the concrete according to Eq.3.38.

The determination of the effective chloride diffusion coefficient has also been studied extensively. A detailed literature review on this topic was provided in Chapter 2. If we summarize the literature, it can be said that chloride diffusion coefficient is coupled with many variables such as temperature, moisture content, time of exposure, concrete type, porosity, presence of cracks, etc. and a comprehensive and satisfactory model that accounts for the effects of all of the parameters of the problem is yet to be formulated.

As mentioned previously, it is not the intention of this study to develop material models; therefore, one of the existing models developed for chloride diffusion coefficient will be used.

Previous studies have shown that (Saetta et al., 1993, Martín-Pérez, 1999), similar to the moisture diffusion coefficient, the effective chloride diffusion coefficient of concrete, determined at some reference conditions, $D_{Cl,ref}$, can be modified according to Eq.3.39 in order to account for the influence of temperature, the time of exposure and humidity.

$$D = D_{ref} \cdot \alpha_T \cdot \alpha_E \cdot \alpha_H \quad (3.39)$$

where α values, which are explained below, are the factors which reflect the effects of temperature, time of exposure and humidity on the chloride diffusivity of concrete.

The effect of temperature on chloride diffusivity can be expressed by using an Arrhenius type equation as in Eq.3.40. (Saetta et al., 1993; Tang and Nilsson, 1996; Amey et al., 1998).

$$\alpha_T = e^{\left[\frac{U}{R} \left(\frac{1}{T_r} - \frac{1}{T} \right) \right]} \quad (3.40)$$

where α_T is the diffusion modification factor due to temperature, U [kJ/mol] is the activation energy of the chloride diffusion process, R is the gas constant, T_{ref} [K] is the reference temperature at which reference chloride diffusivity is measured, and T [K] is the absolute temperature.

As concrete matures, the chloride diffusivity decreases (Nilsson et al., 1996). The effect of time of exposure on chloride diffusivity can be explained by using the following decay function (Mangat and Molloy, 1994, Bamforth, 1998):

$$\alpha_E = \left(\frac{t_r}{t} \right)^m \quad (3.41)$$

where α_E is the diffusion modification factor due to age of concrete, t [s] is the actual time of exposure, t_r [s] is the time of exposure at which the relative diffusivity is measured, and m is the age reduction factor which can be calculated (Mangat and Mollloy, 1994) using:

$$m = 2.5w / c - 0.6 \quad (3.42)$$

where w/c is the water-cement ratio of the concrete.

The amount of water in the pores of concrete plays an important role in the diffusion of chloride in concrete because a decrease in the moisture content in concrete can reduce the diffusion rate of the chloride ions. The same relationship proposed for moisture diffusion coefficient in Eq.3.27 can be used to represent the effect of relative humidity:

$$\alpha_H = \frac{1}{1 + \frac{(1-h)^4}{(1-h_c)^4}} \quad (3.43)$$

where α_H is the diffusion modification factor due to relative humidity, h is the concrete pore relative humidity, h_c is the humidity at which the diffusivity drops halfway between its maximum and minimum values which is calculated as 0.75 by Bazant and Najjar (1971).

Among other acceptable models (Steward and Rosowsky, 1998; Hobbs, 1998) the model proposed by Papadakis et al. (1996) is one of the best fits for the chloride diffusion coefficient found in the literature (Vu and Steward, 2000) and can be represented as:

$$D_{Cl} = 0.15 D_{inf} \frac{1 + \rho_c \frac{c}{w}}{1 + \rho_c \frac{c}{w} + \frac{\rho_c}{\rho_a} \frac{a}{c}} \left(\frac{\rho_c \frac{w}{c} - 0.85}{1 + \rho_c \frac{w}{c}} \right)^3 \quad (3.44)$$

where D_{inf} [m²/s] is the chloride diffusion coefficient in an infinite solution (1.6×10^{-9} m²/s for NaCl solution).

3.4.1. Chloride Binding

Most of the chloride in concrete is bound by C_3A (tricalcium aluminate) to form Friedel's salt (calcium-chloro-aluminate-hydrate). Therefore, the more C_3A content cement has, the more chloride is bound. Since only free chlorides can cause corrosion, determination of the amount of bound and free chloride in the concrete is very important. In addition to this, Glass (2000) has suggested that bound chlorides could be released and would participate in the corrosion process as the pH in concrete falls to certain levels. In any case, determination of the amount of chlorides bound by the concrete is an important aspect of modeling corrosion.

Since the chloride diffusion is a very slow process, thermodynamic equilibrium between free and bound chlorides can be assumed. Therefore, the relationship between the bound and free chlorides can be represented in terms of binding isotherms. Although extensive studies have been carried out with respect to chloride binding isotherms, only the most widely used ones; i.e., Linear, Langmuir and Freundlich, which are given by Eq.3.45, Eq.3.46 and Eq.3.47, respectively, are presented here. A review of the literature on the topic can be found in Chapter 2.

Linear binding isotherm (Tuuti, 1982; Seatta, et al., 1993) can be written as:

$$C_b = \alpha C_f \quad (3.45)$$

where C_b (kg/m³ of pore solution) is the bound chloride concentration, C_f (kg/m³ of pore solution) is the free chloride concentration and α is the proportionality constant which may be modified depending on the type of the concrete.

Similarly Langmuir isotherm (Sergi et al., 1992) has the following form:

$$C_b = \frac{\alpha C_f}{1 + \beta C_f} \quad (3.46)$$

where α (m³ of pore solution per m³ of concrete) and β (m³ of pore solution per kg of concrete) depend on the concrete composition. It has to be noted that the slope of the Langmuir isotherm approaches zero as the concentration of the free chlorides increases, suggesting that there is an upper limit for chloride binding (Martín-Pérez, 1999).

Finally, one of the most widely used binding isotherms; i.e., Freundlich isotherm (Nilsson et al. 1994) is given as:

$$C_b = \alpha C_f^\beta \quad (3.47)$$

where α and β are binding constants which are dependent on the cementitious system used and the units employed.

The effect of chloride binding has been generally introduced in the solution of Eq.3.38 by modifying the effective chloride diffusion coefficient (Martín-Pérez, 1999; Glass, 2000). In other words, the chloride diffusion coefficient, which has been calculated without considering the effect of chloride binding, is reduced by a coefficient as follows:

$$D' = \frac{D}{1 + \frac{1}{w_e} \frac{\partial C_b}{\partial C_f}} \quad (3.48)$$

where D' is the apparent coefficient. The same approach is also adopted in the proposed model.

Depending on the pH level of the pore solution (i.e. hydroxyl concentration), some of the bound chlorides can be released and these released chlorides may contribute to the corrosion process of steel reinforcement (Glass, 2000). Carbonation is one of the reasons of pH reduction in concrete and it has been shown that coupled carbonation and chloride attack increases the rate of corrosion of steel in concrete significantly compared to the cases in which the carbonation or chloride attack is considered separately (Papadakis, 1993). Although currently there is not a well-defined numerical model representing this phenomenon, the most realistic way of defining the process is through employing a net sink term into Eq.3.38 by writing Q_{Cl} as:

$$Q_{Cl} = Q_{Cl, released} \quad (3.49)$$

where $Q_{Cl, released}$ [$\text{kg/m}^3 \cdot \text{s}$] is the source term representing the released chloride ions. As new models for representing chloride release mechanism emerge, accurate calculation of the $Q_{Cl, released}$ term will become possible. Until that time, the current study will use the constant release isotherm, which will be activated as the pH level of the concrete pore solution drops below a user defined value:

$$Q_{Cl, released} = \omega \quad (3.50)$$

where ω is also a user defined value. The recently published equilibrium solid-solution pH values (Birnin-Yauri and Glasser, 1998) for Friedel's salt ranges between 11.99 and

12.14. Therefore, it would be an appropriate approximation to choose a value of pH in this range below which the chloride release mechanism will be activated.

3.5. Oxygen Diffusion in Concrete

The oxygen used in the electrochemical corrosion reaction is in the dissolved state. It can be assumed that oxygen does not participate in any chemical reaction but is simply dissolved in concrete pore water. The amount of O₂ initially present in the concrete pore solution can be assumed to be in the range of 0.005 kg/m³ of pore solution (Bazant, 1979).

The oxygen distribution inside the concrete will be determined by the solution of the following differential equation:

$$\frac{\partial C_o}{\partial t} = \frac{\partial}{\partial x} \left(D_o \frac{\partial C_o}{\partial x} \right) + \frac{\partial}{\partial y} \left(D_o \frac{\partial C_o}{\partial y} \right) \quad (3.51)$$

where D_o [m²/s] is the effective oxygen diffusion coefficient and C_o [kg/m³ pore solution] is the concentration of the oxygen permeating into concrete. Papadakis et al. (1991) have proposed the following effective oxygen diffusion coefficient to be used in Eq.3.51:

$$D_o = 1.92 \times 10^{-6} \mu_p(t) (1 - h)^{2.2} \quad (3.52)$$

where h is the relative humidity at time t and $\mu_p(t)$ is the porosity of the hardened cement paste given by Eq.3.37.

4. Corrosion of Steel in Concrete

4.1. General

The study of reinforcement corrosion in concrete structures requires understanding the theory of the corrosion process. This chapter will explain the details of the corrosion process in general as well as more specifically its relevance to reinforced concrete which will furnish the background for the corrosion model used in the current study.

4.2. Basic Thermodynamic Principles of Corrosion

Metals have a tendency to minimize their total energy level to become stable. Corrosion of metals is the result of this thermodynamically favoured energy minimization process and can be defined as the deteriorative loss of a metal due to dissolution environmental reactions (Scully, 1990).

Metal atoms characteristically give up electrons in what is called an oxidation reaction. The oxidation reaction of a hypothetical metal M can be written as:

where E_a is the electrode potential of the reaction and n is the number of electrons. The location on the metal at which the oxidation takes place is called anode.

The corollary of the oxidation reaction is “reduction” in which electrons given up by oxidation are captured by other species. A typical reduction reaction of an element, N , in a solution can be written as:

where E_r the electrode potential of the reaction. The location at which the reduction occurs is called cathode.

In the majority of practical situations, the cathodic reaction is either oxygen reduction which occurs in the neutral environments or hydrogen evolution which occurs in the acidic environments (Scully, 1990), as given by Equations 4.3 and 4.4, respectively.

In the case of an acid solution containing dissolved oxygen molecules, a combination of oxygen reduction and hydrogen evolution can be observed as shown by the following equation (Scully, 1990):

An example of a corrosion process can be demonstrated by a metal which is submerged in a conducting acid solution (electrolyte) as shown in Figure 4.1. The corrosion is initiated by the potential difference that exists between two locations on the metal, the more active zone acting as the anode and the other acting as the cathode, where some oxidizing species is reduced. The corrosion occurs at the anode where the M atoms oxidize and become ions in the solution. The electrons released from the anode travels through the body of the metal and are reduced at the cathode. Since there can be

no electrical charge accumulation in the total reaction, the total rate of the oxidation must be equal to the total rate of reduction. This implies that the electrons produced by the oxidation must be used by the reduction.

All electrochemical reactions consist of at least one oxidation and one reduction reactions, and are the sum of the two. A typical electrochemical reaction which is the sum of the oxidation of element M and reduction of element N can be written as:

where ΔE is the electric potential difference which can be calculated as:

$$\Delta E = E_r - E_a \quad (4.7)$$

Figure 4.1: Corrosion of a metal in an acid solution

Table 4.1: Standard electrode potentials of important reactions (Scully, 1990)

Reaction	Electrode Potential (volts)
$O_2 + H^+ + 4e^- \rightarrow 2H_2O$	1.229
$Fe^{3+} + 3e^- \rightarrow Fe$	0.771
$O_2 + 2H_2O + 4e^- \rightarrow 4(OH)^-$	0.401
$Cu^{2+} + 2e^- \rightarrow Cu$	0.340
$2H^+ + e^- \rightarrow H_2$	0.000
$Fe^{2+} + 2e^- \rightarrow Fe$	-0.440
$Na^+ + e^- \rightarrow Na$	-2.714
$K^+ + e^- \rightarrow K$	-2.924

It has to be noted that for the electrochemical reaction given in Eq.4.6 to occur spontaneously, ΔE must be positive. The values of the equilibrium potentials of typical electrode reactions are given in Table 4.1. For oxidation potentials, the reaction direction and the sign of the potential must be reversed. A negative value means that energy is given out by the reaction; i.e., that reaction will occur spontaneously without any external help. Positive values show that in order for the corresponding reaction to take place, an external energy must be supplied to the system. The table also implies that as we go from top to bottom, the reactions become more anodic (active). For example, Potassium (K) and Sodium (Na) are two of the most active (susceptible to corrosion) elements available.

It is important to understand that the electrode potentials given in Table 4.1 are determined at standard conditions, which can be calculated by (Scully, 1990):

$$E^{\circ} = \frac{-\Delta G^{\circ}}{nF} \quad (4.8)$$

where E° is the potential of typical electrode reaction, ΔG° is the Gibbs free energy for the reaction, n is the number of electrons participating in the half cell reaction and F is the Faraday's constant which is equal to 96,500 °C/mol.

Under non-standard conditions, the electrode potential can be calculated by Nernst equation (Scully, 1990), which is derived from the basic principles of thermodynamics and given as:

$$E = E^\circ - \frac{RT}{nF} \ln \frac{[Ox]}{[Rx]} \quad (4.9)$$

where R is the universal gas constant (8.31143 J/Kmol) and T is the absolute temperature and $[Ox]$ and $[Rx]$ are the activities (concentrations) of the oxidized and reduced species, respectively.

While metals can dissolve and form ionic solution, they can also undergo other reactions with water. In order to account for all likely corrosion phenomena, it is necessary to know what end products are possible. Pourbaix (1949) collected thermodynamic data on the reactions between many metals and water and combined them with solubility data on oxides and hydroxides and with the equilibrium constants for these reaction to produce the so-called Pourbaix diagrams. Pourbaix diagrams indicate the thermodynamically stable phases as a function of electrode potential and the pH of the electrolyte. The exact procedure for the construction of the Pourbaix diagrams can be obtained from Pourbaix (1949, 1970) and therefore will not be presented here.

A simplified form of Pourbaix diagram for iron is given in Figure 4.2. As it can be seen from this figure, the Pourbaix diagram of iron illustrates clearly that the possibility of reaction between iron and water falls in three different regions. A soluble product is formed under a range of acidic and under a very narrow range of extremely

alkali conditions which have been designated as the corrosion zones. Between these regions an insoluble film (passivating layer) is formed where the corrosion is impeded. The third region shows a thermodynamically stable phase where the iron is immune from corrosion. The main difference between the passivity and immunity is the fact that passivity can be destroyed, but not immunity. The consequence of a passivating film breakdown, chemically or mechanically, may be very high dissolution rates.

Figure 4.2: Simplified form of Pourbaix diagram for iron

Although Pourbaix diagrams provide a strong thermodynamic basis for understanding corrosion reactions, they have two important limitations while predicting the corrosion mechanism and must be used cautiously. The first limitation arises from the fact that no considerations of the kinetic phenomena are included in them since they

are based on thermodynamic data. It has been shown (Pourbaix, 1970) that some reactions may occur in regions of Pourbaix diagram where they are not found to occur in reality and sometimes these meta-stable regions can be of significant importance. The second limitation comes from the fact that the diagrams were derived from the known reactions between pure metals and pure water. In practice, corrosion problems occur in water containing dissolved salts. Therefore, additional reactions can occur due to their presence and these effects must be incorporated into the diagrams. The depassivation of the passivating layer of iron in a chloride-containing electrolyte is an example of this process. Impurities in a metal may also generate reactions that do not occur on a pure metal and must be taken care of in Pourbaix diagrams. Although important studies have been carried out for this purpose (Pourbaix, 1970), unfortunately, for most situations, no such diagram exists.

For these reasons, in order to model the corrosion process as accurately as possible, it is important to understand the kinetics of the electrode reactions which will be presented in the following section.

4.3. Electrode Kinetics and Polarization

When a reaction current, i , flows from an electrode, there are in fact two opposing currents, one anodic, i_a , and one cathodic, i_c . At equilibrium, the rate of reversible anodic and cathodic reactions are equal and opposite and the corroding metal undergoes dissolution and deposition at the same rate which can be expressed as:

$$i_0 = i_c = i_a \quad (4.10)$$

where i_o is the exchange current density in A/m^2 . In these conditions there is no net change in the system. In order to cause a net change, so that some net amount of dissolution or deposition occurs, the potential must be changed away from the equilibrium state.

The divergence from equilibrium is actually a very complex process, which will not be discussed here in detail, but more information can be obtained from such references as Evans (1960) and Scully (1990). Here, a relatively cursory discussion will be provided. The metal atoms on the surface are in energy wells and in order to dissolve into the solution, they have to acquire a certain amount of energy, which is called the activation energy. Some of the atoms have a higher chance to become activated than the others. There are several reasons for this, and some of them can be outlined as follows:

1. On the microscopic scale, metals and their alloys are composed of different crystals. For example steel, which is an iron-carbon alloy, consists of the α -iron crystal, also known as ferrite, and an iron-carbide compound (Fe_3C), known as cementite. These constitute the majority of the structural steel microstructure. Chemically, atoms from the ferrite phase are more active than the ones from the cementite phase.
2. The atoms near the grain boundaries of the crystals tend to be more active than other sites and are more likely to form anodic sites.
3. Stresses due to cold working of metals can lead to effects similar to those produced by grain boundaries. The strained zones will be more active than the non-strained zones.
4. Differences in actual stresses in the different portions of a single metal can also create active sites.

5. Local environmental variations along the same piece of metal can also create active and passive sites. This type of corrosion generally occurs when there exists local differences in the dissolved oxygen concentration. The zones with high concentration of dissolved oxygen become cathodic, and the less aerated zones tend to become active and anodic. This type of corrosion is generally referred to as “aeration cell corrosion”.

6. Certain imperfections in metal crystals such as dislocations or point defects tend to create active sites.

Since the active sites tend to dissolve more metals, the current flowing in the system, i , shifts the potentials of the anode and cathode away from the equilibrium state. This situation is known as polarization, more specifically activation polarization. If the potential of the anode is greater than the equilibrium potential, anodic process will be favoured ($i_a > |i_c|$). If the potential of the cathode is less than the equilibrium potential, cathodic process will be favoured ($i_a < |i_c|$). In either case, the electrode is said to be polarized by activation and the net anodic (or cathodic) reaction is related to its over-potential, η , which is given by the following equation known as “Butler-Volmer equation” (Oldfield, 1988):

$$i = i_o \left[e^{\frac{\alpha n F \eta}{RT}} - e^{-\frac{(1-\alpha) n F \eta}{RT}} \right] \quad (4.11)$$

where α is the transfer coefficient and the exchange current density can be calculated from:

$$i_o = n F k_o [Ox_s]^a [Rx_s]^{a-1} \quad (4.12)$$

where k_o [m/s] is the reaction rate constant, $[Ox_s]$ and $[Rx_s]$ are the activities of the oxidized and reduced species at the electrode surface at equilibrium. The Arrhenius form

of Eq.4.11 can easily be understood since the polarization process is controlled by the activation energy of the dissolution of the metal atoms from the surface of the metal.

Eq.4.11 is usually used in its simplified format, which is known as the “Tafel equation”. At high over-potentials (over-voltages), where the reverse reaction current can be neglected, Tafel equation can be written as (Oldfield, 1988):

$$i = i_o e^{\frac{\alpha n F \eta}{RT}} \quad (4.13)$$

and gives quite accurate approximation for the current density if $\frac{\alpha n F \eta}{RT} > 1.5$.

At low over-potentials, a linear expansion of the exponential term in Eq.4.13 can be carried out to give (Oldfield, 1988):

$$i = i_o \frac{n F \eta}{RT} \quad (4.14)$$

where it has been assumed that $\alpha = 0.5$. Eq.4.14 gives very good approximation for the current density if $\frac{\alpha n F \eta}{RT} < 0.5$. For the cases where, $0.5 < \frac{\alpha n F \eta}{RT} < 1.5$, an error up to 16% can be observed in the estimation of the current density if Eq.4.13 or Eq.4.14 is used instead of Eq.4.11.

Eq.4.11 and its approximations, i.e. Eq.4.13 and Eq.4.14, are derived considering the activation processes that govern the dissolution of a metal only. On the other hand two more polarization effects have to be considered for a more comprehensive examination of the corrosion process: concentration and resistance polarization.

In simple activation dissolution processes described previously, it was assumed that the dissolved ions move away from the anode without any obstruction. On the other hand, the movement of ions in a solution is controlled by diffusion, which is a thermally

activated process, and the electric resistance of the media that they are traveling in. It has been observed in experiments (Scully, 1990) that as the dissolution current density is increased, the rate of removal of the anodic products does not increase proportionally. One of the reasons for this phenomenon is the concentration polarization. As more atoms dissolve in the anolyte, the part of the electrolyte where the anode is in contact with, the concentration of the ions increases significantly since they cannot be transferred towards the cathode with the same rate. This creates a counter electromotive-force (emf) that decreases the rate of dissolution. The influence of concentration polarization can be introduced into Eq.4.11 as follows (Oldfield, 1988):

$$i = i_o \left[\frac{i_{La}}{i_{La} - 1} e^{\frac{\alpha n F \eta}{RT}} - \frac{i_{Lc}}{i_{Lc} - 1} e^{\frac{(1-\alpha) n F \eta}{RT}} \right] \quad (4.15)$$

where the concentration terms in i_o (given by Eq.4.12) refer to the bulk concentrations in the solution around the anodes and cathodes, instead of the surface concentrations, and i_{La} and i_{Lc} are anodic and cathodic diffusion limited current densities which can be calculated as (Oldfield, 1988):

$$i_{La} = \frac{nFD_c}{\delta} ([Rx_B] - [Rx_s]) \quad (4.16)$$

$$i_{Lc} = \frac{nFD_a}{\delta} ([Ox_B] - [Ox_s]) \quad (4.17)$$

where D_c and D_a are the diffusion coefficients of the anions and the cations, respectively, δ is the thickness of the diffusion layer and $[Ox_B]$ and $[Rx_B]$ are the bulk concentrations of the oxidized and reduced species in the solution around the anodes and cathodes instead of the surface.

At high over-voltages, Eq.4.15 is generally simplified by ignoring the reverse reaction; thus cathodic reaction is written as (Oldfield, 1988):

$$i = \frac{i_o e^{\frac{\alpha n F \eta}{RT}}}{1 + \frac{i_o}{i_{La}} e^{\frac{\alpha n F \eta}{RT}}} \quad (4.18)$$

Similarly, the anodic reaction takes the following form:

$$i = \frac{i_o e^{-\frac{\alpha n F \eta}{RT}}}{1 + \frac{i_o}{i_{Lc}} e^{-\frac{\alpha n F \eta}{RT}}} \quad (4.19)$$

It has to be noted that concentration polarization becomes very important when the dissolution current density, i_a , approaches the limiting current density, i_{La} .

As mentioned previously, another polarization effect may be introduced through the electric resistance of the medium that the current passes through. It is generally assumed that electrons do not experience any resistance while traveling through the metal but the resistance of the electrolyte may affect the ion movement. In certain cases, the electric resistance of the electrolyte can be very high due to the moisture and the temperature level of the medium, which resistance is generally referred to as “*ir drop*” (Scully, 1990). Thus an accurate modeling of the process requires that the resistance polarization be taken into account. The effect of electrolyte resistance on the current density can be calculated through the following equation which is an expanded form of Eq.4.15 (Oldfield, 1988):

$$i = i_o \left[\frac{i_{La}}{i_{La} - 1} e^{\frac{\alpha n F \eta}{RT}} - \frac{i_{Lc}}{i_{Lc} - 1} e^{-\frac{(1-\alpha) n F \eta}{RT}} \right] + \frac{\eta}{r} \quad (4.20)$$

where r is the resistance of the medium. The effect of different polarization mechanisms is demonstrated via a sample anodic polarization curve (over-potential vs. logarithm of current density) in Figure 4.3. Some of the metals, on the other hand, do not follow the pattern shown in Figure 4.3. Whether a metal can produce a protective (or passivating) film, which is generally a form of oxide of that metal, has a strong influence on the electrode kinetics of that metal. A typical anodic polarization curve of metal which can exhibit passivity is shown in Figure 4.4.

In Figure 4.4, the region B-C is highly unstable and a potential in this region cannot be maintained. If the potential is raised in this region beyond the critical current density, i_{crit} , it will automatically jump to region C-D and a passivating layer will start to form on the surface of the metal. The small passive current density, i_{pp} , which is the remaining current density at the passivated locations helps to maintain the oxide film, which continues to dissolve in the solution albeit in small amounts. The passive film has significantly high electrical resistivity but still conducts some electricity. Therefore, only small electric potentials can be maintained across passive films (about 1 volt). If higher electric potentials are applied, then the potential on the solution side of the film will rise and anodic reaction will re-start. This can be observed along line DE in Figure 4.4. This region is generally called the trans-passive zone

Another important aspect of the passivity is that it cannot be established nor maintained in the presence of aggressive ions such as chlorides. The reasons behind this phenomenon have different roots and the topic is still under investigation (Scully, 1990). One of the most important reasons is the effect of chlorides on the critical current density. As the concentration of the aggressive ions increase, the critical current density also

increases as can be seen in Figure 4.5. This results in a drop in the passive potential range, AB, to A'B'. The reason behind this behaviour is the high charge density of the chloride ions, their capacity to form soluble species and their entry into the crystal structure of the metals, causing lattice defects. It has to be understood that the presence of chlorides does not stop the formation of the oxide film around the metal, but it affects its protective nature by making it more soluble. The reduction in the passive potential range may result in the depassivation of the anodic regions and, eventually, the corrosion of the metal. This topic will be explained further in the next section.

Figure 4.3: An anodic polarization curve showing the affects of different polarization mechanisms

Figure 4.4: Schematic representation of passivation, passivating film formation and passivating film breakdown (pitting) processes on an anode

Figure 4.5: The effect of aggressive ions on the anodic polarization curve

4.4. Corrosion Kinetics

As explained before, in order for corrosion to occur, there have to be two electrode reactions: oxidation (anodic) and reduction (cathodic). Figure 4.6 shows the most general form of the potential (E) vs. current density (i) relationship of an electrochemical system as shown in Figure 4.1.

Figure 4.6: Combined polarization curves of an anodic and a cathodic reaction on a corroding specimen

Figure 4.6 indicates that corrosion takes place at the intersection of the anodic and cathodic polarization curves. Therefore, in order for corrosion to start, the anodic electrode potential must increase by the anodic polarization, η_a , and the cathodic

electrode potential must decrease by the cathodic polarization, η_c . The rate of corrosion and the corrosion potential that the system will experience are i_{corr} and E_{corr} , respectively.

Rearranging Eq.4.20, for the anodic polarization, η_a , and the cathodic polarization, η_c , to reach the corrosion point (E_{corr} , i_{corr}) from their equilibrium potentials, E_a^0 and E_c^0 can be written as the sum of the activation, the concentration and the resistance polarizations as follows:

$$\eta_a = \frac{RT}{\alpha nF} \ln \left(\frac{i_{corr}}{i_{oa}} \right) - \frac{RT}{nF} \ln \left(1 - \frac{i_{corr}}{i_{La}} \right) + i_{corr} r \quad (4.21)$$

$$\eta_c = \frac{RT}{\alpha nF} \ln \left(\frac{i_{corr}}{i_{oc}} \right) - \frac{RT}{nF} \ln \left(1 - \frac{i_{corr}}{i_{Lc}} \right) + i_{corr} r \quad (4.22)$$

Therefore, at the corrosion point (E_{corr} , i_{corr}), we can write:

$$E_{corr} = E_a^0 + \frac{RT}{\alpha nF} \ln \left(\frac{i_{corr}}{i_{oa}} \right) - \frac{RT}{nF} \ln \left(1 - \frac{i_{corr}}{i_{La}} \right) + i_{corr} r \quad (4.23)$$

or

$$E_{corr} = E_c^0 - \left[\frac{RT}{\alpha nF} \ln \left(\frac{i_{corr}}{i_{oc}} \right) - \frac{RT}{nF} \ln \left(1 - \frac{i_{corr}}{i_{Lc}} \right) + i_{corr} r \right] \quad (4.24)$$

Equations 4.23 and 4.24 are general and not encumbered by the approximations mentioned earlier. Given these equations, the corrosion rate at any point on a metal surface submerged in an electrolyte can be predicted if the electrochemical potential in the electrolyte adjacent to that point is known. It has to be noted that in a dynamic system where the temperature, humidity, electric resistance and the ionic composition of the electrolyte and the concentrations of the oxidizing and reducing atoms change continuously, the determination of the corrosion rate requires the estimation of these variables at every instant during the corrosion process.

4.5. Governing Equation of Corrosion

The equation governing the potential distribution in an electrochemical system is given by Poisson's equation (Scully, 1990):

$$\frac{\partial^2 E}{\partial x^2} + \frac{\partial^2 E}{\partial y^2} + i_p = \frac{\partial E}{\partial t} \quad (4.25)$$

where i_p represents the external polarization currents entering or exiting the system. If these external sink or source terms are not present, Eq.4.25 can be written as:

$$\frac{\partial^2 E}{\partial x^2} + \frac{\partial^2 E}{\partial y^2} = \frac{\partial E}{\partial t} \quad (4.26)$$

Solution of this equation with appropriate anodic and cathodic polarization expressions and the relevant boundary conditions will give the potential distribution throughout the electrolyte from which the corrosion rates can be calculated. At the free and isolated surfaces of the system the following boundary condition based on Ohm's law can be imposed:

$$i = \frac{1}{r} \frac{\partial E}{\partial n} = 0 \quad (4.27)$$

where n represents the direction normal to the surface under consideration.

At the anodic and cathodic locations respectively the following polarized electrode potentials can be used as boundary conditions:

$$E_a = E^o_a + \frac{RT}{\alpha n F} \ln \left(\frac{i_a}{i_{oa}} \right) - \frac{RT}{n F} \ln \left(1 - \frac{i_a}{i_{La}} \right) + i_a r \quad (4.28)$$

$$E_c = E^{\circ}_c - \left[\frac{RT}{\alpha n F} \ln \left(\frac{i_c}{i_{oc}} \right) - \frac{RT}{n F} \ln \left(1 - \frac{i_c}{i_{Lc}} \right) + i_c r \right] \quad (4.29)$$

where E_a and E_c are the anodic and cathodic potentials at the anodic and cathodic locations on the metal. In the present study Eq.4.26 will be solved by using a nonlinear finite element scheme. The details of the solution algorithm are presented in the following chapter.

The effect of aggressive ions, such as chlorides, on the anodic polarization curve of metals, which can develop a protective film, was discussed in the previous section and was shown in Figure 4.5. With reference to Figure 4.5, it was mentioned that the shift of the critical current density, i_{crit} , and the decrease in the passive potential range, A-B, results in the de-passivation (or re-activation) of the metal. This can be better understood now from the shift in the corrosion point C to C'. Without the chloride ions, the intersection of the anodic and cathodic polarization curves, the corrosion point, is the point C where the metal is covered with a passive film. After the introduction of chlorides, due to a shift in the anodic polarization curve, the corrosion point shifts to point C' where the metal is in an active state and free to corrode.

4.6. Corrosion of Steel in Concrete

The corrosion of steel reinforcement in concrete follows the same thermodynamic principles and kinetics that were presented in the previous sections. Generally, the steel in concrete has a passivating layer (around 10 nm thick) which is generally in the form of Fe_2O_3 and possibly other oxides. If the steel is in its active state where the passivating layer cannot provide a protective environment, a series of oxidation and reduction

reactions take place on the steel surface with the concrete pore solution acting as the electrolyte. These reactions are the iron dissolution for the anode and the oxygen reduction for the cathode and can be written as:

Since the concrete provides an alkali environment, the hydrogen evolution for the reduction, which generally takes place in acidic solutions, can be ignored.

As indicated by Eq.4.28, the iron atoms are ionized to ferrous ions (Fe^{2+}), which dissolve in the pore solution around the anodic sites. The electrons released by the anodic reaction are deposited on the steel surface and they raise its electric potential. These electrons then flow through or along the steel to a lower potential (cathodic) site. The iron dissolution process will proceed only if there is a cathodic reaction which will act as a sink for the electrons produced at the anodic site. Therefore, if the oxygen and water are not available at the cathodic sites; i.e., the reaction in Eq.4.29 cannot occur, the corrosion will stop.

Beside the internal current taking place inside the steel (electron movement), there is also ion movement in pore solution of the concrete surrounding the steel. This external current consists of hydroxide ions (OH^{-}) moving from the cathode to the anode and ferrous ions (Fe^{2+}) moving in the opposite direction. It is important to understand that the water in the concrete pores is actually a dilute solution of several alkali and calcium hydroxide. It is this fluid that serves as a medium for ionic flow. If the pores are dried out, or if the structure of the concrete is dense such that the pores are not sufficiently interconnected, the flow of ions through the pores becomes very difficult.

The entire process, which is demonstrated in Figure 4.7, leads to the formation of corrosion products. The actual loss of steel involved in the corrosion process takes place at the anodic sites, with the reaction of Fe^{2+} and OH^- ions, as follows:

Combining equations 4.28, 4.29 and 4.30 yields the following total electrochemical reaction:

Ferrous oxide, $Fe(OH)_2$, can further react with the available oxygen and water at the anode according to the following reaction:

$Fe(OH)_3$, the so-called hydrated red rust, is the final corrosion product whose volume is four times as large as the volume of the steel with the same mass. Therefore the formation of red rust may cause internal stresses and consequently the cracking and spalling of the concrete covering the reinforcement.

If the oxygen concentration in the pore solution is not adequate for the formation of the red rust according to Equations 4.30 and 4.32, a thickening of the oxide film on the steel surface can be observed with the formation of black rust, Fe_2O_3 . The formation of black rust can be explained by the following equation:

The volume of the black rust is only twice as large as the volume of the steel with the same mass; therefore it is less dangerous compared to the red rust. However, it is significant since it is the predominant corrosion product when the oxygen supply in the anodic sites is not enough.

The formation of anodic and cathodic sites on steel surface follows the same principles described in the previous section and depends on the microstructure and the environmental conditions around the steel. Although, it is very difficult to model the formation of the anodic and cathodic sites based on these principles, the compositional and structural variations in steel, local differences in the applied stresses, or local changes in the environmental conditions along the reinforcement, can provide a guideline for this difficult task.

The electrical resistivity of the concrete, which is affected by the pore structure of the concrete, the degree of water saturation, temperature, and the total ionic concentration of the pore solution, is also important in the corrosion of steel reinforcement. For example, fully saturated ordinary portland cement has an approximate electrical resistivity of 15 ohm-m; but this value increases three orders of magnitude by progressively drying the concrete. At higher temperatures, more ions will dissolve in the pore solution and hence the resistivity will decrease. The relationship between concrete resistivity and temperature can be obtained from Hinchinson-Rash law (Martín-Pérez, 1999):

$$r_2 = r_1 e^{\left[\frac{U}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \right]} \quad (4.34)$$

where r_1 and r_2 are the electrical resistivities of concrete in $\Omega \cdot m$ at temperatures T_1 and T_2 , respectively, U is the activation energy and R is the universal gas constant. Hope (1987) suggested that the $U/R = 2900$ K is a good approximation.

It has been discussed that the presence of chlorides may cause the de-passivation of the protective layer and act as a catalyst in the corrosion process. It has been shown by many researchers that there is a threshold concentration of chloride that must be exceeded

in order to start the depassivation of the protective layer (Glass and Buenfeld, 1995). Although there is a common acceptance of this theory qualitatively, there is little agreement on how to determine this threshold value quantitatively. The threshold value depends on several factors many of which are still imperfectly understood. Haussman (1967) proposed that the chloride threshold concentration is about 0.6 times the $(OH)^-$ concentration. This suggestion is made based on data from laboratory experiments on steel immersed in calcium hydroxide solution. Gouda (1970) conducted similar experiments with potassium and sodium hydroxide solutions and suggested a logarithmic relationship between chloride ion concentration and pH of the pore solution. Diamond (1986) used Gouda's experimental data and recalculated the threshold as 0.3 versus the 0.6 reported by Haussman. Glass and Buenfeld (1995) suggested that the $[Cl^-]$ to $[OH^-]$ ratio should be between 0.26 to 0.40.

It was also stated that in order for the passivating film to form and to continue protecting the steel against general corrosion, the pH level of the pore solution must be high (above 11.5). This high pH level ensures that there are enough hydroxide ions in the system to keep the passivating film effective. Carbonation reduces the pH (alkalinity) of the pore water from 12-13 to levels below 9. Therefore, if the alkalinity of the pore water surrounding the steel is lowered due to carbonation, de-passivation of the steel and the consequent corrosion processes need to be considered.

Another side effect of carbonation process is the release of the already bound chloride ions to the pore water, which can create further depassivation if they reach the reinforcing steel. Many researchers (Neville, 1996) have observed increased concentrations of chloride ions in pore water adjacent to the carbonation front.

4.7. Corrosion Rates in Concrete

The corrosion rate can be defined as the rate of material removal as a consequence of corrosion. This rate can be expressed as *CPR* (corrosion penetration rate), or thickness loss of material per unit time. The formula for the calculation is as follows:

$$CPR = \frac{KW}{\rho At} \quad (4.35)$$

where W [mg] is the weight loss after time t [h], ρ [g/cm³] is the density of the material, A [mm²] is the area of the exposed specimen; and $K = 0.876$ when *CPR* is expressed in millimeters per year [mpy].

Another way of representing the corrosion rate is through the electric current density, i , which is also used in the current study. The rate of corrosion J [mol / m².s], can be determined by:

$$J = \frac{i}{nF} \quad (4.36)$$

where n is the number of electrons participating in the reaction and F is the Faraday's constant.

It is assumed that the oxygen supply from the concrete and the surrounding environment equals the amount of oxygen consumed by the cathodic reaction and by the oxidation of ferrous hydroxide at the anode (Bazant, 1979). According to Eq.4.29, since one mole of O₂ is consumed to produce 4 moles of OH⁻, n can be taken as 4; therefore, Eq.4.34 can be rewritten as:

$$J_{oc} = -8.291 \times 10^{-8} i_c \text{ [kg/m}^2\text{.s]} \quad (4.37)$$

The rate of ferrous oxide, Fe(OH)₂, production, J_{fh} , at the anode according to Eq.4.30 can be written as:

$$J_{fh} = \frac{i_a}{zF} = 4.656 \times 10^{-7} i_a \quad [\text{kg/m}^2.\text{s}] \quad (4.38)$$

where $z = 2$ from Eq. 4.16.

Ferrous oxide, $\text{Fe}(\text{OH})_2$, can further be oxidized based on Eq. 4.32 and this will result in the production of $\text{Fe}(\text{OH})_3$ for which the rate of oxygen consumption at the anode can be calculated as:

$$J_{oa} = -4.144 \times 10^{-8} i_a \quad [\text{kg/m}^2.\text{s}] \quad (4.39)$$

The total amount of oxygen reaching the steel surface must be equal to the total amount of oxygen consumed at the anode and the cathode. Therefore the rate of total oxygen consumption is:

$$J_{oa} + J_{oc} = -4.144 \times 10^{-8} i_a - 8.291 \times 10^{-8} i_c \quad (4.40)$$

Since one mole of $\text{Fe}(\text{OH})_2$, which is 89.845 g, produces one mole of $\text{Fe}(\text{OH})_3$ (106.845 g) according to Eq.4.32, the rate of rust production can be determined by:

$$J_{oa} = -\frac{106.845}{89.845} J_{fh} = 5.536 \times 10^{-7} i_a \quad [\text{kg/m}^2.\text{s}] \quad (4.41)$$

This means that, one can determine the amount of rust formed on a steel reinforcement if i_a is known (Martín-Pérez, 1999).

Figure 4.7: Process of corrosion of steel in concrete

5. The Proposed Durability Model and Its Finite Element Implementation

5.1. General

The proposed durability model consists of two parts: the initiation stage and the propagation (corrosion) stage. In the initiation stage, the transport of the corrosive agents (heat, moisture, CO₂, O₂ and chloride ions) through the concrete is modeled. The corrosion of the reinforcement is modeled in the propagation stage. Both stages work in a common time–2D space domain. This chapter explains the details of the initiation and propagation stages of the model as implemented in the computer program CONDUR developed in the current study.

5.2. Initiation Stage Model

Due to the complex and nonlinear nature of the initiation stage, a finite element solution scheme has been adopted. The model works in a time-2D space domain. A summary of the equations used and the associated material models are given in Table 5.1 and Table 5.2, respectively. A general flowchart of the solution procedure for the initiation stage is presented in Figure 5.1 and the details of the individual analyses for heat, moisture, CO₂, Cl⁻ and O₂ transport are provided in the flowcharts given in Figures 5.2 to 5.6.

As indicated in Figure 5.1, the analysis commences with definition of the geometry of the problem, the specification of the material properties, the initial boundary conditions for temperature, relative humidity, O_2 , Cl^- and CO_2 concentrations, $Ca(OH)_2$ content and the pH.

The first step in the initiation stage is determination of the temperature profile by solving the homogeneous boundary value problem for heat transfer given in Table 5.1, subject to the specified boundary and initial conditions. The solution provides the spatial and temporal distribution of the temperature in the structure. As discussed previously, although the coefficient of thermal conduction, k , and specific heat, c , depend on the moisture content of the medium, the effect is not significant for the temperature range one normally encounters in concrete structures; therefore, they are assumed to be independent of the moisture content. As shown by previous studies (Hartley and Black, 1981; Basha and Salveduria, 1998), this assumption gives satisfactory results. In addition, if there is no radiation in the system and there is no temperature-dependent heat sink or source term, the solution of the heat transfer equation follows a linear solution algorithm; otherwise a nonlinear analysis is used. A summary of the thermal properties used in the model, which is a combination of defined relations and user-defined parameters, and a flowchart of the solution algorithm are provided in Table 5.2 and Figure 5.2, respectively.

The heat transfer results are used in conjunction with the governing equation of moisture transport (See Table 5.1) to calculate the moisture distribution within the structure. As explained in Chapter 3, the type of moisture transport analysis (in terms of liquid water content or relative humidity) depends on whether the structure is exposed to

wetting-and-drying cycles. If the structure is exposed to wetting and drying cycles, Eq.3.14 is solved in which liquid water content is used as the state variable. Otherwise, Eq.3.16 is solved in which relative humidity, h , is the state variable. The main reason of representing the moisture transport problem in terms of liquid water content, w_L , is to calculate the amount of chloride ions carried into the concrete by the advection of the liquid water.

When Eq.3.16 is used to represent the moisture transport problem, the relationship between the relative humidity and the liquid water content is determined by the adsorption isotherms. The adsorption isotherms used in the current model are listed in Table 5.3. The material models for isothermal moisture diffusion coefficients, D_h and D_w , and the thermal moisture diffusion coefficient, D_T are provided in Table 5.2. Since the moisture diffusion coefficients are functions of the moisture content of concrete, a nonlinear solution algorithm is followed.

As indicated in Figures 5.2 and 5.3, since carbonation produces water, which affects the moisture content of concrete, the moisture transfer analysis is coupled with the CO_2 transfer analysis (i.e. carbonation). However, it is a one-way coupling in that the water produced by the carbonation reaction is introduced as a source term (Q_h or Q_w), in the moisture diffusion equation as shown in Table 5.1 and its quantity is determined by the rate of carbonation reaction according to Equations 3.31 and 3.32. Another important consequence of the carbonation process is its affect on the porosity of the concrete. The change in the porosity is assumed to affect the moisture, CO_2 , Cl^- and O_2 diffusivity and is modeled by using a bilinear decay function. It has to be noted that the change in the pH

of the pore solution is monitored and recorded at each time step since it will be used as a criterion for the chloride release process and in the propagation stage of the model.

The diffusion coefficients for chloride ions and oxygen, as well as other properties such as electrical resistivity, which depend on temperature and moisture, are calculated after the moisture and CO₂ transfer analyses are completed. Following the calculation of the diffusion coefficients, finite element analyses are carried out to determine the chloride and O₂ concentrations at each node. Flowcharts for the chloride and oxygen diffusion analyses are given in Figures 5.5 and 5.6.

As discussed in Chapter 3, some of the chloride ions are bound by the hydration products (C₃A) and released when the pH of the pore solution drops below 8.5. Chloride binding is modeled by modifying the chloride diffusion coefficient by using one of the binding isotherms which are given in Table 5.3. Chloride release process is treated as a source term in the finite element calculations. In the proposed model, a user defined chloride release isotherm is used.

Table 5.1: The summary of the governing equations of the initiation stage of the proposed durability model

Analysis	Governing Equation	Initial and Boundary Cond.'s	Material Prop's	Notes
<i>Heat Transfer</i>	$k \nabla^2 T + Q_T = \rho c \frac{\partial T}{\partial t}$	$\frac{\partial T}{\partial n} + \alpha_1 T = f_1(s, t)$ on S_1 $T = f_2(s, t)$ on S_2 $T(x, y, 0) = T(x, y)$ on S_2	$k, c, \varepsilon, \alpha, h_c, h_r$	Unidirectional coupling with moisture transfer analysis is assumed
<i>Moisture Transfer in terms of w_L</i>	$D_w \nabla^2 w_L + Q_w = \frac{\partial w_L}{\partial t}$	$\frac{\partial w_L}{\partial n} + \alpha_1 w_L = f_1(s, t)$ on S_1 $w_L = f_2(s, t)$ on S_2 $w_L(x, y, 0) = w_L(x, y)$ on S_2	$D_w = f(T, S, t_e, \mu_p)$	Used to model chloride ingress through convection, Q_w due to carbonation
<i>Moisture Transfer in terms of h</i>	$D_h \nabla^2 h + D_T \nabla^2 T + Q_h = \frac{\partial w_L}{\partial h} \frac{\partial h}{\partial t}$	$\frac{\partial h}{\partial n} + \alpha_1 h = f_1(s, t)$ on S_1 $h = f_2(s, t)$ on S_2 $h(x, y, 0) = h(x, y)$ on S_2	$D_T = f(h),$ $D_h = f(T, h, t_e, \mu_p)$	$\frac{\partial w_L}{\partial h}$ is determined by adsorption isotherms, Q_h due to carbonation

Table 5.1: Continued...

Analysis	Governing Equation	Initial and Boundary Cond.'s	Material Prop's	Notes
Chloride Transport	$D_{cl} \nabla^2 C_f + Q_{cl} = \frac{\partial C_f}{\partial t}$	$\frac{\partial C_f}{\partial n} + \alpha_1 C_f = f_1(s, t)$ on S_1 $C_f = f_2(s, t)$ on S_2 $C_f(x, y, 0) = C_f(x, y)$ on S_2	$D_{cl} = f(T, h, t_c)$	Chloride ingress through diffusion, binding and release through Q_{cl}
CO₂ Transport	$D_c \nabla^2 C_c + Q_c = \frac{\partial C_c}{\partial t}$	$\frac{\partial C_c}{\partial n} + \alpha_1 C_c = f_1(s, t)$ on S_1 $C_c = f_2(s, t)$ on S_2 $C_c(x, y, 0) = C_c(x, y)$ on S_2	$D_c = f(T, h, \mu_p)$	Changes the pore structure; i.e., η_p ; produces water; Q_c represents the carbonation reaction
O₂ Transport	$D_o \nabla^2 C_o + Q_o = \frac{\partial C_o}{\partial t}$	$\frac{\partial C_o}{\partial n} + \alpha_1 C_o = f_1(s, t)$ on S_1 $C_o = f_2(s, t)$ on S_2 $C_o(x, y, 0) = C_o(x, y)$ on S_2	$D_o = f(T, h, \mu_p)$	Assumed to diffuse without any reaction with concrete. Although the functionality is in the model, Q_o is not used.

Table 5.2: The summary of the equations for determining the material properties

Analysis	Material Property	Equation	Unit
Heat Transfer	Coefficient of Conduction (<i>User input</i>)	$k = 0.1 - 5$	W/m°C
	Surface Heat Transfer Coefficient	$h_c + h_r = 13.5 + 3.88v$	W/m ² °C
	Specific Heat (<i>User input</i>)	$c = 840 - 1170$	J/kg°C
	Density of Concrete (<i>User input</i>)	$\rho = 1600 - 2500$	kg/m ³
	Absorptivity (<i>User input</i>)	$\alpha = 0.5 - 1.0$	-
	Emissivity (<i>User input</i>)	$\epsilon = 0.5 - 1.0$	-
Moisture Transfer in terms of w_L	Moisture Diffusion Coefficient	$D_w = D_{w,ref}(1 - S)^{-1.7} \left(\frac{S_c - S}{S_c} \right)^{2.2}$	m ² /s
Moisture Transfer in terms of h	Isothermal Moisture Diffusion Coefficient	$D_h = D_{h,ref} \left[0.05 + \frac{0.95}{1 + \left(\frac{1-h}{0.25} \right)^n} \right] \left(e^{\left[\frac{U}{R} \left(\frac{1}{T_{ref}} - \frac{1}{T} \right) \right]} \right) \left(0.3 + \sqrt{\frac{13}{t_c}} \right)$	m ² /s
	Thermal Moisture Diffusion Coefficient	$D_T = 0.001D_h$	m ² /s

Table 5.2: Continued

Analysis	Material Property	Equation	Unit
Chloride Transport	Chloride Diffusion Coefficient	$D_{Cl} = 0.15D_{inf} \frac{1 + \rho_c \frac{c}{w}}{1 + \rho_c \frac{c}{w} + \frac{\rho_c a}{\rho_a c} \left(\frac{\rho_c \frac{w}{c} - 0.85}{1 + \rho_c \frac{w}{c}} \right)^3}$	m ² /s
CO₂ Transport	CO ₂ Diffusion Coefficient	$D_c = 1.64 \times 10^{-6} \mu \left(1 + \frac{\frac{a}{c} \frac{\rho_c}{\rho_w}}{\frac{a}{c} \frac{\rho_c}{\rho_w}} \right) (1-h)^{2.2}$	m ² /s
O₂ Transport	O ₂ Diffusion Coefficient	$D_o = 1.92 \times 10^{-6} \mu \left(1 + \frac{\frac{a}{c} \frac{\rho_c}{\rho_w}}{\frac{a}{c} \frac{\rho_c}{\rho_w}} \right) (1-h)^{2.2}$	m ² /s

Table 5.3: Adsorption isotherms used in the program CONDUR

Isotherm	Equation	Notes
BET Isotherm	$\frac{V}{V_m} = \frac{C \left(\frac{P}{P_0} \right)}{\left(1 - \frac{P}{P_0} \right) \left[1 + (C - 1) \left(\frac{P}{P_0} \right) \right]}$	$C = e^{\frac{Q_g - Q_L}{RT}}$
FHH Isotherm	$V = V_m \left[\frac{a}{\ln \left(\frac{P_0}{P} \right)} \right]^b$	a and b are user defined
H&J Isotherm	$\log \left(\frac{P}{P_0} \right) = B - \frac{A}{V^2}$	A and B are user defined

Table 5.4: Chloride binding and release models used in the program CONDUR

Model	Equation	Notes
Linear Binding Isotherm	$C_b = \alpha C_f$	α is user defined
Langmuir Binding Isotherm	$C_b = \frac{\alpha C_f}{1 + \beta C_f}$	α and β are user defined
Freundlich Binding Isotherm	$C_b = \alpha C_f^\beta$	α and β are user defined
Linear Release Isotherm	$C_r = \omega C_b$	<ul style="list-style-type: none"> - When pH drops below a user defined value - ω is user defined

Figure 5.1: Nonlinear solution scheme for the initiation stage

Figure 5.2: Flowchart of the heat transfer analysis

Figure 5.3: Flowchart of the moisture transfer analysis

Figure 5.4: Flowchart of the CO₂ transfer analysis

Figure 5.5: Flowchart of the chloride transfer analysis

Figure 5.6: Flowchart of the O_2 transfer analysis

5.3. Propagation (Corrosion) Stage Model

The propagation stage cannot start until the reinforcing steel becomes active; i.e. depassivated, which can occur in different ways. As discussed in Chapter 4, one of the mechanisms of depassivation is triggered by the presence of the chloride ions and their effect on the anodic polarization. As the chloride concentration exceeds a threshold value, which is a user-defined parameter in this thesis, depending on the $[Cl^-]$ to $[OH^-]$ ratio in the concrete pore solution around the steel reinforcement, the passive film becomes unprotective. If the depassivation occurs locally, pitting corrosion will start along the reinforcement. On the other hand, if the passivating layer disappears completely, general corrosion starts. Complete depassivation can be observed when the pH of the concrete pore solution drops below a certain value which is often the case when there is carbonation. Whether the steel will be completely depassivated or not is determined by appealing to the Pourbaix diagram for iron which is given in Figure 4.2. It has to be noted that this is an approximation since Pourbaix diagrams are constructed for ideal conditions.

As shown in Figure 5.7, the next step is to determine the anodic and cathodic locations along the steel reinforcement. In the pitting corrosion case, the determination of anodic and cathodic locations is relatively straightforward. The locations where the passivating layer is lost act as the anodes and the remaining parts of the reinforcement act as the cathodes. In the general corrosion case, an accurate determination of the anodic and cathodic sites becomes almost impossible. In the current work, two options have been provided for the determination of the anodic and cathodic locations when complete depassivation of the reinforcement occurs: In the first option, the user defines the anodic

and cathodic locations by selecting the nodes on the steel surface. In the second option, the user defines the proportion of the anodic and the cathodic areas or lengths, and according to this ratio, the anodic and cathodic sites are distributed evenly along the reinforcement.

After this determination, electric circuits are formed between the anodes and cathodes along the steel reinforcement. The corrosion takes place when the anodic and cathodic polarization curves, as shown in Figure 4.6, intersect in the active region, and the rate of corrosion is determined by the corrosion current density, i_{corr} . The amount of rust produced due to the corrosion reaction depends on the corrosion current density.

Figures 5.8 and 5.9 give the general flowchart of the numerical procedure to be followed to obtain the current densities along the reinforcement. The determination of the electrode potentials requires the solution of Eq.4.26 which shows a nonlinear behaviour due to the polarization effects. In the present study, three types of polarization (activation, concentration and resistance) for the anodic and cathodic locations have been considered as indicated in Figure 5.8. The selection of small time increments in the finite element analysis assures an accurate determination of the corrosion point coordinates in the electric potential vs. current density diagram; i.e, i_{corr} and E_{corr} .

The amount of rust produced around the reinforcement is calculated using Eq. 4.41 which is a function of the anodic current density, i_a . The propagation stage continues until a predefined amount of rust is produced due to corrosion.

Figure 5.7: Initiation of the corrosion process

Figure 5.8: Modeling electrode polarization

Figure 5.9: Flowchart for the propagation stage

6. Finite Element Formulation

6.1. General

The durability model, which was explained in the previous chapter, requires the solution of the heat and moisture transport and of chloride, CO₂ and O₂ ingress into concrete as well as the distribution of the electric potential around the reinforcing steel. Each of these problems is governed by a general quasi-harmonic equation as discussed before and can be solved numerically using the finite element method. This chapter explains the details of the finite element implementation to solve these equations.

6.2. The General Quasi-Harmonic Equation

In the problem of diffusion or flow of a physical quantity such as heat, mass, or a chemical agent, the rate of transfer per unit area (flux) can be written in terms of its Cartesian components as:

$$\{q\} = \begin{Bmatrix} q_x \\ q_y \\ q_z \end{Bmatrix} \quad (6.1)$$

If the rate at which the relevant quantity is generated or removed per unit volume is Q , the continuity requirement gives:

$$\frac{\partial q_x}{\partial x} + \frac{\partial q_y}{\partial y} + \frac{\partial q_z}{\partial z} = Q \quad (6.2)$$

In general, the rate of flow is related to the gradient of some potential quantity ϕ , as given in Eq.6.3. In the case of heat flow, for instance, this potential is the temperature while in the case of diffusion it is the concentration of the diffusing species. The flux is related to the potential via:

$$\{q\} = -[k] \begin{Bmatrix} \frac{\partial \phi}{\partial x} \\ \frac{\partial \phi}{\partial y} \\ \frac{\partial \phi}{\partial z} \end{Bmatrix} \quad (6.3)$$

where $[k]$ is a diagonal conductivity matrix. The final form of the pertinent steady state differential equation after substituting Eq.6.3 into Eq.6.2 is:

$$\frac{\partial}{\partial x} \left(k_x \frac{\partial \phi}{\partial x} \right) + \frac{\partial}{\partial y} \left(k_y \frac{\partial \phi}{\partial y} \right) + \frac{\partial}{\partial z} \left(k_z \frac{\partial \phi}{\partial z} \right) + Q = 0 \quad (6.4)$$

where k_x , k_y and k_z are the appropriate conductivities in the x , y and z directions, respectively.

Eq.6.4 is called the general steady-state quasi-harmonic equation, or Laplace's equation, and can be used to represent many physical problems such as heat transfer, fluid flow and other transport phenomena in porous media. In the case of heat transfer, the potential, ϕ , represents the temperature, T ; and k_x , k_y , and k_z are the thermal conductivities in x , y and z directions, respectively. For a moisture transfer problem, the potential, ϕ , is the relative humidity, h ; and k_x , k_y , and k_z are the moisture diffusion coefficients in x , y and z directions, respectively. Similarly, in chemical diffusion problems, the potential represents the concentration of the diffusing agent and k_x , k_y , and k_z are the diffusion coefficients in the x , y and z directions, respectively.

6.3. Finite Element Modeling of the Quasi-Harmonic Problems

The concrete durability model presented in the previous chapter is a combination of several field problems such as heat transfer, moisture transfer, chloride, CO₂ and O₂ ingress, as well as electric potential distribution, each of which can be represented by a quasi-harmonic equation as shown in Table 5.1. In this section, the solution algorithm of the general quasi-harmonic equation will be presented. All of the particular cases follow the steps described in this section.

As the current investigation is limited to two-dimensional problems, the two-dimensional steady-state case will be considered first. The corresponding transient, or time-dependent, boundary value problem will be dealt with later in this chapter.

Any two-dimensional steady-state quasi-harmonic problem can be represented by Eq.6.5, which is the two dimensional form of Eq.6.4.

$$\frac{\partial}{\partial x} \left(k_x \frac{\partial \phi}{\partial x} \right) + \frac{\partial}{\partial y} \left(k_y \frac{\partial \phi}{\partial y} \right) + Q = 0 \quad (6.5)$$

If we assume the material to be isotropic, then Eq.6.5 and its associated boundary conditions can be written compactly as [Brickford, 1994]:

$$\nabla^2 \phi + f(x, y) = 0 \quad (\text{in } D) \quad (6.5a)$$

$$\frac{\partial \phi}{\partial n} + \alpha(s)\phi = h(s) \quad (\text{on } S_1) \quad (6.5b)$$

$$\phi = g(s) \quad (\text{on } S_2) \quad (6.5c)$$

where D is the interior and S_1 and S_2 are the boundaries of the domain of interest. When the term $f(x, y)$ in Eq.6.5a is absent, it is referred to as Poisson's equation and its solution closely follows that of Laplace's equation. The corrosion problem is governed by

Poisson's equation. In Eq.6.5 α , h and g are functions of the boundary coordinate s and n is the unit normal to the boundary.

Eq.6.5 represents a two-dimensional elliptic boundary value problem which can be solved by the finite element method using either the Ritz or the Galerkin formulations. As usual in the finite element model, the domain of interest is divided into discrete elements of known shape and the field variable is approximated over each element using nodal values of the variable and predefined interpolation functions, known as shape functions. Two-dimensional triangular, quadrilateral or general isoparametric elements can be used in the discretization. The computer program that is developed in this work is able to handle triangular as well as four, eight and nine node quadrilateral elements. For simplicity, only the formulation based on the three-node triangular element, as shown in Figure 6.1, will be described.

6.3.1. Element Formulation

As stated earlier, finite element solution of differential equations begins with the selection of a suitable finite element(s) used to discretize the domain of interest. The procedure used to develop the element properties are practically independent of the shape and order of the element, therefore for clarity, we illustrate the procedure using a simple three node triangular element.

Figure 6.1 shows a triangular finite element where (x_i, y_i) , (x_j, y_j) , and (x_m, y_m) represent the coordinates of the nodes i , j , and m , respectively. It has to be noted that nodes i , j , and m are labeled in the counterclockwise direction and it is essential that this sign convention is adhered to in the finite element model.

Figure 6.1: Basic three-noded triangular element

The current formulation is based on Ritz method (Heinrich and Pepper, 1999). Let us start with the selection of a field variable (e.g. temperature in the case of heat transfer) and its functional representation within the element. We approximate the field variable, ϕ , within each element in terms of the interpolation or shape functions, $[N]$, and the nodal values of the field variable, $\{a\}$, as:

$$\phi = [N] \{a\} \quad (6.6)$$

where

$$\{a\} = \begin{Bmatrix} a_i \\ a_j \\ a_m \end{Bmatrix} \quad (6.7)$$

in which a_i , a_j , and a_m represent the nodal values of the field variable ϕ (e.g. temperature); and the shape function matrix has the following form:

$$[N] = [N_i \quad N_j \quad N_m] \quad (6.8)$$

The choice of the shape functions depends on the type of the element as well as the type and order of the governing equation of the problem. For this specific formulation; i.e., for a three node triangular element, the shape functions can be written as:

$$\begin{aligned} N_i &= \frac{1}{2A}(\alpha_i + \beta_i x + \gamma_i y) \\ N_j &= \frac{1}{2A}(\alpha_j + \beta_j x + \gamma_j y) \\ N_m &= \frac{1}{2A}(\alpha_m + \beta_m x + \gamma_m y) \end{aligned} \quad (6.9)$$

where

$$\begin{aligned} \alpha_i &= x_j y_m - y_j x_m \\ \alpha_j &= y_i x_m - x_i y_m \\ \alpha_m &= x_i y_j - y_i x_j \\ \beta_i &= y_j - y_m \\ \beta_j &= y_m - y_i \\ \beta_i &= y_i - y_j \\ \gamma_i &= x_m - x_j \\ \gamma_j &= x_i - x_m \\ \gamma_m &= x_j - x_i \\ 2A &= \begin{vmatrix} 1 & x_i & y_i \\ 1 & x_j & y_j \\ 1 & x_m & y_m \end{vmatrix} \end{aligned} \quad (6.10)$$

where A is the area of the triangular element. More information on the calculation of the shape functions can be found in Logan (1993); Zienkiewicz (1989).

The second stage in the formulation of the element equations is the establishment of a relationship between the potential gradient and the flux. If we define the gradient matrix as:

$$\{g\} = \begin{Bmatrix} \frac{\partial \phi}{\partial x} \\ \frac{\partial \phi}{\partial y} \end{Bmatrix} \quad (6.11)$$

then the flux can be written as:

$$\begin{Bmatrix} q_x \\ q_y \end{Bmatrix} = -[D] \{g\} \quad (6.12)$$

where the material property matrix is

$$[D] = \begin{bmatrix} k_x & 0 \\ 0 & k_y \end{bmatrix} \quad (6.13)$$

Using the Ritz formulation, the functional corresponding to Eq.6.5 may be written as π_h (Logan, 1993):

$$\pi_h = U + \Omega_\Omega + \Omega_q + \Omega_h \quad (6.14)$$

Where

$$U = \frac{1}{2} \iiint_V \left[k_x \left(\frac{\partial \phi}{\partial x} \right)^2 + k_y \left(\frac{\partial \phi}{\partial y} \right)^2 \right] dV \quad (6.15)$$

$$\Omega_\Omega = - \iiint_V Q \phi dV \quad (6.16)$$

$$\Omega_q = - \iint_{S_1} q \phi dS \quad (6.17)$$

$$\Omega_h = \frac{1}{2} \iint_{S_2} h (\phi - \phi_\infty)^2 dS \quad (6.18)$$

where S_1 and S_2 are portions of the boundary S over which potential flow q^* and convection loss $h(\phi - \phi_\infty)$ are specified, respectively and V is the element volume.

Substituting for ϕ and its spatial derivatives from Eq.6.6 into Equations 6.15 to 6.18,

Eq.6.14 can be written in matrix form as:

$$\begin{aligned} \pi_h = & \frac{1}{2} \iiint_V \{g\}^T [D] \{g\} dV - \iiint_V \{a\}^T [N]^T Q dV \\ & - \iint_{S_1} \{a\}^T [N]^T q^* dS \\ & + \frac{1}{2} \iint_{S_2} h \left(\{a\}^T [N]^T - \phi_\infty \right)^2 dS \end{aligned} \quad (6.19)$$

where the matrix $\{g\}$ is given by:

$$\{g\} = \begin{bmatrix} \frac{\partial N_i}{\partial x} & \frac{\partial N_j}{\partial x} & \frac{\partial N_m}{\partial x} \\ \frac{\partial N_i}{\partial y} & \frac{\partial N_j}{\partial y} & \frac{\partial N_m}{\partial y} \end{bmatrix} \begin{Bmatrix} a_i \\ a_j \\ a_m \end{Bmatrix} \quad (6.20)$$

which can also be written in compact form:

$$\{g\} = [B] \{a\} \quad (6.21)$$

where after substituting for N_i , N_j and N_k from Eq.6.9 into Eq.6.20, the matrix $[B]$ is:

$$[B] = \frac{1}{2A} \begin{bmatrix} \beta_i & \beta_j & \beta_m \\ \gamma_i & \gamma_j & \gamma_m \end{bmatrix} \quad (6.22)$$

If we substitute Eq.6.21 into Eq.6.19, and take the nodal values of the field variable outside the integrals, we obtain:

$$\begin{aligned}
\pi_h = & \frac{1}{2} \{a\}^T \iiint_V [B]^T [D][B] dV \{a\} - \{a\}^T \iiint_V [N]^T Q dV \\
& - \{a\}^T \iint_{S_1} [N]^T q^* dS \\
& + \frac{1}{2} \iint_{S_2} h \left(\{a\}^T [N]^T [N] \{a\} - (\{a\}^T [N]^T + [N] \{a\}) \phi_\infty + \phi_\infty^2 \right) dS
\end{aligned} \tag{6.23}$$

We now invoke the principle of minimum potential, by taking the derivative of Eq.6.23 with respect to the nodal values of the field variable and setting it equal to zero, we obtain:

$$\begin{aligned}
\frac{\partial \pi_h}{\partial \{a\}} = & \iiint_V [B]^T [D][B] dV \{a\} - \iiint_V [N]^T Q dV \\
& - \iint_{S_1} [N]^T q^* dS \\
& + \iint_{S_2} h [N]^T [N] \{a\} dS \\
& - \iint_{S_2} [N]^T h \phi_\infty dS = 0
\end{aligned} \tag{6.24}$$

Simplifying Eq.6.24, we obtain:

$$\left[\iiint_V [B]^T [D][B] dV - \iint_{S_2} h [N]^T [N] dS \right] \{a\} = \{f_Q\} + \{f_q\} + \{f_h\} \tag{6.25}$$

where

$$\begin{aligned}
\{f_Q\} &= \iiint_V [N]^T Q dV \\
\{f_q\} &= \iint_{S_1} [N]^T q^* dS \\
\{f_h\} &= \iint_{S_2} [N]^T h \phi_\infty dS
\end{aligned} \tag{6.26}$$

In Eq.6.26, the term $\{f_Q\}$ represents the source/sink, such as internal heat generation, $\{f_q\}$ is the specified flux on the boundary and $\{f_h\}$ is the convection. Eq.6.25 may be written more succinctly as:

$$[k]\{a\} = \{f\} \quad (6.27)$$

where

$$[k] = \left[\iiint_V [B]^T [D] [B] dV + \iint_{S_2} h [N]^T [N] dS \right] \quad (6.28)$$

is the element transfer matrix (e.g. element conduction matrix in the heat transfer problem). If we substitute Equations 6.8, 6.13, and 6.22 into Eq.6.28, we obtain the transfer matrix for a three node triangular element:

$$[k] = \iiint_V \frac{1}{4A^2} \begin{bmatrix} \beta_i & \gamma_i \\ \beta_j & \gamma_j \\ \beta_m & \gamma_m \end{bmatrix} \begin{bmatrix} k_x & 0 \\ 0 & k_y \end{bmatrix} \begin{bmatrix} \beta_i & \beta_j & \beta_m \\ \gamma_i & \gamma_j & \gamma_m \end{bmatrix} dV \quad (6.29)$$

$$+ \iint_{S_2} h \begin{bmatrix} N_i N_i & N_i N_j & N_i N_m \\ N_j N_i & N_j N_j & N_j N_m \\ N_m N_i & N_m N_j & N_m N_m \end{bmatrix} dS$$

The integrals in Eq.6.29 can be explicitly evaluated due to the simplicity of the shape functions used in the formulation. For more complex elements, the integration is generally performed using numerical integration techniques.

6.3.2. Assembly of Global Equations

The global finite element equations, which are a set of algebraic equations with their unknowns being the nodal values of the field variable (Bickford, 1994; Logan, 1993), are formed by summing the individual element equations, through the process of matrix assembly, and are solved by first imposing the proper boundary conditions and then solving them using one of the methods such as Gaussian elimination for solving simultaneous equations.

It should be pointed out that if the conductivity of the material is a function of the field variable, then the problem becomes nonlinear and an iterative scheme must be used to solve the problem.

6.4. Time-Dependent Formulation

When the governing differential equation of a physical problem is time-dependent, a different approach has to be followed during the formulation of the element equations and the solution of the global equations.

In the case of transient heat transfer in two dimensions, the governing equation is:

$$k\nabla^2 T = \rho c \frac{\partial T}{\partial t} \quad (6.30)$$

where T is the temperature, ρ is the density of the medium, c is its specific heat and t is the time. In the case of moisture transport in porous media, the following time-dependent governing equation must be solved:

$$D_h \nabla^2 h + D_T \nabla^2 T + Q_h = \frac{\partial w_L}{\partial h} \frac{\partial h}{\partial t} \quad (6.31)$$

where D_h is the isothermal moisture diffusion coefficient, D_T is the thermal moisture diffusion coefficient, h is the relative humidity, Q_h is the sink or source term, $\frac{\partial w_L}{\partial h}$ is the relationship between the liquid water and the relative humidity in the pore space, which under equilibrium conditions, can be approximated by using the adsorption isotherms.

If we consider the transient heat transfer problem, then the governing Eq.6.30 must be solved subjected to the following boundary conditions:

$$\frac{\partial T}{\partial n} + \alpha T = h(s, t) \quad \text{on } S_1 \quad (6.32)$$

$$T = g(s, t) \quad \text{on } S_2 \quad (6.33)$$

and the initial conditions:

$$T(x, y, 0) = c(x, y) \quad \text{on } S_2 \quad (6.34)$$

Using the procedures and notations of Section 6.3.1, the functional corresponding to Eq.6.30 can be written as (Logan, 1993):

$$\begin{aligned} \pi_h = & \frac{1}{2} \iiint_V \left[k_x \left(\frac{\partial T}{\partial x} \right)^2 + k_y \left(\frac{\partial T}{\partial y} \right)^2 - 2 \left(Q - c\rho \frac{\partial T}{\partial t} \right) T \right] dV \\ & - \iint_{S_1} q^* T dS \\ & + \frac{1}{2} \iint_{S_2} h (T - T_\infty)^2 dS \end{aligned} \quad (6.35)$$

Eq.6.32 can be written in the matrix form as:

$$\begin{aligned} \pi_h = & \frac{1}{2} \{a\}^T \iiint_V [B]^T [D] [B] dV \{a\} - \{a\}^T \iiint_V [N]^T Q dV + \\ & \iiint_V \rho c [N]^T \{a\} [N] \frac{\partial \{a\}}{\partial t} dV - \{a\}^T \iint_{S_1} [N]^T q^* dS \\ & + \frac{1}{2} \iint_{S_2} h \left(\{a\}^T [N]^T [N] \{a\} - (\{a\}^T [N]^T + [N] \{a\}) \phi_\infty + \phi_\infty^2 \right) dS \end{aligned} \quad (6.36)$$

where $\{a\}$ represents the nodal temperatures.

By using the principle of stationary potential, we take the derivative of Eq.6.36 with respect to nodal values of the field variable, $\{a\}$, to obtain:

$$\begin{aligned} \frac{\partial \pi_h}{\partial \{a\}} = & \iiint_V [B]^T [D] [B] dV \{a\} - \iiint_V [N]^T Q dV + \frac{\partial \{a\}}{\partial t} \iiint_V \rho c [N]^T [N] dV \\ & - \iint_{S_1} [N]^T q^* dS + \iint_{S_2} h [N]^T [N] \{a\} dS - \iint_{S_2} h [N]^T \phi_\infty dS = 0 \end{aligned} \quad (6.37)$$

Using the previous definitions for the transfer and force matrices, Eq.6.37 leads to the following element equations:

$$[k]\{a\} + [m]\{\dot{a}\} = \{f\} \quad (6.38)$$

Where $[k]$ and $[m]$ are the same as in Eq.6.27,

$$[m] = \iiint_V c\rho[N]^T[N]dV \quad (6.39)$$

and the superscript dot denotes differentiation with respect to time.

For an element of constant thickness, b , Eq.6.39 can be rewritten as:

$$[m] = c\rho b \iint \begin{bmatrix} N_i N_i & N_i N_j & N_i N_m \\ N_j N_i & N_j N_j & N_j N_m \\ N_m N_i & N_m N_j & N_m N_m \end{bmatrix} dA \quad (6.40)$$

The solution of Eq.6.38 has to be carried out by using one of the numerical time integration schemes. In the current implementation, Newmark's method (Newmark, 1959), which is one of the most widely used numerical time integration schemes, has been used.

The numerical integration methods start with the assumption of two initial states of the physical variable; ϕ_i at time t_i and ϕ_{i+1} at time t_{i+1} which are related by:

$$\phi_{i+1} = \phi_i + [(1 - \beta)\dot{\phi}_i + \beta\dot{\phi}_{i+1}](\Delta t) \quad (6.41)$$

Eq.6.41 is known as the *general trapezoidal rule*, where the parameter, β , is chosen by the user. The global equation corresponding to the entire domain of interest:

$$[K]\{A\} + [M]\{\dot{A}\} = \{F\} \quad (6.42)$$

If we write Eq.6.42 for time t_i and t_{i+1} , then if we multiply the former with $(1-\beta)$ and the latter with β , we obtain:

$$(1 - \beta)(\mathbf{K}\mathbf{A}_i + \mathbf{M}\dot{\mathbf{A}}_i) = (1 - \beta)\mathbf{F}_i \quad (6.43)$$

$$\beta(\mathbf{K}\mathbf{A}_{i+1} + \mathbf{M}\dot{\mathbf{A}}_{i+1}) = \beta\mathbf{F}_{i+1} \quad (6.44)$$

where the bold symbols denote vectors and matrices.

Adding Equations 6.43 and 6.44, we obtain:

$$\mathbf{M}\left[(1 - \beta)\dot{\mathbf{A}}_i + \beta\dot{\mathbf{A}}_{i+1}\right] + \mathbf{K}\left[(1 - \beta)\mathbf{A}_i + \beta\mathbf{A}_{i+1}\right] = (1 - \beta)\mathbf{F}_i + \beta\mathbf{F}_{i+1} \quad (6.45)$$

If we eliminate the derivative terms and rearrange the equation, we get:

$$(\mathbf{M} + \mathbf{K}\beta\Delta t)\mathbf{A}_{i+1} = [\mathbf{M} - \mathbf{K}(1 - \beta)\Delta t]\mathbf{A}_i + [(1 - \beta)\mathbf{F}_i + \beta\mathbf{F}_{i+1}]\Delta t \quad (6.46)$$

Eq.6.46 provides the time-marching scheme to solve $\mathbf{A}_{i+1}$ using a time step Δt , and knowing the initial conditions $\mathbf{A}_i$ at the beginning of the time step. Any standard method of solution for simultaneous algebraic equations can be employed to solve the system of equations in Eq.6.46.

It has been shown that (Hughes, 2000) depending on the value of β , the time step may have an upper limit for the numerical integration to be stable. If $\beta < 0.5$, the largest value of Δt can be:

$$\Delta t = \frac{2}{(1 - 2\beta)\lambda_{\max}} \quad (6.47)$$

where $\lambda_{\max}$ is the largest eigenvalue of

$$(\mathbf{K} - \lambda\mathbf{M})\mathbf{A}' = 0 \quad (6.48)$$

where $\mathbf{A}'$ represents the natural modes.

For $\beta \geq 0.5$, the numerical analysis is unconditionally stable. It has to be noted that this does not mean that the accuracy of the solution is guaranteed. If $\beta = 0$, the

method is called “Forward Difference” or “Euler Method” (James and Smith, 1985) which is said to be conditionally stable in which Δt must be less than the value given by Eq.6.47; while when $\beta = 0.5$, it is referred to as “Crank-Nicolson” or “Trapezoid” Rule which is unconditionally stable. When $\beta = 3/2$ or $\beta = 1$, the methods are unconditionally stable and are called the “Galerkin’s” and the “Backward Difference” methods, respectively. It has to be noted that all of the methods explained above can be used in the proposed finite element model. In the examples solved in the current thesis, the Crank-Nicolson rule was utilized.

6.5. Nonlinear Solution Scheme

In the previous sections, we addressed the solution of linear differential equations such as Eq.6.30 and 6.31, in which the material properties, i.e. k , D_h , D_T , were constants. The finite element formulation of linear differential equations leads to a set of linear algebraic equations, which can be solved simultaneously by using one of the known methods such as Gaussian elimination. The linear algorithm is often used in practice and is deemed satisfactory in general. However, in certain cases the material properties can be strongly dependent on the magnitude of the field variable. For example, as implied in Eq.3.27, the moisture diffusion coefficient, D_h is a function of the relative humidity, h . In these situations, the finite element formulations lead to a nonlinear system of equations as given in Eq.6.49, which have to be treated differently, and generally require a numerical solution scheme.

Ignoring the $\{\dot{A}\}$ term, the nonlinear form of the global equation of the system given in Eq.6.42 can be written as:

$$[K(A)]\{A\} = \{F\} \quad (6.49)$$

where K is a function of the nodal values of the field variable, A . Generally, the solution scheme follows a trial and error process in which an initial estimate for the solution is refined through a series of iterations.

There are several methods (Isaacson and Keller, 1966; Ortega and Rheinboldt, 1970; Bicanic and Johnson, 1979; Gill et al., 1981) for the numerical solution of nonlinear differential equations, but since in this study only the Substitution, the Newton-Rapson and the Modified Newton-Rapson Methods are used, they will be explained in the following sections.

6.5.1. The Substitution Method

The substitution method (Dhatt and Touzot, 1984) consists of constructing a series of solutions $\{A^0\}$, $\{A^1\}$, $\{A^2\}$, ... $\{A^i\}$, where $\{A^i\}$ is calculated from the previous value $\{A^{i-1}\}$ and solving the linear system:

$$[K(A^{i-1})]\{A^i\} = \{F\}; \quad i = 1, 2, 3, \dots \quad (6.50)$$

Note that at the end of each solution, $[K]$ is updated and the calculated nodal values are compared with the corresponding values in the previous iteration and by using a convergence norm, the iterations are terminated when the norm is satisfied. The rate of convergence is dependent on the initial estimate, $\{A^0\}$, and the nature of the problem. The substitution method is generally used when the physical problem is mildly nonlinear

or the severity of the nonlinearity is not known. This method is also useful if the response to only one value of maximum applied effect; i.e. $\{F\}$, is sought.

6.5.2. The Newton-Rapson Method

The Newton-Rapson Method (Bicanic and Johnson, 1979) is probably the most rapidly converging process for the solution of nonlinear equations. The formulation of the method is also very simple and follows the following steps.

Presume that an approximation of $\{A^{i-1}\}$ has the following residual:

$$\{R(A^{i-1})\} = \{F\} - [K(A^{i-1})]\{A^{i-1}\} \neq 0 \quad (6.51)$$

For iteration i , we look for an approximation A^i such that:

$$\{R(A^i)\} = \{R(A^{i-1} + \Delta A^i)\} \approx 0 \quad (6.52)$$

If the residual function is expanded as a Taylor series in the neighborhood of A^i :

$$\{R(A^{i-1} + \Delta A^i)\} = R(A^{i-1}) + \left[\frac{\partial R}{\partial A} \right]_{A=A^{i-1}} \{\Delta A^i\} + \dots = 0 \quad (6.53)$$

Neglecting all terms of orders higher than one, we obtain:

$$-\left[\frac{\partial R}{\partial A} \right]_{A=A^{i-1}} \{\Delta A^i\} = R(A^{i-1}) \quad (6.54)$$

where $-\left[\frac{\partial R}{\partial A} \right]_{A=A^{i-1}}$ can be obtained by differentiating Eq.6.51 with respect to $\{A\}$ at A^{i-1} :

$$[K_T] = -\left[\frac{\partial R}{\partial A} \right]_{A=A^{i-1}} = [K(A)] + \left[\frac{\partial [K(A)]}{\partial A} \{A\} \right] \quad (6.55)$$

where $[K_T]$ is the Jacobian matrix corresponding to the tangent direction. This gives an iterative correction as:

$$\{\Delta A^i\} = [K_T]^{-1} R(A^{i-1}) \quad (6.56)$$

The improved value, $\{A^i\}$, can be calculated as:

$$\{A^i\} = \{A^{i-1}\} + \{\Delta A^i\} \quad (6.57)$$

When a convergence norm between the current and the previous values of the iterations becomes smaller than a user defined value, the iterations can be terminated.

Although it provides the fastest rate of convergence, the Newton-Rapson method has two disadvantages: First of all, a new $[K_T]$ matrix has to be formed and solved for in each iteration. Secondly, in certain cases, the $[K_T]$ matrix, which is initially symmetric, may become non-symmetric which may require non-symmetric solvers. To overcome these problems, the Modified Newton-Rapson method has been developed.

6.5.3. The Modified Newton-Rapson Method

The Modified Newton Rapson method (Ortega and Rheinboldt, 1970) uses exactly the same solution algorithm as the Newton-Rapson method with a small difference. It replaces the variable Jacobian matrix $[K_T]$ by a constant approximation:

$$[K^m_T] \approx [K_T] \quad (6.58)$$

where $[K^m_T]$ is the modified constant Jacobian matrix and is generally chosen as the Jacobian corresponding to the first iteration at any increment or step. The procedure will generally converge at a slower rate but the difficulties mentioned in relation to the Newton-Rapson method will disappear (Zienkiewicz, 1991).

6.5.4. Convergence Norms

In nonlinear solutions, the iteration continues until the convergence norm is satisfied. Two norms are commonly used in the convergence test: the maximum norm and the Euclidian norm. The maximum norm can be defined as (Heinrich and Pepper, 1999):

$$\|n\| = \text{Max}|\Delta A_j^i| \quad (6.59)$$

where j is the number of nodes in the model and the norm $\|n\|$ represents the largest difference in the absolute values of the nodal values of the field variable between current and previous iterations.

The Euclidian norm can be defined as (Heinrich and Pepper, 1999):

$$\|n\| = \sqrt{\sum_j \{\Delta A^i\}^2} \quad (6.60)$$

where the norm $\|n\|$ represents the square root of the sum of the squares of all of the nodal differences between the current and the previous iterations. When the norm is smaller than a predefined convergence criterion, ϵ , the iterations is terminated. For the proposed finite element model ϵ is selected to be 10^{-6} .

As stated earlier, in the current study the choice of the solution scheme is left to the user, but the modified Newton-Rapson method is adopted as the default option.

7. The Program: CONDUR

7.1. General

The proposed durability model, which was explained in Chapter 5, is implemented in a two-dimensional time-dependent nonlinear finite element program, called CONDUR (CONcrete DURability). This chapter will give general information about the program including its specifications and capabilities. How to use the program will be demonstrated through actual screen shots from CONDUR.

7.2. Program Development and Specifications

CONDUR runs under Microsoft Windows (Windows 95 or higher) and comprises two main modules: The Graphical User Interface (GUI), which is responsible for data input and storage and presentation of the results, and the Engineering module, which handles all of the engineering routines including the finite element solver. GUI has been developed by using Microsoft Visual C++ Version 6.0 to achieve the standards of the highest quality commercial software packages and makes the program as user friendly as possible. Object oriented programming (OOP) technique has been used to accommodate the complicated data structures and Windows features. The engineering routines are developed by using Digital FORTRAN Version 6.0A Standard Academic Edition.

There are several reasons for choosing these compilers for the development of the engineering and GUI routines and these can be outlined as follows:

1. Both compilers work under 32-bit memory allocation system that is assumed to be the current industry standard. This guarantees a long shelf life for the program and easy upgrade possibilities when the standards change in the future.
2. Fortran is the most widely used programming language in engineering calculations, particularly in the field of finite element analysis. Using Fortran for programming allows us to utilize existing finite element routines that can be found in the literature, and save significant amount of time by avoiding repetitive work.
3. Digital Fortran 6.0A and Microsoft Visual C++ 6.0 are fully compatible with each other such that GUI and engineering routines can be compiled under one project without any conflict issues. This means that any engineering function developed by Fortran can be called directly by the GUI functions developed in Visual C++. This allows us to develop a fast, efficient, and an industry standard program, which are missing generally in the civil engineering software applications.
4. Microsoft Visual C++ 6.0 compiler is the industry standard for developing high-end commercial software packages with user-friendly GUI's. Any program developed by this compiler will be upgraded easily as the technology improves. Any other software package that is developed by C++ can be incorporated in the program. There are a significant number of data manipulation and graphics software packages that can improve the capabilities of the program.

CONDUR is designed to solve problems up to 10,000 nodes. This allows us to model the structures as realistically as possible by using very fine meshes and accurately model local imperfections such as cracks in concrete. In order to handle the load created by the intensive finite element processes when a large number of nodes are used in fine meshes, CONDUR requires at least 128MB of RAM. Although the program requires only 20 MB of hard disk space for installation, due to the large size of the output files, at least 500 MB of free space is recommended.

7.3. Data Input Module (GUI)

As explained in the previous chapters, the modeling of the service life of a reinforced concrete structure by the finite element method is a very complex problem which requires the analysis of heat and moisture transfer as well as of chloride, carbon dioxide and oxygen transport in the concrete and their effects on the corrosion of the steel reinforcement. Each of these analyses requires the definition of the geometry, the selection of the finite elements and discretization of the geometry, the identification of the material properties, and material models, and the specified initial and boundary conditions. The required data for such a set of analyses is significantly large and difficult to input for the user. Similarly, the results of each analysis can be quite voluminous and difficult for the user to interpret. For instance, consider the analysis of a 1000-node finite element model, comprising triangular elements, for the determination of temperature, moisture, chloride, carbon dioxide, oxygen profiles and amount of rust formation. If we wish to run the analyses for five years of exposure with a time increment of one day, the

required input data, in the text format, occupies more than 5 MB of disk space. The output generated by the program, i.e. the daily nodal temperatures, relative humidities, chloride, carbon dioxide and oxygen concentrations as well as the amount of rust produced, over a five-year period occupies almost 100 MB of disk space. The program CONTUR is designed to be as user friendly as possible to handle these issues. The input data generation is achieved through a series of easy-to-use screens as indicated in Figures 7.1 to 7.20. In order to minimize errors in input, the values are checked as the user enters the data. The results obtained by the program are presented in text and graphical formats.

The main screen of the program can be seen in Figure 7.1. This screen contains four parts: data input section, analysis section, mesh plot screen and activity log screen. The data input section is composed of a series of buttons, which activate the dialog boxes that are used to input the general project information, the exposure conditions, the geometry, and the concrete and reinforcement properties. After the data input is completed, the analyses to be run can be selected by checking the boxes provided in the analysis section. Clicking on the ANALIZE button activates the analysis. Once the analysis is completed, the results can be seen by clicking on the RESULTS button. Each step of the analysis process is logged in the activity log screen.

Every analysis starts with the definition of the general project parameters as indicated in Figure 7.2. In this screen, the user can input information about the project as well as the latitude and longitude of the location of the structure to be analyzed.

Figure 7.1: The main screen for the program CONDUR

Project Information

[Empty Box]

Jul/8/2001

40. North

[Empty Box]

74. East

[Empty Box]

[Empty Box] [OK]

Figure 7.2: Project information screen

As shown in Figure 7.3, the user can define different and unlimited number of exposure profiles, which simulate the temperature, moisture, chloride, O_2 and CO_2 variations on the boundary of the structure under consideration. Each profile can be entered either manually, by clicking on the EDIT which activates the screen shown in Figure 7.6, or loaded from a predefined library by clicking on "Load From Library" which activates the screen shown in Figures 7.5. The libraries can be customized as shown through the Library dialog box indicated in Figure 7.4 and saved with a CDL extension so that it can be used later by other projects. The boundary conditions can be defined monthly, daily or hourly which allows the user to select the accuracy level of the analysis.

Figure 7.3: Exposure profile screen

Figure 7.4: Library edit screen

Figure 7.5: Library loading dialog box

Figure 7.6: Exposure profile edit screen

The nodes and the elements are defined in the geometry screen shown in Figure 7.7. The nodes and elements can be defined manually by using ADD, MODIFY and DELETE buttons or can be generated automatically by clicking on the GENERATE button which activates the screen indicated in Figure 7.8.

The proposed durability model and the accompanying program CONDUR can use four, eight and nine node quadrilateral and three and six node triangular elements. The program allows the user to create transition elements to refine the mesh in zones where the gradient of the field variables may be steeper.

For each node, the user can define the initial conditions and a boundary value profile as indicated in Figures 7.9 and 7.10, respectively. The user can select a boundary value profile over time (monthly, daily or hourly), or a constant pattern can be used. The zero diffusion nodes (isolated surfaces, etc) can be easily modeled by selecting "Use constant temperature", "Use constant moisture", "Use constant chloride concentration", "Use constant oxygen concentration" or "Use constant carbon dioxide concentration" and setting the values to zero.

All of the elements are initially generated as concrete elements. The elements, which will be used to model the reinforcement, must be converted to steel elements by the dialog box, which is shown in Figure 7.11 that can be activated by clicking on the "Steel/Conc." button in geometry screen.

Figure 7.7: Geometry (mesh generation) screen

Generate Nodes and Elements

Block #1

Cartesian

4-node elements

3-node triangles (type 1)

3-node triangles (type 2)

3-node triangles (type 3)

0	0	0	0	0
0	0	0	0	0
0	0	0	0	0
0	0	0	0	0
0	0	0	0	0

Figure 7.8: Automatic node and element generation screen

Initial Conditions

22

0.6

50

0.

0.

Figure 7.9: Initial conditions edit screen

Loading

☐	0.	☐	0.
	0		1
☐	1 2 3 0	☐	0.
	0		1
☐	0.	☐	0.
	0		0

Figure 7.10: Nodal prescribed value editing screen

Figure 7.11: Element material selection dialog box

Concrete properties can be entered from the screen shown in Figure 7.12. General properties of the cement used to produce the concrete; the heat and mass transfer properties, adsorption isotherms, chloride binding / release models and the carbonation decay functions are input in this screen. There is also the possibility of overwriting any diffusion coefficients with the reference values by selecting the corresponding option.

The final stage of the data input involves entry of information about the steel reinforcement. If the program is used to determine the heat, moisture, chloride, oxygen, or carbon dioxide profiles only; i.e., if a corrosion analysis is not performed, this stage of the data input is not necessary. The main purpose of the reinforcement properties screen is to determine the steel elements which will act as anodes and cathodes during the corrosion process. There are three options for the determination of the anodic and cathodic sites: The first option is to leave the selection process to the program which will identify the elements where the passivating layer is lost and assign those sites as anodes. In order for this process to run correctly, the initiation stage analyses must be completed before the corrosion analysis and there must be local concentration or pH differences at the end of these analyses. For example, if the concentration of the chloride ions and the pH of the pore solution is the same at each node along the steel surface, the program will

Figure 7.13: Adsorption isotherm selection dialog box

Figure 7.14: Chloride binding isotherm selection and edit dialog box

Figure 7.15: Reinforcement properties screen

7.4. Engineering Module

Once the input data is complete, the user can use the program CONDUR to conduct different analyses to determine the service life of the reinforced concrete structure, which are executed by the engineering module. The engineering module, which is written in Fortran language, runs in the background of the GUI as a separate executable and consists of a two-dimensional transient nonlinear finite element engine

and subroutines which are used to prepare the input data for the finite element routines and post-process the results.

7.4.1. Phenomena Analyzed

The purpose of the program CONDUR is to model the chloride and carbonation induced reinforcement corrosion phenomena in concrete structures. The carbonation process, which is a chemical reaction between Ca(OH)_2 in the hydrated cement paste and the dissolved CO_2 , reduces the alkalinity (pH) of the pore solution which may cause the depassivation of the protective layer around the reinforcement. Similarly, if the chloride ion concentration exceeds a threshold value, the steel may also lose its protecting layer. Therefore, the modeling of CO_2 and chloride ingress in concrete is crucial in the determination of the beginning of the corrosion process. When the protective layer is lost, in the presence of oxygen and water, the reinforcing steel may corrode, eventually resulting in the failure of the concrete structure. Hence, the amount of oxygen and moisture around the steel reinforcement during the service life of the structure must also be monitored. Since the CO_2 , chloride, oxygen and moisture transport processes are dependent on the temperature, a heat transfer analysis has to be conducted to determine the temperature profile within the concrete structure. The estimation of the rate and amount of corrosion in steel requires the determination of the current densities at the anodic and cathodic locations on the steel surface. These current densities can be calculated if the electric potential distribution in the concrete surrounding steel reinforcement is known.

Summarizing, the corrosion of steel reinforcement in concrete, as a result of carbonation and chloride attack, is a transient electrochemical process, which is dependent on many factors such as temperature, moisture content, pH, chloride and oxygen concentrations of the concrete surrounding the reinforcement and can be quantified by calculating the amount of rust produced around the reinforcement. All of these phenomena mentioned above are governed by the general quasi-harmonic equation whose solution can be obtained by using the finite element method if the initial and boundary conditions of the problem are known.

The engineering module of the program CONDUR uses a transient finite element technique to solve the nonlinear two-dimensional equations governing heat, moisture, chloride, carbon dioxide and oxygen transfer as well as the electric potential distribution in concrete.

7.4.2. Finite Element Formulation

Finite element solution of differential equations governing the phenomena explained in the previous section begins with the selection of a suitable finite element(s) of known shape used to discretize the domain of interest. The program CONDUR can use triangular as well as four, eight and nine node quadrilateral and transition elements. The field variable is approximated over each element using predefined interpolation functions, known as shape functions, and nodal values of the variable.

The equations are cast as a system of algebraic equations based on the Ritz finite element formulation (Heinrich and Pepper, 1999), which requires the representation of the governing differential equation as a functional and the implementation of principle of

minimum potential. The resulting nonlinear equations are solved using an iterative technique based on one of the available numerical solution algorithms; i.e. modified Newton-Rapson, Newton-Rapson or Substitution methods. The Newmark method (Newmark, 1959) is adopted as the numerical integration scheme to solve the time-dependent problems.

7.5. Program Execution

Once the data input is complete, the user can select the type of analysis; i.e. "Heat Transfer", "Moisture Transfer", "Chloride Transfer", "CO₂ Transfer and Carbonation", "O₂ Transfer" or "Corrosion Analyses", that he wants to run by checking the boxes in the analysis section as shown in Figure 7.1. Individual or a combination of analyses may be selected for execution. For example, the program can be used just to determine the temperature profile by selecting only the "Heat Transfer" or to determine heat, moisture and CO₂ profiles by selecting the corresponding options.

It is important to mention that some of the analyses need the results of the other analyses. For example, the moisture transfer analysis requires the temperature profile in concrete to determine the moisture diffusion coefficients in each element. Similarly, the chloride, CO₂ and O₂ transfer analyses require the temperature and moisture profiles in concrete. When the required analyses are not complete, the program asks the user either to run the required analyses or to enter values for the required values as indicated in Figure 7.16. For example, if the corrosion analysis option is checked in the main screen indicated in Figure 7.1, and if the initiation stage analyses (heat, moisture, chloride, CO₂ and O₂ transfer) have not been completed previously, the dialog box, which is indicated

in Figure 7.16, pops up and asks for the manual entry of the missing profiles around the steel reinforcement. Once this step is complete, the analysis starts and runs the corrosion analysis.

Figure 7.16: Missing data warning screen

After the selection of the type of analysis to be carried out, the analysis can be activated by clicking on the ANALYZE button. This activates the “Analysis Data” dialog box shown in Figure 7.17, wherein the user selects the start and the end dates of the analysis and the time increments that will be used during this time span. The user has the option of selecting the nonlinear solution algorithm to be used by the program. The default option is the modified Newton-Rapson method, but the Newton-Rapson or Substitution methods can also be used. The number of maximum iteration steps must be

entered to limit the number of iterations for convergence during the nonlinear analysis. If the intention of the user is just to check the input data and not run the analysis, “Only create input data field without running analysis”, which can be seen in Figure 7.16, box can be checked. In addition to this, the results represented as colour coded contour plots can be printed as postscript files if the corresponding option is selected.

Figure 7.17: Analysis data screen

Once the OK button in the “Analysis Data” dialog box is clicked, a text file is generated for each of the selected analyses in which all of the information, which is required to conduct the finite element analyses, is written. The engineering module of the program CONDUR reads this file, solves the problem and writes the results to another

text file, which is read by the GUI. When more than one type of analysis is selected, the execution follows the following order:

1. Heat transfer
2. Moisture transfer
3. CO₂ transfer and carbonation
4. Chloride transfer
5. O₂ transfer
6. Corrosion analysis

7.6. Program Results

When the selected analyses are completed and the results are stored by the GUI, the user has different options to view them. As it can be seen in Figure 7.18, there is an option of batch printing in CONDUR. The user may select any of the input data or the results and print them on paper, on screen or into a text file. The screen output of a sample heat transfer analysis can be seen in Figure 7.19. As a second option, the results of the analyses can also be viewed as colour coded contour plots as indicated in Figure 7.20. These plots can also be printed as postscript files.

Figure 7.18: Print screen

Print Screen

HEAT TRANSFER RESULTS

Units: oC

NODE	t = 0%	t = 25%	t = 50%	t = 75%	t = 100%
1	-10.000	8.000	28.000	22.000	2.000
2	-10.000	8.000	28.000	22.000	2.000
3	-10.000	8.000	28.000	22.000	2.000
4	-10.000	2.966	23.654	27.767	2.651
5	-10.000	1.661	22.523	29.170	2.905
6	-10.000	0.999	21.947	29.829	3.081
7	-10.000	0.653	21.645	30.139	3.206
8	-10.000	0.461	21.476	30.289	3.295
9	-10.000	0.354	21.382	30.361	3.355
10	-10.000	0.300	21.334	30.393	3.390
11	-10.000	0.283	21.319	30.402	3.401
12	-10.000	4.769	25.215	25.796	2.330
13	-10.000	4.644	25.106	25.929	2.355
14	-10.000	3.804	24.379	26.854	2.498
15	-10.000	2.684	23.409	28.071	2.705
16	-10.000	1.520	22.400	29.315	2.938
17	-10.000	0.947	21.902	29.876	3.099
18	-10.000	0.629	21.624	30.157	3.217
19	-10.000	0.449	21.465	30.296	3.303
20	-10.000	0.347	21.375	30.364	3.361
21	-10.000	0.295	21.329	30.394	3.395
22	-10.000	0.278	21.315	30.402	3.406

Figure 7.19: Presentation of analysis results

Figure 7.20: Presentation of analysis results in the contour format

8. Verification of the Proposed Model and Numerical Simulations

8.1. General

In this chapter, the initiation and propagation stages of the proposed durability model and its associated computer program, CONDUR, will be tested and verified by several examples. Despite the fact that a significant amount of experimental data exists for the initiation stage, albeit most are from one-dimensional simulations, and some for the reinforcement corrosion, i.e. propagation stage, it is difficult to obtain experimental studies that test the combined processes of initiation and propagation. A recent study conducted by Li (2001) provides probably one of the most comprehensive examinations of chloride-induced reinforcement corrosion with special attention to both initiation and propagation stages and is used in this chapter for the verification of the proposed model.

8.2. Heat Transfer Model

The heat transfer module of the proposed service life model and its associated computer program, CONDUR, are compared with the results of the problem defined and solved by Sucec (1985). In conformity with his solution and to simplify the comparison, we maintain the original US customary units in this problem.

Figure 8.1(a) shows a plate, insulated on two sides, as indicated by the hatched lines, and exposed to two temperature levels on the other two faces. Initially, the plate and its upper and the lower faces are at 100°F. Suddenly, the lower face is exposed to 1000°F fluid with a surface coefficient of heat transfer of 30 Btu /hr ft² °F between the fluid and the lower face. The fluid bounding the upper face remains at 100°F with a surface coefficient of heat transfer of 100 Btu /hr ft² °F. The coefficient of heat conductivity, k , is given as 30 Btu /hr ft °F.

Sucec (1985) used a finite difference computer program and ran the program over six time intervals up to 17 minutes and presented the temperature variation at points A, B, C, D, E, F, G and H (see the location of these points in Figure 8.1(a)). In the present analysis, the plate is divided into 600 triangular elements comprising 352 nodes as shown in Figure 8.1(b) and solved by using the program CONDUR. The analysis is run for 20 minutes with 10-second time intervals. The results of the finite element analysis are compared with Sucec's finite difference results in Figure 8.2.

It can be seen from Figure 8.2 that the proposed FEM method agrees closely with Sucec's finite difference solution at all times. The small differences are expected due to the difference in the accuracy of the two methods. The largest difference is 2.929% at point E at $time = 17$ minutes.

(a)

(b)

Figure 8.1: (a) Plate subjected to prescribed temperature on its edges
 (b) The finite element mesh used to model the heat transfer in the plate

Figure 8.2: Comparison of the proposed FEM and Sucec's solution

8.3. Chloride Ingress Model

The proposed finite element model and its associated computer program, CONDUR, are compared with a one-dimensional experimental study on chloride transfer in concrete conducted by Costa and Appleton (1999), and two two-dimensional studies conducted by Suryavanshi et al. (1998) and Zemajtis and Weyer (1999).

8.3.1. Experimental Data from Costa and Appleton (1999)

Costa and Appleton (1999) tested fifty-four 1000 x 500 x 120-mm concrete panels for one-dimensional chloride ingress. All faces, except one, were protected with epoxy paint so that the chloride penetration could take place through one face only. Three concrete mixes, whose properties are given in Table 8.1, were studied. An ordinary portland cement with the following mineral composition was used to prepare the specimens: C₃S: 53.86%, C₂S: 15.58%, C₃A: 8.12%, C₄AF: 9.42%.

The tests were conducted in the naval complex of Setenave located in the river Sado estuary in Setubal peninsula facing the Atlantic Ocean towards South and West. It has to be noted that the estuary water contained 16-21 g/l Cl⁻ ions. The environmental characteristics reported in this location in the period from 1974 to 1990 are (Costa and Appleton, 1999): annual average temperature: 16.8°C; monthly average temperature: 11.1°C (January), 22.7°C (July); annual average relative humidity: 70%; monthly average relative humidity: 80% (January), 60% (July). Costa and Appleton (1999) also provided the monthly atmospheric chloride content in this location, which is given in Table 8.2.

Concrete panels were tested at five locations, each representing different exposure conditions. These zones were: Zone A: spray zone, Zone B: tidal zone, Zone C:

atmospheric zone, Zone D: dockyard 20 and Zone E: dockyard 21. Among 54 panels, which were prepared using three types of concrete, C1, C2 and C3, and tested under five exposure conditions, three panels from Zone C (atmospheric zone) and three panels from Zone D (dockyard 20) were analyzed by the proposed finite element model. Since the information provided for other exposure conditions was not enough, panels in these zones were not analyzed.

The panels in Zone C (atmospheric zone) were analyzed by using the exposure conditions given in Table 8.2. The panels in Zone D were also under the same environmental conditions, but in addition they were subjected to 22 wetting and drying cycles over a four-year period due to the filling and emptying of the dockyard 20 by estuary water. During the wetting cycles, the panels were assumed to be exposed to the chloride ions dissolved in the estuary water, which was penetrating the concrete through convection. A constant chloride concentration of 20 g/l for the estuary water is used in the current analysis. During the drying cycles, the atmospheric chloride, whose concentration variation is given in Table 8.2, was assumed to be penetrating the concrete through diffusion.

**Table 8.1: Mix proportions of the concrete specimens tested by
Costa and Appleton (1999)**

Concrete Type	Water-cement ratio	Aggregate-cement ratio
	(w/c)	(a/c)
C1	0.35	3.50
C2	0.30	4.49
C3	0.50	6.51

Table 8.2: The natural exposure conditions of Costa's specimens

Month	[Cl] (mg/m ² /day)	RH (%)	T (°C)	Exposure
Jan.	260	80	11.1	6, 12, 24, 36 and 48 Months
Feb.	45	76	14	
Mar.	80	72	16	
Apr.	20	68	18	
May	40	64	20	
Jun.	15	62	21.5	
Jul.	20	60	22.7	
Aug.	25	60	21	
Sep.	20	65	17	
Oct.	40	70	15	
Nov.	155	73	13.5	
Dec.	95	77	12	

Table 8.3: Input parameters used in the modeling of Costa's specimens

Parameter	Value
Longitude	9° W
Latitude	38.7° N
Specific heat	1000 J/kg°C
Coefficient of conduction	2 W/m°C
Coefficient of convection	3 W/m ² °C
Coefficient of radiation	13.5 W/m ² °C
Emissivity of gray concrete	0.9
Absorptivity	1
Density of concrete	2400 kg/m ³
Adsorption isotherm	BET
Chloride binding	Freundlich: $\alpha = 1.0$, $\beta = 0.3$
Chloride release	No release
Carbonation decay	No carbonation

The assumed input parameters necessary for the finite element analysis are given in Table 8.3. BET adsorption isotherm was used to relate the evaporable water content with the water vapour content. Chloride binding was simulated by Freundlich isotherm in which α and β were taken as 1.0 and 0.3, respectively. Since the effect of carbon

dioxide exposure was not considered, no model for carbonation decay or chloride release has been used.

(a)

(b)

Figure 8.3: (a) The finite element mesh used to model one-dimensional chloride ingress
(b) Chloride diffusion front plot from CONDUR for the model in (a)

The finite element mesh in Figure 8.3(a) was used to simulate this one-dimensional chloride diffusion problem in the panels. 160 triangular elements were used to discretize the geometry, Figure 8.3(a). Only the nodes along the bottom edge of the mesh was exposed to chlorides while the other edges were assumed to be insulated. Analysis was carried out over a 36-month period with time increments of one day. Figure 8.3(b) shows a typical profile of this one-dimensional chloride ingress obtained from the current analysis.

We notice that the proposed finite element model and its associated computer program, CONDUR, predict the experimental results provided by Costa and Appleton (1999) quite accurately as indicated in Figures 8.4 to 8.6. Figure 8.4 shows the chloride penetration depth through C1-type panels under the exposure conditions of dockyard 20 (Zone D) after 6, 24 and 36 months. The effect of concrete type and quality on the chloride penetration can be observed in Figure 8.5 which shows the chloride penetration depth through the C1, C2 and C3-type panels after 36 months of exposure in dockyard 20 (Zone D). The chloride penetration is significantly larger for C3-type panels, whose water-cement-ratio is higher, than the C1 and C2-type panels. Higher w/c results in higher porosity, which causes larger diffusion coefficients for the liquid water and chloride ions. This shows the importance of the quality of concrete on the ingress of the corrosive agents in concrete.

Figure 8.6 shows a comparison between the chloride penetration in C1-type panels in the exposure conditions of Zone C (atmospheric exposure) and Zone D (dockyard 20) after 36 months. It has to be noted that there is no wetting or drying in Zone C, where the main source of chlorides is the natural exposure. The penetration of

these chloride ions also follows a diffusion type flow, which is at a slower rate than the transport through convection of liquid water. On the other hand, the panels in Zone D are exposed to wetting and drying cycles. During wetting, chloride ions are transported into concrete by the convection of liquid water. During drying, the water evaporates but the chloride ions remains in the concrete. This zone, which can be defined in Figure 8.6 as the region 15 mm from the exposed boundary, is called the convection zone. Chloride ions, which are deposited in the convection zone by the liquid water, follow a diffusion-type flow afterwards.

Figure 8.4: Chloride penetration profile of C1-type panels under the exposure conditions of Dockyard 20 (Zone D) after 6, 24 and 36 months

Figure 8.5: Chloride penetration profile through the C1, C2 and C3-type panels after 36 months of exposure in Dockyard 20 (Zone D)

Figure 8.6: Chloride penetration profile in C1-type panels in exposure zones C and D after 36 months

8.3.2. Experimental Data from Suryavanshi et al. (1998)

Suryavanshi et al. (1998) tested a number of slabs to investigate the effect of lateral gradient on the chloride penetration. Some of the slabs were partially coated with a surface coating system known to be highly resistant to chloride penetration. Figure 8.7 shows the experimental setup and the dimensions of the specimens used in this study.

Figure 8.7: The test setup used by Suryavanshi et al (1998)

Although six types of slabs were tested in the study, only three were partially coated, the fully coated slabs were not used in the current verification study because they simulate one-dimensional flow. The water-cement ratio and the aggregate-cement ratio of the three specimens, i.e. specimens S1, S2 and S3, selected for analysis are provided in Table 8.4. Ordinary portland cement with the following composition was used to produce the slabs: C_3S : 60%, C_2S : 24%, C_3A : 9%, C_4AF : 7%.

Table 8.4: Mix proportions of the concrete specimens tested by Suryavanshi et al. (1998)

Slab No.	Water-cement ratio	Aggregate-cement ratio
	(w/c)	(a/c)
S1	0.45	5.26
S2	0.60	5.26
S3	0.75	5.26

All the slabs were exposed to a series of wetting and drying cycles every 10 days. During each wetting cycle, slabs were ponded by a 4% NaCl solution for seven days, and then allowed to dry for three days. They were subjected to 70 cycles over a 2.5-year period. The chloride content of the specimens were measured by coring at locations X1, X2 and X3 as well as in the uncoated zone. The cores were sliced at the following depths: 0-5, 5-25, 25-45, 45-65, 65-85, and 85-105 mm and the chloride content in each slice was reported.

Figure 8.8 shows the finite element mesh used to simulate this experiment. The finite element mesh represents the cross section of the slab with dimensions of 125 x 1000 mm. A total of 1000 elements of equal size were used in the discretization.

Figure 8.8: The finite element mesh used to model the partially coated slabs tested by Suryavanshi et al. (1998)

The input data, including material properties for the analysis are given in Table 8.5. Since no information regarding the temperature and relative humidity of the environment were provided in the referred paper (Suryavanshi et al., 1998), for the purpose of verification, they were assumed to be kept constant at 22°C and 65%, respectively. BET adsorption isotherm was used to relate the evaporable water content with the water vapour content. Chloride binding was simulated by the Freundlich isotherm in which α and β were taken as 1.05 and 0.35, respectively. Once again, since the effect of carbon dioxide exposure is not considered, no model for carbonation decay or chloride release was used.

Figure 8.9 shows the chloride ingress profile in the three slabs after 4 years of exposure obtained by the present analysis. Notice the progressively greater depth of intrusion as we compare slabs S1, S2 and S3. The reason is the significant increase in the w/c ratio from slab S1 to S3. Once again, a higher w/c indicates a more porous concrete with greater susceptibility to chloride diffusion.

Figures 8.10 to 8.12 present the comparison between the experimental data and the proposed FEM analysis. The comparison has been made for chloride content at depths of 2.5, 15, 35, 55, 75 and 95 mm.

Table 8.5: Input parameters used in the finite element modeling of Suryavanshi's specimens

Parameter	Value
Specific heat	1000 J/kg°C
Coefficient of conduction	2 W/m°C
Density of concrete	2400 kg/m ³
Adsorption isotherm	BET
Chloride binding	Freundlich: $\alpha = 1.05$, $\beta = 0.35$
Chloride release	No release
Carbonation decay	No carbonation

As it can easily be seen from the contour plots indicated in Figure 8.9, chlorides did not reach locations X2 and X3 (see Figure 8.7), which are 210 mm and 350 mm laterally away from the edge of the uncoated (exposure) zone. Figure 8.10 shows the chloride profile at the center of the uncoated zone at the end of the experiment. We observe that the finite element analysis results agree closely with the corresponding experimental data for all three slabs. Similarly, Figure 8.11 shows the chloride profile at section X1 for the three slabs. The results for slabs S1 and S2 agree closely with the experimental data, but not for slab S3. Since the experimental results for S3 seem to fluctuate rather haphazardly, it is likely that either the coating was not effective or some other flow existed in the slab. Not knowing the nature of the flow, it cannot be modeled by the finite element program. The presence of the flow is further corroborated by the chloride content profile at location X2 in Figure 8.12. We can see that the experimental data indicates 0.5% chloride immediately under the coating, which shows that the coating may not have been fully effective. Clearly, such vagaries of the experimental program cannot be simulated by finite element method unless the exact nature of the problem is known.

Figure 8.9: The finite element simulation of the experiments by Suryavanshi et al. (1998)
(a) Specimen S1 (b) Specimen S2 (c) Specimen S3
(All values are given in terms of % Chloride by mass of cement)

Figure 8.10: Comparison of experimental chloride content profile with results of proposed FEM analysis at the center of the uncoated zone

Figure 8.11: Comparison of experimental chloride content profile with results of proposed FEM analysis for location X1^(*)

(*) Note that according to Suryavanshi et al. (1998) correct measurements could not be obtained for some of the depths

Figure 8.12: Comparison of experimental data with results of proposed FEM analysis at location X2

8.3.3. Zemajtis and Weyer Experiments (1999)

Zemajtis and Weyer (1999) constructed six concrete specimens whose dimensions are given in Figure 8.13. All of the specimens had a w/c of 0.45. Since five of the specimens are prepared by using corrosion inhibitors and mineral admixtures, only one of them will be used in the current analysis. The a/c of the specimen was 4.59. Each specimen was placed into 0.71 m deep tanks and exposed to wet-and-dry cycles, using 6 % by weight NaCl solution for wetting. Each cycle was one week in duration and was

divided into two stages. In the first stage, the wetting solution was at high tide level (610 mm from the bottom of the specimen), therefore the tidal and immersed zones were covered with NaCl solution. In the second stage, the wetting solution, while at low tide level (305 mm from the bottom of the specimen), was pumped to the top of the specimen, thus wetting the surfaces in the horizontal and vertical zones. At the same time surfaces in the tidal zone were allowed to air dry. The vertical, horizontal and tidal zones were subjected to 3.5 days wetting and 3.5 days drying cycles. The immersed zone was subjected to wetting solution for 7 days a week. Powder samples were collected after 33 weeks, one year and 1.5 years of ponding. Each sample set consisted of chloride samples from depths of 13 mm, 25 mm and 38 mm. An additional sample was collected from the horizontal surface at a depth of 51 mm after 1.5 years of exposure.

Figure 8.13: Test setup used by Zemajtis and Weyer (1999)

The input data, including material properties for the analysis are given in Table 8.5. Since no information regarding the temperature and relative humidity of the environment was given, for the purpose of verification, they were assumed to be kept constant at 22°C and 65%, respectively. Also, immersed zone of the specimens was assumed to be fully saturated. BET adsorption isotherm was used to relate the evaporable water content with the water vapour content. Chloride binding was simulated by Freundlich isotherm in which α and β were taken as 1.05 and 0.35, respectively. Since the effect of carbon dioxide exposure is not considered, no model for carbonation decay or chloride release was used.

Figure 8.14 shows the finite element mesh used to simulate this experiment. Due to symmetry, only half of the specimen was modeled. A total of 2600 elements of equal size were used in the discretization. The analysis was run for 1.5 years with time increments of 1 day.

The results of the proposed finite element model are presented in Figures 8.15, 8.16 and 8.17. These figures show the chloride content variation along the highest of the wall at depths of 13 mm, 25 mm and 38 mm, respectively, after 33 weeks, one year and 1.5 years of exposure. As it can be seen from the figures the finite element model predicts the available experimental data results quite accurately. It should be noted that a one-dimensional analysis used by Zemajtis and Weyer (1999) could not simulate the experiments accurately. Hence, a two-dimensional analysis is necessary to correctly model the effect of lateral gradient on the chloride penetration.

Figure 8.14: The finite element mesh used to model specimens tested by Zemajtis and Weyer (1999)

Figure 8.15: The chloride penetration along the vertical wall at a depth of 13mm

Figure 8.16: The chloride penetration along the vertical wall at a depth of 25mm

Figure 8.17: The chloride penetration along the vertical wall at a depth of 38mm

8.4. CO_2 Transfer and Carbonation Model

In this section the proposed finite element method is used to model the one-dimensional experimental studies on CO_2 transfer and carbonation conducted by Papadakis et al. (1991) and CEN (1997). Figure 8.18 shows a typical setup for the one-dimensional CO_2 penetration and carbonation experiments analyzed in the current study. The one-dimensional CO_2 transfer and carbonation problem was discretized using a mesh similar to that in Figure 8.4(a). The carbonation depth in each of the experimental studies considered in this section was measured by spraying phenolphthalein on the sliced surfaces of the specimens. A detailed explanation about the experimental studies that are simulated here can be obtained from Papadakis et al. (1999) and CEN (1997). Hence, only the information required to simulate the experiments using the program CONDUR is presented.

Figure 8.18: Typical concrete specimens used by Papadakis et al (1999) and CEN (1997)

8.4.1. Papadakis et al. (1991) Experiments

Papadakis et al. (1991) conducted a series of accelerated carbonation tests. In this study, eight concrete specimens, which were similar to the one shown in Figure 8.18, were tested. The dimensions of the specimens were $H = 100 \text{ mm}$, $W = 100 \text{ mm}$ and $L = 300 \text{ mm}$. After 90 days of moist curing at 30°C to assure complete hydration, the specimens were oven-dried and all surfaces were covered with a gas-tight paint except for the two opposite lateral surfaces with $100 \times 300 \text{ mm}$ dimensions. The specimens were placed in a control chamber and exposed to a continuous flow of air with 50% CO_2 . The temperature and relative humidity of the chamber were controlled in each test, but different levels of relative humidity and temperature were considered in their experiments. Carbonation depth measurements for the specimens were taken at 1, 3, 5, 10, 15 and 20 days under various temperature (at 22°C , 30°C and 42°C) and relative humidity (at 35%, 45%, 55%, 65%, 70% and 85%) conditions. Mix proportions of the concrete specimens are given in Table 8.6. The cement used to prepare the specimens was composed of 65.28% CaO , 23.55% SiO_2 , 6.12% Al_2O_3 , 5.1% gypsum, 2.51 % Fe_2O_3 , 1.3% MgO and 0.47% SO_3 . Based on the preceding chemical composition, the following mineral composition was assumed in the current verification: C_3S : 55%, C_2S : 20%, C_3A : 12%, C_4AF : 13%. The exposure conditions of the specimens are given in Table 8.7.

Table 8.6: Mix proportions of the concrete specimens tested by Papadakis (1991)

Mix Type	Water-cement ratio (w/c)	Aggregate-cement Ratio (a/c)
S1	0.5	0
S2	0.5	3
S3	0.65	3
S4	0.8	3
S5	0.65	3
S6	0.65	5
S7	0.65	5
S8	0.65	7

Table 8.7: The exposure conditions for the specimens tested by Papadakis et al. (1991)

Specimen #	CO₂ (%)	RH (%)	T (°C)	Exposure	Concrete Mix
1	50	65	30	1, 3 5, 10, 15, 20 Days	S1
2	50	65	30		S2
3	50	65	30		S3
4	50	65	30		S4
5	50	65	30		S5
6	50	65	30		S6
7	50	65	30		S7
8	50	65	30		S8
9	50	35	30	5 days	S6
10	50	45	30		S6
11	50	55	30		S6
12	50	65	30		S6
13	50	70	30		S6
14	50	85	30		S6
15	50	65	22	5 days	S6
16	50	65	30		S6
17	50	65	42		S6

Figure 8.19: The finite element mesh used to model the one-dimensional CO₂ ingress

The input data, including material properties for the analysis are given in Table 8.8. BET adsorption isotherm has been used to relate the evaporable water content with the water vapour content. The bi-linear carbon dioxide decay function, with $a = 0.5$ and $b = 90$ was used to simulate the change in porosity due to carbonation. Since there is no chloride exposure, no binding or release isotherm was selected.

The finite element mesh in Figure 8.19, which is composed of 160 triangular elements, was used for the analysis of this one-dimensional carbonation problem. Only the nodes along the top and the bottom edges of the mesh were exposed to the carbon dioxide while the other edges were assumed to be insulated. The analysis was carried out for 30 days with 1-hour time increments.

Table 8.8: Input parameters used in the finite element modeling of Papadakis' specimens

Parameter	Value
Specific heat	1000 J/kg°C
Coefficient of conduction	2 W/m°C
Density of concrete	2400 kg/m ³
Adsorption isotherm	BET
Chloride binding	No binding
Chloride release	No release
Carbonation decay	Bi-linear: $a = 0.5$, $b = 90$

Figures 8.20 and 8.21 illustrate the carbonation depth for the various specimens as measured experimentally and as obtained by FEM analysis. The finite element model results are in close agreement with the carbonation measurements reported by Papadakis et al.. It has to be mentioned that the proposed durability model and its associated computer program, CONDUR, uses the carbonation diffusion coefficient proposed by Papadakis et al. (1991).

Figure 8.20: Comparison of the results of Papadakis et al. (1991) with CONDUR (Specimens 1 to 8)

Figure 8.21: Comparison of the results of Papadakis et al. (1991) with CONDUR (Specimens 9 to 17)

8.4.2. Experimental Data from CEN Report: CR 12793 (1997)

The experimental study conducted by the authors of the CEN test method for the measurement of the carbonation depth of hardened concrete was presented by Jones et al. (2000). The specimens were similar to the one shown in Figure 8.18 with the following dimensions: $H = 100 \text{ mm}$ $W = 100 \text{ mm}$ and $L = 400 \text{ mm}$. All of the specimens were cured under impermeable plastic sheeting for 24 hours and three days uncovered in the mould. All surfaces except one were covered with a gas-tight paint. A water-cement-ratio (w/c) of 0.55 and an aggregate-cement-ratio (a/c) of 5 were used in the concrete mix. The exposure conditions of the specimens are given in Table 8.7. Carbonation readings were taken at 29, 91, 182, 273 and 364 days.

Table 8.9: The exposure conditions for the specimens tested by CEN (1997)

Specimen #	CO ₂ (%)	RH (%)	T (°C)	Exposure
1	0.035	70	22	1 year
2	0.035	65	20	
3	0.035	65	20	
4	0.035	70	20	
5	0.035	65	20	
6	0.035	50	20	
7	0.035	55	20

Figure 8.22: The finite element mesh used to model one-dimensional CO₂ ingress

The input data, including material properties for the analysis are given in Table 8.8. BET adsorption isotherm was used to relate the evaporable water content with the water vapour content. A bi-linear carbon dioxide decay function with $a = 0.6$ and $b = 90$ was used to simulate the change in porosity due to carbonation. Since there is no chloride exposure, no binding or release isotherm needs to be selected. Since no information was provided about the mineral composition of the cement used in the study,

the mineralogical characteristics of a typical ordinary portland cement; i.e. C_3S : 55%, C_2S : 20%, C_3A : 12%, C_4AF : 13%, is assumed in the current verification.

The finite element mesh in Figure 8.19, which is composed of 160 triangular elements, was used for the analysis of a one-dimensional carbonation problem. Only the nodes along the bottom edge of the mesh was exposed to the carbon dioxide while the other edges were assumed to be insulated. The analysis was carried out for one year with 1-day time increments.

Table 8.10: Input parameters used in the modeling of CEN specimens

Parameter	Value
Specific heat	1000 J/kg°C
Coefficient of conduction	2 W/m°C
Density of concrete	2400 kg/m ³
Adsorption isotherm	BET
Chloride binding	No binding
Chloride release	No release
Carbonation decay	Bi-linear: $a = 0.6$, $b = 90$

Figure 8.23 shows the comparison between the FEM prediction of carbonation depth after one year of exposure and the experimental data. Once again, the comparison is reasonable.

Figure 8.23: Comparison of CEN data (Jones et al., 2000) with results of proposed FEM analysis after one-year of exposure

8.5. Reinforcement Corrosion

Li (2001) conducted an extensive experimental study on the chloride-induced steel corrosion in concrete structures. This comprehensive study is very important since it is one of the few works, which investigate the combined processes of initiation and propagation stages of the service life problem in detail. The effects of cement type, presence and size of cracks, wetting and drying cycles, variable exposure conditions and concrete cover on the corrosion of steel reinforcement were investigated by testing model and full-size beams. Half-cell potentials (HCP) readings with respect to saturated calomel electrode (SCE) were made continuously during the day.

A total of 219 model beams whose geometric properties are shown in Figure 8.24 were tested under the accelerated exposure conditions given in Table 8.12. The main reason why such a large number of beams was tested is due to the fact that some of the beams had to be broken at certain intervals to take the necessary chloride content measurements and to visually inspect the corrosion state. As it can be seen in Figure 8.24, there are two types of model beams of 300 mm length, but with cross section of either 62 x 62 mm or 82 x 82 mm. Type 1 beams (with 62 x 62 mm cross section) had a concrete cover of 25 mm, while Type 2 beams had 35 mm cover. Each model beam was reinforced with a 12 mm diameter 400 MPa steel bar along the centerline. Although three types of cement; i.e. ordinary portland cement (OPC), fly ash blended cement (FAC) and blast-furnace slag blended cement (BFSC), were used in the original study, only the samples prepared with OPC are analyzed by the program CONDUR. Two types of mixes, with $w/c = 0.45$ and $w/c = 0.6$, were compared.

The effect of cracking on the initiation and propagation stage was studied by using four groups of model beams with different crack widths: uncracked, <0.05 mm, 0.1-mm and 0.2-mm. It has to be noted that for the finite element solution, the crack width has no effect on the chloride penetration since cracks are modeled as free boundaries. Therefore only the uncracked and the cracked cases will be analyzed with the proposed durability model. It was observed by Li (2001) that the primary cracks occurred at the midspan of the model beams. A total of 8 model beams were analyzed by the program CONDUR and the results are compared with the experimental results of Li (2001).

In addition to the model beams, 14 full-size beams whose dimensions and reinforcement layout are shown in Figure 8.25 were tested under the accelerated conditions given in Table 8.12. The results of only one of these 14 beams, whose crack pattern and properties are shown in Figure 8.26 and Table 8.13, respectively, was reported in the referred paper (Li, 2001). Therefore, only this beam was analyzed by the program CONDUR.

Figure 8.24: The dimensions of the (a) Type 1 (b) Type 2 model beams tested by Li (2001)

Table 8.11: Properties of the model beams (Li, 2001) tested by CONDUR

Beam No	Beam Type	w/c	Crack Width (mm)	Crack Depth (mm)
1	Type 1	0.45	No cracking	No cracking
2	Type 1	0.6	No cracking	No cracking
3	Type 1	0.45	N/A	15
4	Type 1	0.6	N/A	15
5	Type 2	0.45	No cracking	No cracking
6	Type 2	0.6	No cracking	No cracking
7	Type 2	0.45	N/A	15
8	Type 2	0.6	N/A	15

Table 8.12: Typical weekly exposure conditions for the specimens

Day	Temperature (°C)	Relative Humidity (%)	Spray of NaCl Solution*	Note
Monday	25	N/A	2 hours on 1 hour off (for 8 hours)	Wetting
Tuesday	25	60	Off	Natural conditions
Wednesday	50	20	Off	Drying
Thursday	25	N/A	2 hours on 1 hour off (for 8 hours)	Wetting
Friday	25	60	Off	Natural conditions
Saturday	50	20	Off	Drying
Sunday	25	60	Off	Extra day

(*) 3.5% by weight NaCl solution

Figure 8.25: Dimension and reinforcement layout of full-size beams (Li, 2001)

Figure 8.26: Crack formation along the full-size beam analyzed by CONDUR

Table 8.13: Location, depth and width of the cracks for the full-size beam shown in Figure 8.17

Crack No.	Crack Location* (mm)	Crack Width (mm)	Crack Depth (mm)
1	772	0.01	36
2	829	0.02	16
3	968	0.02	29
4	1096	0.04	49
5	1250	0.05	37
6	1432	0.21	72
7	1637	0.2	89
8	1771	0.04	99
9	1993	0.04	22
10	2078	0.02	32

(*) Measured from the left end

The input parameters used in the finite element analysis are presented in Table 8.14. Figure 8.27 shows the finite element meshes used to simulate the uncracked and cracked model beams as well as the full beam. Uncracked beams were modeled by one-dimensional finite element mesh with 21 quadrilateral elements. A total of 2100 and 3091 quadrilateral elements were used in the discretization of cracked model and the full-size beams as shown in Figure 8.27 (b) and (c), respectively.

Table 8.14: Input parameters used in the finite element analysis

Parameter	Value
Specific heat	1000 J/kg°C
Coefficient of conduction	2 W/m°C
Density of concrete	2400 kg/m ³
Adsorption isotherm	BET
Chloride binding	Langmuir: $\alpha = 0.40$, $\beta = 0.08$
Chloride release	No release
Carbonation decay	No carbonation
Initial Concrete resistivity	15 ohm-m
Initial oxygen concentration	0.005 kg/m ³ solution
External oxygen concentration	0.0085 kg/m ³ solution
Chloride threshold value	0.06% of concrete weight

(a) **(b)** **(c)**

Figure 8.27: The finite element mesh for
(a) Uncracked model beams **(b)** Cracked model beams **(c)** Full beam

The chloride penetration depths of some of the model beams were reported in the experimental study. Once again, the proposed finite element method predicts the chloride penetration depths accurately as indicated in Figures 8.28 and 8.29. The effect of water-

cement-ratio on the chloride diffusivity of concrete can be observed in Figure 8.28. As discussed before, the higher w/c results in higher chloride diffusivity. It should also be noticed from this figure that, the steel in Beam 3 ($w/c = 0.45$) experiences depassivation after 7 cycles (47.6 days); whereas the steel in Beam 4 ($w/c = 0.6$) experiences depassivation after 3 cycles (20.3 days).

Figure 8.29 shows the effect of cracking on the chloride diffusivity of concrete. The chloride penetration depths of the uncracked and cracked beams, with crack widths <0.05 , 0.1 and 0.2 -mm, are compared with the finite element results obtained by analyzing uncracked and cracked finite element models. As mentioned before, the proposed finite element model assumes the cracks as free surfaces; therefore, different crack widths do not affect the finite element solution. Figure 8.29 shows that the proposed finite element method predicts the chloride profile of the uncracked beams quite accurately. According to the experimental results shown in Figure 8.29, the chloride permeability in cracked beams increases as the crack width gets larger. Although the proposed finite element model cannot identify different crack widths, its prediction of the chloride penetration depth is reasonably accurate. It can be observed in Figure 8.29 that, finite element solution is approximately the average of the experimental results of the beams with different crack widths.

For the model beams, the comparison between the half-cell potential measurements by Li (2001) and the potential distribution obtained by the proposed durability model is presented in Figures 8.30 and 8.31. The half-cell potentials are for the center of the beam. Several important observations can be made from these results. First, by increasing the cover thickness from 25 mm to 35 mm, the half-cell potentials on

average dropped by 30%. This observation is true both for the cracked and uncracked beams. Therefore, the service life of the concrete structures can be significantly increased by increasing the concrete cover thickness.

Figure 8.28: Chloride content at the steel level in cracked model beams with 25-mm cover

Figure 8.29: Chloride content at the steel level in cover cracked and uncracked model beams with the 25-mm cover after 4 cycles

Another observation can be made about the effect of cracking on the corrosion of steel reinforcement. As it can be seen in Figure 8.30 and 8.31, the cracked beams; i.e. beams 3,4,7 and 8, show a larger jump in the half-cell potential compared to the uncracked beams: 1, 2, 5 and 6. A higher half-cell potential shows greater polarization and consequently faster corrosion rate.

A final observation can be made on the effect of water-cement-ratio on the corrosion of the steel reinforcement. Increasing w/c from 0.45 to 0.60, which is the difference between the pair of beams 1 and 2; 3 and 4; 5 and 6; and 7 and 8, can increase the half cell potential by 20%. This shows the importance of high quality concrete, with low porosity and permeability, in the durability of the concrete structures.

Figure 8.32 shows the effect of the cracks, caused by the loading, on the potential distribution; i.e. polarization behavior, of the full-size beam. It can be observed that the electric potential on the surface of the reinforcement increases around the main cracks in the midspan of the beam. The proposed finite element model shows excellent agreement with the experimental data.

A more detailed potential distribution along the beam calculated by the proposed finite element model is given in Figure 8.33. It can be observed in this figure that due to the depassivation of the protective layer in the presence of chloride ions, anodic sites form at the crack locations, which also confirms the fact that corrosion is actually a local phenomena and occurs at different locations along the reinforcement. Figure 8.34 shows the corrosion current density at the anodic sites along the beam after 24 cycles calculated by the proposed finite element program. Once the corrosion current densities are known, the rate of rust ($\text{Fe}(\text{OH})_3$) production along the beam can be determined easily by the proposed finite element model. Figure 8.35 shows the rate of rust production along the beam after 24 cycles. Finally, the calculated amount of rust produced after 1, 2, 5 and 10 years of exposure is shown in Figure 8.36. As it can be observed from this figure, after 10 years, almost 20 grams of rust will be produced at the midspan of the beam due to corrosion. This example illustrates the detailed capabilities of CONDUR.

Figure 8.30: Comparison of the experimental half-cell values at the center of the reinforcing bar and their FEM prediction for the Type 1 beams (25 mm cover)

Figure 8.31: Comparison of the experimental half-cell values at the center of the reinforcing bar and their FEM prediction for the Type 2 beams (35 mm cover)

Figure 8.32: The comparison of the finite element analysis results for half-cell potential with the experimental data at the crack locations

Figure 8.33: The potential distribution along the beam at the crack locations determined by the proposed finite element model after 24 cycles

Figure 8.34: The corrosion current density at the anodic sites along the beam determined by the proposed finite element model after 24 cycles

Figure 8.35: The rate of Fe(OH)_3 production along the beam determined by the proposed finite element model after 24 cycles

Figure 8.36: The amount of Fe(OH)_3 production along the beam determined by the proposed finite element model

8.6. Numerical Simulations

In order to simulate the carbonation induced steel corrosion in a real-life structure, the example, which is illustrated in Figure 8.37, is solved by using the program CONDUR. We consider a beam, which is located in a very corrosive environment; with flexural cracks 20 mm deep (through the concrete cover) and 0.2 mm wide on the surface. The composition of the cement used in the beam, whose specific gravity and fineness are taken as 3.15 and $300\text{m}^2/\text{kg}$, is given in Table 8.15. Based on this chemical composition, the following mineral composition is used: C_3S : 55%, C_2S : 20%, C_3A : 12%, C_4AF : 13%.

The water-cement-ratio (w/c) and aggregate-cement-ratio (a/c) of the initial mix are assumed to be 0.65 and 5, respectively. The average specific gravity of the aggregates is taken as 2.6. Initially, the concrete is assumed to have 65% relative humidity and 0% CO_2 content. The monthly temperature, relative humidity, and the CO_2 profiles during a year are given in Table 8.16. Exposure to CO_2 starts in May and continues for ten years.

The input data, including material properties for the analysis are given in Table 8.17. BET adsorption isotherm is used to relate the evaporable water content with the water vapour content, and a bi-linear carbon dioxide decay function with $a = 0.5$ and $b = 85$ is used to simulate the change in porosity due to carbonation. Since there is no chloride exposure, no binding or release isotherm needs to be considered.

Table 8.15: Chemical composition of the cement used in the numerical example

CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	SO ₃	Gypsum
65 wt%	25 wt%	6 wt%	2.5 wt%	1.2 wt%	0.4 wt%	2.9 wt%

Table 8.16: Temperature, relative humidity and CO₂ contents along the exposed surfaces

Months	T (°C)	RH (%)	CO ₂ (%)
January	-10	55	0.3
February	-4	60	0.25
March	1	65	0.2
April	4	70	0.15
May	12	75	0.1
June	21	80	0.1
July	25	85	0.1
August	27	90	0.15
September	18	85	0.2
October	11	75	0.25
November	2	70	0.25
December	-4	65	0.3

Table 8.17: Heat Transfer parameters used in the modeling of panels

Parameter	Value
Specific heat	960 J/kg°C
Coefficient of conduction	1.55 W/m°C
Coefficient of convection	2.8 W/m ² °C
Coefficient of radiation	13 W/m ² °C
Emissivity of gray concrete	0.9
Absorptivity	1
Density of concrete	2400 kg/m ³
Adsorption isotherm	BET
Chloride binding	No binding
Chloride release	No release
Carbonation decay	Bi-linear: a = 0.5, b = 85
Chloride threshold value	[Cl ⁻]/[OH ⁻] = 0.4

To save on computational time, a portion of the beam is selected, as indicated in Figure 8.37, for the purpose of analysis. The selected portion is discretized by four node quadrilateral elements and the prescribed boundary conditions are shown on the finite

element mesh. The three cracks that are within the selected portion are modeled as free surfaces.

Results of the analysis are shown as movement of the carbonation front. The movement of the carbonation front over ten years can be observed in Figure 8.38. It should be noted that the results are reported in terms of “% carbonated” which gives the percentage of Ca(OH)_2 used in each element in the mesh. For example, a 60% carbonated element still has 40% of the initial Ca(OH)_2 content and will experience more carbonation.

It is important to notice the effect of cracks on the carbonation of the concrete beam. An analysis without considering the cracks would not be able to adequately simulate the carbonation accurately. To confirm this assertion, the same problem was analyzed without considering the cracks. The results of the later analysis are shown in Figure 8.39, and compared with cracked beam analysis. It is clear that the two models give substantially different results.

It is important to mention that a one-dimensional analysis would not be appropriate for simulating the cracked beam problem and its results may not be realistic either. The orientation of the cracks and the variable exposure conditions require a two-dimensional model similar to the developed in the present investigation.

Figure 8.37: Finite element modeling of a cracked beam for coupled heat, moisture, CO₂ transfer and carbonation analysis

Figure 8.38: Annual carbonation front over a 10-year period

Figure 8.39: Effect of the presence of cracks on the carbonation of concrete

Next, in order to demonstrate the effect of coupling between chloride ingress and carbonation, let us now assume that the preceding structure is exposed to chloride ions in addition to the carbonation conditions given in Table 8.16. The atmospheric chloride concentrations that are assumed in the analysis are given in Table 8.17. Chloride binding is modeled by the Freundlich isotherm with the following parameters: $\alpha = 1.05$, $\beta = 0.35$, and the initial pH of the concrete is assumed to be 13.5. The chloride release due to carbonation is set to start when pH drops below 12 and a linear chloride release isotherm is used with $w = 0.05$.

Table 8.18: Atmospheric chloride concentration along the exposed surfaces

Months	[Cl] (kg/m³ solution)
January	20
February	15
March	10
April	5
May	2
June	0
July	0
August	0
September	3
October	5
November	10
December	18

Figure 8.40 shows the effect of carbonation on the pH of the concrete after 1, 5 and 10 years of exposure. It can be observed from the figure that as the carbonation front penetrates into the concrete, the pH also drops. Figure 8.41 shows the chloride penetration in concrete with and without the carbonation process. As it can be seen from the figure, after 10 years of exposure to chlorides, there is a significant difference in the

amount of free chloride ions in the concrete with and without concurrent exposure to carbonation.

Figure 8.40: Effect of carbonation on the alkalinity (pH) of concrete

Figure 8.41: The free chloride ion profile after 10 years
 (a) Without carbonation
 (b) With carbonation

Figure 8.41 also shows the importance of the variation in exposure on the transport properties of concrete. As it can be seen in Table 8.18, the chloride concentration on the exposed surface of the structure drops significantly, and even becomes zero, during the summer months. During the period, the chloride concentration inside the concrete is generally larger than the chloride concentration along the exposed surface. Therefore, reverse diffusion towards the exposed surface of the concrete occurs during the summer months. This process can be clearly observed in Figure 8.41.

Finally let us examine the amount of rust produced as a result of the depassivation of the reinforcing bar in this structure. Figure 8.42 shows the potential distribution along the reinforcement after 10 years of exposure to chlorides alone or to chlorides and carbonation. As expected, the potentials due to combined chloride ingress and carbonation is higher than the potentials due to chloride ingress alone. The combined effect leads to higher corrosion rate in the bar. The amount of rust produced in the process after 10 years is shown in Figure 8.43.

Figure 8.42: The potential distribution along the steel surface after 10 years of exposure

Figure 8.43: The amount of rust produced along the steel surface after 10 years of exposure

It is clear from the later simulation that the program CONDUR provides designers of reinforced concrete structures with a tool to carry out realistic simulations with respect to the service-life performance of structures exposed to aggressive environments. The level of information that is provided by this detailed quantitative program will make the task of the designer somewhat easier. Undoubtedly, as more detailed experimental data becomes available, the validity of the program models can be further ascertained, but for the purpose of this study, the results confirm the reasonable assumptions made in the development of the models incorporated in this program.

9. Conclusions and Recommendations

9.1. Summary

A robust two-dimensional time-dependent nonlinear finite element technique and an associated Windows-based computer program, CONDUR, have been developed for modeling chloride and carbonation induced steel corrosion in reinforced concrete structures.

The significant phenomena that contribute to the rate and amount of corrosion of reinforcement; i.e. heat and moisture transfer, chloride, CO_2 and O_2 transport, are modeled by the two-dimensional time-dependent nonlinear finite element method. The governing equations of the various transport phenomena are solved numerically in the time and the space domains. The coupling effects among the different transport phenomena and the chloride binding/release mechanisms as well as the carbonation process are modeled in order to simulate the field conditions reasonably closely. The chemical reactions such as carbonation and chloride binding are incorporated as sink and source terms in the governing differential equations.

The proposed finite element model and its associated computer program, CONDUR, are designed to accommodate any geometry (including cracks), prescribed initial and boundary conditions and pertinent material nonlinearities.

The corrosion of the reinforcement is treated as an electrochemical process and is modeled by using a two-dimensional time-dependent nonlinear finite element method as corrosion is assumed to be a spatial and temporal function of temperature, moisture, and

ionic or molar concentration of various chemicals within the pore solution. The corrosion analysis provides the rate and amount of reinforcement corrosion in a reinforced concrete structure operating within a prescribed environment.

To verify the finite element model and its associated computer program, its results are compared with available experimental data. Further numerical simulations have been carried out to demonstrate the capabilities of the developed methodology and its associated computer program.

9.2. Conclusions

The following conclusions can be reached based on the findings of this study:

1. The modeling of corrosion of steel reinforcement in concrete is a very complex problem, which requires a systematic and robust finite element approach which must be cast in a common time and two- (but preferably, three-) dimensional space domain for a realistic simulation. The finite element method must handle the coupling effects and material nonlinearities, which are in the nature of the reinforced concrete durability problem, and be capable of defining different geometries, initial and boundary conditions.
2. The initiation and propagation stages should not be separated in a reinforced concrete service life model. Corrosion of reinforcement is a dynamic phenomenon whose boundary conditions change even after the corrosion has begun. Corrosion process can start, stop and re-start depending on the boundary

conditions and this can only be modeled when there is full-integration of the initiation and propagation stages.

3. One-dimensional initiation stage models, which are widely used to model chloride and CO₂ penetration into concrete, have limited applicability. In practice, many problems in the field are not governed by one-dimensional transport phenomena. Even in the obvious cases like concrete bridge decks, the presence of local imperfections such as cracks may violate the one-dimensional flow assumption.
4. The corrosion of reinforcement is actually a three-dimensional problem. A two-dimensional approximation may be adequate in most cases, however, a three-dimensional finite element model is preferable to accurately model the corrosion of reinforced concrete structures, especially when the reinforcement detailing is complicated with steel rebars located in different planes and directions, and with the presence of stirrups and splices, which is generally the case for most of the structural members.
5. The presence of cracks has an important effect on the transport properties of concrete and on the corrosion of reinforcement. The cracks may not affect the corrosion rate but they accelerate the corrosion initiation process. Since it is almost impossible to find concrete structures without cracks, reinforced concrete durability models should have the capability to simulate cracks.
6. The finite element method can easily model discrete cracks, while smeared or micro-cracks can be accounted for via the material transport properties.
7. The quality of the concrete significantly affects the durability of the structures. Structures constructed with high quality concrete; i.e. with low water-cement-

ratio, low porosity and permeability, are more durable than the others. It has been observed in the present study that an increase in w/c from 0.45 to 0.60 may increase the rate of corrosion up to 20%.

8. One of the easiest ways of protecting reinforced concrete structures is to use a thicker cover. It has been observed in this study that an increase of 10 mm may decrease the rate of corrosion by 30%.
9. The combined effect of chloride diffusion and carbonation on steel corrosion in concrete is more severe than their separate effects.
10. The available models for chloride diffusion and carbonation, although primarily developed based on test data simulating one-dimensional flow can be extended to two-dimensional transport conditions.
11. The proposed electrochemical corrosion model, which includes the effect of various kinds of polarization, can accurately predict electric potential measurements from an extensive experimental program. It can also provide an estimate of the rate and amount of corrosion once the corrosion current is accurately determined.
12. Computer programs such as CONDUR require a great amount of data about concrete and steel material properties, therefore, the input data should be carefully examined before the output can be judged and interpreted.

9.3. Recommendations for Future Work

The following recommendations for future work can be made:

1. Implementation of the three-dimensional finite element modeling of the transport phenomena and the reinforcement corrosion in concrete.
2. Incorporation of the electric coupling between ions and its effect on the ionic movement in concrete.
3. Investigation of the effects of other ions such as sulfates and magnesium on the durability of reinforced concrete structures and incorporation of the corresponding coupled ionic transport mechanisms into the existing model.
4. Modification of the existing durability model and associated computer program to include the effects of service loads, creep, shrinkage and freeze-and-thaw action.
5. Implementation of a finite element module to couple environmental and mechanical stresses in order to automatically detect the failure mechanism of the structure.
6. Addition of a cost analysis module to CONDUR.
7. Modification of the developed finite element model and associated computer program such that they can be used for modeling durability problems in other types of building materials such as wood and FRP. An example is the modeling of bio-chemical degradation mechanism of wood.
8. Greater investigation of the significance of various transport phenomena in different environments and the incorporation of these in the program.
9. Investigation of the effect of aging on concrete durability and its incorporation in computer simulation models.

10. Development of an extensive and detailed database of experimental results for the individual and combined effects of various parameters on concrete durability in order to verify and/or improve the results of computer simulations.
11. Gathering of more field data on the performance of actual structures under natural conditions and the analysis of these structures by the computer models, to correlate the physical data with the computer model predictions.
12. Performance of detailed sensitivity analyses using the current computer program in order to determine the degree to which the final results depend upon variation in input data and on the assumptions made in the numerical analysis procedures.

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