THE EFFECTS OF GLOBAL CLIMATE CHANGE ON CARBONATION INDUCED CORROSION OF REINFORCED CONCRETE STRUCTURES

by

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Abstract

There is nearly unanimous consensus amongst scientists that increasing greenhouse gas emissions, including CO₂ generated by human activity, are affecting the Earth's climate. Climate change has the potential to overwhelm existing capacities, as well as durability of concrete infrastructure. Carbonation of concrete occurs due to a reaction between atmospheric CO₂ and the hydrated phases of concrete, leading to a drop in its pH and the depassivation of embedded rebar. Therefore, increases in carbonation rates of reinforced concrete structures are expected as a result of increased temperatures and CO₂ concentrations, with the enhanced risk of carbonation induced corrosion likely affecting the longevity of our concrete infrastructure.

This thesis considered the potential consiquences of global climate change on our concrete infrastructure, with the objective being to determine if there is an increased risk of deterioration due to carbonation induced corrosion. A unique numerical model was developed to determine carbonation rates in structures, and verified through experimental tests. The model was applied to a number of cities in locations throughout the world to determine where structures were most vulnerable. Additionally, a number of other laboratory experiments were carried out to supplement the numerical model and provide insights as to how carbonation progress can be monitored within a structure.

Using the model developed, and inputting forecasts for increases in future atmospheric CO₂ concentrations and weather conditions, it was shown that for medium quality, non-pozzolonic concrete in geographic areas where carbonation induced corrosion is a concern, global climate change will affect its progress in our concrete infrastructure. We will see much higher ultimate carbonation depths in the long term. The use of non-destructive testing (NDT) methods, and structural health monitoring (SHM) techniques could be invaluable in monitoring the progress of carbonation in a structure, but the data generated by the methods and techniques used must be analyzed carefully before making any conclusions. For the NDT methods and carbonation pH sensors

which were evaluated in this study, it was found that ambient test conditions had a major impact on results.

Preface

This statement confirms that the author of this thesis is the primary person responsible for the research contained. All experimental designs and procedures were conceived by the author with input from the supervisory committee, namely Dr. Nemkumar Banthia, Dr. John Grace, Dr. Pat McGrath, and Dr. Sidney Mindess. The specific names of those who assisted in conducting several of the experiments have been gratefully recognized in the Acknowledgments section of this thesis.

Several manuscripts have been published or are under consideration for publication pertaining to the results of this thesis. The following is a list of such manuscripts which have been published or are currently under review:

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या देवी सर्वभूतेषु विद्यारूपेण संस्थिता, नमस्तस्यै नमस्तस्यै नमस्तस्यै नमो नमः ||

Chapter 1: Introduction

1.1 Research Rationale, Objectives and Scope

There is nearly unanimous consensus amongst scientists that increasing greenhouse gas emissions, including CO_2 generated by human activity, are affecting the Earth's climate. The global average surface air temperature has increased over the 20th Century by about 0.6°C, and is projected to increase by a further 1.4-5.8°C by 2100. Some of the potential effects of climate change include (Solomon, 2009):

- Rising sea levels, decreased snowpacks and increased glacial melting
- Increased heat waves and drought occurrences, and
- Increased extreme precipitation events, leading to increased flood risks.
- The risk of decreases in global food production.
- The potential for the extinction of up to 30 per cent of the Earth's plant and animal species.

Until recently, one overlooked area of research is the impact of climate change on our concrete infrastructure. Reinforced concrete structures form an essential part of our world. Climate change has the potential to overwhelm existing capacities, as well as durability of concrete infrastructure. Limited work has been carried out on the effects that global climate change may have on concrete infrastructure, mainly because the issue has only been recently recognized. Carbonation of concrete occurs due to a reaction between atmospheric CO₂ and the hydrated phases of concrete, leading to a drop in its pH and the depassivation of embedded rebar. Therefore, increases in carbonation rates of reinforced concrete structures are expected as a result of increased temperatures and CO₂ concentrations, with the enhanced risk of carbonation induced corrosion likely affecting the longevity of our concrete infrastructure.

This thesis explores the consequences of global climate change on our concrete infrastructure, with the objectives being to determine if there is an increased risk of deterioration due to carbonation-induced corrosion, and considering ways to monitor and deal with the effects.

- A unique numerical model was developed to determine carbonation rates in structures, and verified through experimental tests. The model was applied to cities throughout the world to determine if/where structures are most vulnerable.
- 2. A number of other laboratory experiments were carried out to supplement the numerical model and evaluated as potential structural health monitoring (SHM) techniques to provide insights as to how carbonation progress can monitored.
- 3. Finally, based on the results, recommendations as to how to deal with the threat of climate change and carbonation induced corrosion to our infrastructure are developed and presented.

1.2 Outline

The structure of this thesis is presented here. It is consists of nine chapters:

Chapter 1: Introduction

An introduction to the thesis is given in this chapter, summarizing the research objectives and scope.

Chapter 2: Background

A comprehensive summary and discussion of past literature is given, explaining the scientific basis behind climate change, its worldwide effects, and specifically how it could affect infrastructure. A thorough description of carbonation and carbonation-induced corrosion of reinforced concrete is discussed in detail towards the end of the chapter.

Chapter 3: Numerical Modeling and Verification

A unique service life model of concrete structures subjected to carbonation induced corrosion is formulated, along with a unique new carbonation model for structurally cracked concrete. Their development and verification is presented in this chapter.

Chapter 4: Global Service Life Analysis

The service life model developed in Chapter 3 is applied to 6 cities around the world, and the results are presented in this chapter.

Chapter 5: Non-Destructive Testing of Carbonated Concrete

Although it is well known that carbonation alters the properties of concrete which would influence the results of Non-destructive Tests (NDT) on concrete, a comprehensive study on the topic has not yet been conducted. Beyond simply modelling and forecasting carbonation depths due to climate change, it is also important to know what kind of mechanical and chemical response to expect from NDTs in order to assess damage levels within a structure in the future. Therefore, a thorough study is carried out, and in this chapter the results of a variety of NDTs on carbonated concrete are presented.

Chapter 6: Thermogravimetric Analysis

For the first time, an attempt was made to conduct low-temperature thermogravimetric analysis (TGA) on carbonated concrete in order to verify some of the parameters used in the model developed in Chapter 3. The results of the analysis are described in this chapter.

Chapter 7: X-Ray Diffraction Analysis

There is some debate about whether the results of accelerated carbonation tests are truly representative of results obtained when concrete is naturally carbonated. This is due to differences in the crystalline phases of calcium carbonate. X-ray diffraction (XRD) can be used to identify the constituents of concrete and hydrated cement paste, and differentiate between the crystalline phases of calcium carbonate which have been formed by carbonation at various CO₂ concentrations. The results of XRD tests are presented in this chapter to determine just how acute the difference is between the types of calcium carbonate formed in the accelerated processes.

Chapter 8: pH Sensing

This chapter describes the testing of a micro pH sensor which could potentially be used to remotely monitor the pH of concrete as it is carbonating as part of a Structural Health Monitoring (SHM) system. Sensors were embedded at a given depth within a concrete specimen, and then allowed to carbonate. In the future such sensors could be used to monitor susceptibility to carbonation induced corrosion in a non-destructive manner.

Chapter 9: Conclusions and Recommendations

Overall conclusions from each chapter of this thesis are presented and discussed, and a number of recommendations are offered, both general recommendations on how to prepare ourselves to deal with the effects of climate change, and specific research recommendations for what may be done to supplement this study.

Chapter 2: Background

In this chapter, a comprehensive literature review and background is given regarding the topics of climate change and the durability of concrete infrastructure, in particular, the carbonation induced corrosion of concrete infrastructure. A discussion of the interaction between the two topics, and why the effects of climate change on concrete infrastructure may be a cause for concern, is provided.

2.1 Climate Change

There is nearly unanimous consensus amongst scientists that increasing greenhouse gas emissions, including carbon dioxide (CO₂) generated by human activity, are effecting the Earth's climate. In 2007, the Intergovernmental Panel on Climate Change (IPCC), Working Group I (IPCC, 2007) declared that the contribution of human activities to recent global warming is more than 90%. For many key parameters, the climate system is already moving beyond the patterns of natural variability within which our society and economy have developed and thrived. These parameters include global mean surface temperature, sea-level rise, ocean and ice sheet dynamics, ocean acidification, and extreme climatic events. There is a significant risk that many of the trends will accelerate, leading to an increasing risk of abrupt or irreversible climatic shifts. The Earth's average temperature has increased by 0.5°C since the 1970's and is expected to increase by a further 1.4-5.8°C by the end of this century (McMichael et al, 2006).

2.1.1 Radiative Forcing

The Earth's surface temperature is determined by the balance between incoming solar radiation and outgoing infrared radiation. Energy is constantly flowing into the atmosphere in the form of sunlight that always shines on half of the Earth's surface. Some of this sunlight is reflected back to space and the rest is absorbed by the planet. Some energy is also always radiating back out into space as invisible infrared light. The reported values of incoming energy and outgoing energy are shown in Figure 2.1.



Figure 2.1: Atmospheric energy cycle (Cohen and Wadell, 2009)

If the amount of incoming energy (342 W/m^2) is equal to the amount of outgoing energy $(107 + 235 \text{ W/m}^2)$, then there will be no change in the surface temperature of the Earth. However, an increase in concentration of certain gases will cause more energy to remain trapped/reflected by the atmosphere, thereby decreasing the amount of outgoing energy, and causing a net increase in the Earths surface temperature. This concept is referred to as 'radiative forcing' (RF).



Figure 2.2: Radiative forcing components (IPCC, 2007)

Figure 2.2 shows the various anthropogenic and natural radiative forcing components, and their RF values relative to the year 1750 (the beginning of the Industrial Revolution). Since 1750, there has been an increase in RF due to anthropogenic emissions of 1.6 W/m² (Cohen and Wadell, 2009). The major anthropogenic contributor has been CO_2 . While this value may not seem very high, when we consider the surface area of the Earth, and the fact that this additional energy is being absorbed every second of the day by the surface, we realise that this seemingly nominal increase in energy could very much cause a noticeable increase in surface temperatures.

The primary source of the increased atmospheric concentration of CO_2 since the pre-industrial period results from fossil fuel use, with land-use change providing another smaller, but still significant contribution. The removal of CO_2 from the atmosphere involves multiple processes, including rapid

exchange with the land biosphere, and the surface layer of the ocean through air-sea exchange (Solomon, 2009). Solomon et al (2009) reported that even if CO₂ emissions were to cease, it would take at least 1000 years for the effects of climate change to be reversed. Emissions scenarios are therefore extremely important, as they can be input into global climate change models to predict future increases in temperature, and effects on the weather in general.

2.1.2 Emissions Scenarios

The IPCC developed long-term emissions scenarios in 1990 and 1992 (IPCC, 1990, IPCC, 1992). These scenarios have been widely used in the analysis of possible climate change, its impacts, and options to mitigate climate change. In 1995, the IPCC 1992 scenarios were evaluated (IPCC, 1995). The evaluation recommended that significant changes (since 1992) in the understanding of driving forces of emissions and methodologies should be addressed. This led to a decision by the IPCC Plenary in 1996 to develop a new set of scenarios. The IPCC published a new set of scenarios in 2000 for use in the Third Assessment Report (Special Report on Emissions Scenarios - SRES) (IPCC, 2000). The SRES scenarios were constructed to explore future developments in the global environment with special reference to the production of greenhouse gases and aerosol precursor emissions.

The SRES team defined four narrative storylines, labeled A1, A2, B1 and B2, describing the relationships between the forces driving greenhouse gas and aerosol emissions and their evolution during the 21st century for large world regions and globally. Each storyline represents different demographic, social, economic, technological, and environmental developments that diverge in increasingly irreversible ways. In simple terms, the four storylines combine two sets of divergent tendencies: one set varying between strong economic values and strong environmental values, the other set between increasing globalization and increasing regionalization. The storylines are summarized as follows (IPCC, 2000):

• A1 storyline and scenario family: A future world of very rapid economic growth, global population that peaks in mid-century and declines thereafter, with rapid introduction of new and more efficient technologies.

- A2 storyline and scenario family: A very heterogeneous world with continuously increasing global population and regionally oriented economic growth that is more fragmented and slower than in other storylines.
- B1 storyline and scenario family: A convergent world with the same global population as in the A1 storyline but with rapid changes in economic structures toward a service and information economy, with reductions in material intensity, and the introduction of clean and resourceefficient technologies.
- **B2 storyline and scenario family:** A world in which the emphasis is on local solutions to economic, social, and environmental sustainability, with continuously increasing population (lower than A2) and intermediate economic development.

After determining the basic features of each of the four storylines, including quantitative projections of major driving variables such as population and economic development taken from reputable international sources (United Nations, World Bank and IIASA), the storylines were then fully quantified using 6 integrated assessment models, resulting in families of scenarios for each storyline. In all, 40 scenarios were developed by six modeling teams. All are equally valid, with no assigned probabilities of occurrence. Six groups of scenarios were drawn from the four families: one group each in the A2, B1 and B2 families, and three groups in the A1 family, characterizing alternative developments of energy technologies: A1FI (fossil intensive), A1T (predominantly non-fossil) and A1B (balanced across energy sources). Illustrative scenarios were selected by the IPCC to represent each of the six scenario groups.

The SRES report discusses emissions projections produced by a range of Integrated Assessment Models for a range of socio-economic storylines. Four `marker scenarios' (one from each story line) are recommended as the basis of climate model projections. For each of the marker emissions scenarios, CO_2 concentration projections calculated by two different carbon cycle models (ISAM and BERN) were reported in IPCC (2001) and used as the basis for climate model projections.

Using CO_2 concentration projections data provided by the SRES report (for storylines A1F, A2, B1, B2), as well as the original IPCC data (for IS92a), worldwide projected CO_2 increases based on the data are provided in Figure 2.3 for the BERN carbon cycle model:



Figure 2.3: SRES emissions scenarios

2.1.3 Worldwide Effects

As mentioned, the major effect of CO_2 increases will be an increase in global temperature. Projected temperature increases for the various scenarios (IPCC, 2007) are shown in Figure 2.4:



Figure 2.4: Temperature forecasts

Recent observations confirm that, given high rates of observed emissions, the worst-case IPCC scenario trajectories (or even worse) are being realised (Schneider, 2009). Alongside global mean surface temperatures, other natural parameters may be affected (IPCC, 2007). These include:

- Sea-level rise: Melting ice sheets continue to increase sea levels worldwide, leading to potential submerging of coastal and low lying areas.
- Ocean and ice sheet dynamics: Increasing temperatures are affecting ocean currents, thereby influencing weather patterns worldwide.

- Ocean acidification: Increased uptake of CO₂ by the world's oceans may cause a decrease in pH, thereby affecting marine ecology.
- Ecosystem productivity: Due to increasing CO₂ levels, and changing temperatures, some parts of the world will see increases in crop yields, while others will see decreases. Land-based animals, insects and plant life are migrating to different parts of the globe, while changing hydrology and water temperatures will also affect fish stocks.
- Extreme climatic events: Analysis of weather data over the past 50 years indicates that the frequency of heavy precipitation events, more intense, and longer draughts, and the number of hot days yearly have increased, which is likely attributable to global climate change and likely to continue.

2.1.4 Effects on Infrastructure

One overlooked area is the impact of climate change on our concrete infrastructure. We will have to adapt our future designs to ensure that they have adequate capacity and have sufficient durability to deal with the consequences of climate change.

Some researchers have identified potential risks to structural capacity. There is the possibility that design codes need to be revised to consider that the probability of extreme loading events will increase in the future (wind loads, snow loads, rain loads). Furthermore, in general, rain load, snow load, wind load, and temperature stresses will change, depending on location. Steenbergen et al (2009) identified increased potential structural load increases due to climate change in the Netherlands. Specifically, Steenbergen et al (2012) discussed the consequences of climate change on design wind speeds used in building regulations. The Canadian Council of Professional Engineers developed an engineering protocol for climate change related issues and conducted a vulnerability assessment of public infrastructure throughout Canada (PIEVC, 2008).

As discussed previously, some environmental changes that may occur due to climate change include:

- Increasing amounts of air pollutants.
- Increasing temperatures.
- Fluctuations in yearly precipitation amounts.
- Fluctuations in relative humidity levels.
- Fluctuations in the length of seasons.
- More frequent extreme weather events.

All of which will affect the durability of our concrete infrastructure. Researchers have begun to consider the effect of climate change on the durability of our construction materials. Nijland et al (2009), evaluated the effects of expected climate change on the durability of building materials, and offered suggestions for adaption. Naik and Kumar (2010) have summarized the effects of climate change on portland cement based materials specifically.

With regards to concrete durability, three major deterioration threats appear:

• Increase in the risk of carbonation induced corrosion:

Amongst the literature reviewed, Yoon, et al (2007) were the first to assess the effects of climate change on carbonation of concrete. Their simplified model showed that there would be an increase in carbonation depths in concrete for varying w/c ratios. Their simplified model was proposed based on a $t^{0.5}$ relationship between time and carbonation depth. While this provides a reasonable approximation, it fails to account for the finite depth and reaction effects. Moreover, this model does not account for the influence of temperature change, which can significantly affect the diffusion coefficient of CO₂ into concrete, the rate of reaction between CO₂ and Calcium Hydroxide (Ca(OH)₂), and the rate of dissolution of CO₂ and Ca(OH)₂ in pore water. In addition, the model is a point-in-time predictive model, which assumes CO₂ concentrations to be constant up to a given time, thereby overestimating carbonation depths (Bastidas-Arteaga et al, 2011).

Stewart and Ping (2010) expanding upon the earlier work by Yoon et al (2007) by taking into account the effect of temperature on the CO₂ diffusion coefficient, but they did not consider the influence of temperature on the other aforementioned parameters. Their work looked not only at carbonation, but also at the time to crack initiation, crack propagation and failure due to reinforcement corrosion. They also used the same carbonation model as Yoon et al (2007) in their work, but noted that this model was an approximation, and there is a need for an improved model that considers the time-dependent effect of CO₂ concentration and other parameters such as temperature and humidity (Bastidas-Arteaga et al, 2011), (Stewart and Ping, 2010).

Subsequent studies by Stewart et al (2011), Stewart et al (2012) and Wang et al (2012) expanded upon the research base by conducting probabilistic analysis including the uncertainty of CO₂ concentrations, material properties and dimensions. Stewart et al (2011) found that depending on the region, and the scenario considered, the increased risk due to carbonation-induced corrosion in various Australian cities was up to 400%. Also, rather than just looking at increases in carbonation depths, the time to cover cracking and spalling was also investigated, along with the presentation of various adaption measures to ameliorate the effects of a changing climate.

Increase in the risk of chloride induced corrosion:

- Bastidas-Arteaga et al (2010) concluded that global warming may induce lifespan reductions due to chloride induced corrosion from 4% to 18% for a concrete element depending on the exposure environment. The assessment of chloride ingress was carried out on the basis of a comprehensive model that coupled the effects of convection, chloride binding, concrete aging, temperature and humidity. A simplified model of temperature and humidity including seasonal variations and global warming was also proposed in their work.
- Increase in weathering/abrasion due to higher climatic stresses, and increased frequency of extreme weather events:

Areas in low lying, flood prone areas, such as Bangladesh, or the Netherlands, will have their flood protection systems challenged on a more regular basis, as water levels rise, and storm frequency increases (Hanson et al, 2011).

Clearly, overall, global climate change will have significant and wide-ranging effects on our concrete infrastructure. In this study, we look mainly at the effects climate change will have on the increased risk of carbonation induced corrosion of concrete infrastructure. In the next section, carbonation-induced corrosion is described in detail.

2.2 Corrosion of Reinforced Concrete

Concrete is the world's most predominant construction material. Next to water, it is the world's most commonly used material (Meyer, 2005). The exponential growth of infrastructure, especially in developing regions, further increases the demand for concrete materials such that the worldwide production and use of concrete is more than 10 billion tons per year (Meyer, 2005). In the United States, the annual production of over 500 million tons implies about two tons for each man, woman and child (Meyer, 2005). As a construction material, concrete is durable, economical, plentiful, versatile and easy to build with. Vital components such as roads, sidewalks, bridges, buildings, dikes, dams and walls are often constructed at least partially with, if not completely with, reinforced concrete. At its simplest level, concrete can be considered to be a composite material formed by mixing fine and coarse aggregate (sand and gravel) with water and cement powder. However, while tremendously strong in resisting applied compressive stresses, concrete is notoriously weak in coping with imposed tensile stresses. In order to deal with this deficiency, most concrete is cast with continuous steel reinforcement that imparts a sufficient tensile load bearing capacity. Unfortunately, steel is highly susceptible to deterioration via corrosion. Corrosion, manifested as formation of rust, affects load-carrying capacity of structures via loss of rebar cross-section, loss of bond with the concrete, cracking, and subsequent delamination and spalling of the cover concrete. Corrosion of steel in US bridges alone costs \$8.29 billion annually, not counting the indirect cost to users from traffic delays and lost productivity which can be ten times larger (Sohanghpurwala, 2011).

Corrosion is an electrochemical process very much like the one that produces power in an ordinary electrical cell. In a cell which is generating current, the anode is the negative electrode from where electrons are generated and then flow to the positive, cathode electrode. OH ions are reduced at the cathode and flow back to the anode to form rust at the anode. In concrete, the rust can grow to a volume several times that of the steel from which it was formed. Some of the products have a volume upto 6.15 times that of the original rebar (Jamali et al, 2013). The result is that the growing rust will crack the cover through delamination and spalling.

The surface of the corroding steel functions as a mixed electrode that is a composite of anodes and cathodes electrically connected through the body of steel itself, upon which coupled anodic and cathodic reactions take place. Concrete pore water functions as an aqueous medium, i.e., a complex electrolyte (Ahmad, 2003). The areas where iron is more easily oxidized form the anodic regions, while the other areas are cathodic (Zumdahl, 1998) (Figure 2.5).



Figure 2.5: Corrosion of rebar (Ahmad, 2003)

In the anodic regions each iron atom gives up two electrons to form a Fe^{2+} ion:

 $Fe \rightarrow Fe^{2+} + 2e^{-}$

(2.1)

The electrons that are released flow through the steel, as they do through the wire of a galvanic cell, to a cathodic region where they react with oxygen and water:

$$\frac{1}{2}O_2 + H_2O + 2e^- \to 2OH^- \tag{2.2}$$

 OH^{-} ions formed in the cathodic regions travel back to the anodic regions through the moisture on the surface of the steel, just as ions travel through a salt bridge in a galvanic cell. In the anodic regions they react with Fe^{2+} to form rust which is hydrated iron oxide of variable composition:

(rust)

$$Fe^{2+} + 2(OH)^- \rightarrow Fe(OH)_2 \xrightarrow{O_2, H_2, 0} Fe_2O_3 \cdot nH_2O$$
 (2.3)

Fortunately, experience with reinforced concrete structures shows that even under aggressive environmental conditions, the reinforcement embedded in concrete will be protected against corrosion during normal service life, provided that the mix is properly designed, placed, compacted, and sufficient concrete cover is provided (Mindess, 2003). In good quality, well-compacted concrete, reinforcing steel should not be susceptible to corrosion, even though active sites resulting from inhomogeneities in the steel or nonuniform stress concentrations are likely to be prevalent. This is because the high alkaline conditions (pH > 12) present within concrete cause a passive oxide barrier to form on the surface of the steel and prevent corrosion. It is only when this passiviating layer is destroyed that the embedded steel becomes susceptible to corrosion. One of the ways that rebar can become depassivated is through the carbonation reaction of concrete.

2.2.1 Carbonation Induced Corrosion of Reinforced Concrete

Carbonation of concrete occurs due to a reaction between atmospheric CO₂ and the hydrated phases of concrete. Hydration of tricalcium and dicalcium silicates in cement powder (C₃S and C₂S) results in the

formation of calcium silicate hydrates (CSH) and calcium hydroxides (Ca(OH)₂) in hydrated cement paste (Neville, 1996). The cement paste acts a binder for fine and coarse aggregates in hardened concrete.

Natural concrete carbonation is a chemical process by which atmospheric CO_2 reacts with $Ca(OH)_2$ in concrete to form calcium carbonate ($CaCO_3$). The reaction predominately used to describe the chemical reaction is given in Equation 2.4 (Sulapha et al, 2003) and the carbonation process is graphically illustrated in Figure 2.6:



Figure 2.6: CO₂ diffusion into concrete pores

In addition to the primary reaction, there are several other reactions which occur with the other constituents of the concrete to form $CaCO_3$ as well (Equations 2.5-2.7) (Peter et al, 2008):

$$(3CaO \cdot 2SiO_2 \cdot 3H_2O) + 3CO_2 \rightarrow (3CaCO_3 \cdot 2SiO_2 \cdot 3H_2O)$$
 (2.5)

$$(2CaO \cdot SiO_2) + 2CO_2 + nH_2O \rightarrow (SiO_2 \cdot nH_2O) + 2CaCO_3$$

$$(2.6)$$

$$(3CaO \cdot SiO_2) + 3CO_2 + nH_2O \rightarrow (SiO_2 \cdot nH_2O) + 3CaCO_3$$

$$(2.7)$$

While all species compete to react with CO_2 , Peter et al (2008) showed that the amount consumed by carbonation of $Ca(OH)_2$ is three times as great as that of CSH, 20 times as great as that of C_2S and roughly 50 times as great as that of C_3S . Therefore, they concluded that in simulations carbonation of C_2S and C_3S (Equations 2.6 and 2.7) can be ignored. Park (2008) asserted that one-half of CO_2 in concrete reacts with $Ca(OH)_2$ while the other half reacts with CSH. This assertion was further supported by Glasser and Matschei (2007) who showed that the reaction would occur in sequence, with $Ca(OH)_2$ first being fully consumed and then CSH, the reactions thereby densifying the microstructure.

Carbonation is heavily influenced by the type of cement used. Blended cements containing different types of Supplementary Cementitious Materials (SCMs). It has been established (Papadikas, 2000), that the carbonation depth decreases as aggregate replacement by SCM increases and increases as cement replacement by SCM increases. Fly Ash or Silica Fume reduces the amount of calcium hydroxide available for carbonation and thereby increases the overall carbonation rate. However, for aggregate replacement by an SCM the total amount of carbonatable constituents remains almost the same along with a decrease in porosity, resulting in lower carbonation rates. For cement replacement by an SCM the total amount of decreases due to decrease in total Ca(OH)₂, resulting in overall higher carbonation rates. Therefore, when designing mixes with SCMs to protect against carbonation, care must be taken to incorporate the SCM as part of the aggregate replacement, and not just the cement replacement.

The ingress of aggressive ions or molecules into saturated or dry concrete is governed by several transport mechanisms. As far as carbonation is concerned, the main transport mechanism is diffusion (Roziere et al, 2009). Diffusion is defined as the phenomenon of material transport by atomic motion due to a concentration gradient. The CO_2 that reacts with the carbonatable constituents of hardened
cement paste diffuses from the environment into the air-filled fraction of the pores of the concrete or the mortar from regions of high CO₂ concentration to those of low. There it dissolves into the film of water that covers the wall pores and reacts with Ca(OH)₂. Solid Ca(OH)₂ is dissolved from the cement gel into the pore water, and diffuses in it from regions of high alkalinity to those of low. The carbonation process can therefore only proceed to the depth to which there is capillary pore moisture present (Saetta et al, 1993). The end effect is for the pH of the concrete to be reduced from ≥ 12 to ≤ 8.3 in fully carbonated concrete (Huet et al, 2005). The reduction in pH will cause rebar embedded in the concrete to depassivate and become vulnerable to corrosion.

As the volume of rust begins to build up, the concrete begins to delaminate as it begins to crack and becomes hollow underneath the surface. As cracks become more severe, spalling occurs, the concrete cover is pushed off, and the rebar becomes completely exposed, further accelerating the corrosion process. The process is shown in Figure 2.7.



Figure 2.7: Spalling and cracking of concrete

Corrosion, and the consequent delamination and spalling which occurs, can lead to an undesirable aesthetic appearance for the structure. More importantly, the loss in cross-sectional area of the rebar,

as well as deterioration in the concrete can potentially lead to catastrophic structural failure if the corrosion goes unnoticed or is not repaired in time.

Chapter 3: Numerical Modeling and Verification

As described in Chapter 2, increasing atmospheric CO_2 emissions will likely increase the rates of carbonation in reinforced concrete structures. However, there is a lack of a reliable numerical model to predict the depth of carbonation as a function of time.

To address this deficiency, a numerical model involving simultaneous solution of the transient diffusion and reaction equations of CO_2 and $Ca(OH)_2$ is developed. The model includes the effects of variations of various parameters such as porosity, humidity, temperature, atmospheric CO_2 concentrations and chemical reaction rates.

The model is experimentally verified by accelerated carbonation tests, and found to be able to forecast carbonation depths in non-pozzolanic, unloaded, uncracked concrete specimens under conditions of multiple, simultaneous, time-varying concentrations of CO₂, temperature and humidity. This makes it ideal to be able to predict carbonation depths under conditions of climate change. After verifying its applicability to be able to predict corrosion initiation times, the model is extended over an entire serviceable life span to include corrosion propagation times through to cracking and spalling of concrete cover.

Finally, a similar, new, theoretical model is presented for predicting the depth of carbonation in the presence of a structural crack in concrete.

3.1 Model Development: Uncracked Concrete

Natural concrete carbonation is a chemical process by which atmospheric CO_2 reacts with $Ca(OH)_2$ and CSH to form $CaCO_3$. The equations were described in Section 2.2.1, and the process was graphically illustrated in Figure 2.7. The two predominant equations are repeated in Equations 3.1 and 3.2.

$$CO_2 + Ca(OH)_2 \rightarrow CaCO_3 + H_2O \tag{3.1}$$

$$(3CaO \cdot 2SiO_2 \cdot 3H_2O) + 3CO_2 \rightarrow (3CaCO_3 \cdot 2SiO_2 \cdot 3H_2O)$$

$$(3.2)$$

As per Equation 3.2, in addition to its reaction with Ca(OH)₂, CO₂ will also react with CSH in concrete to form additional CaCO₃ (Park, 2008, Wang and Lee, 2009, Peter et al, 2008, Borges et al, 2010, Bahador and Cahyadi, 2009). Consumption of Ca(OH)₂ and formation of CaCO₃ cause a decrease in the pH of the concrete. However, the interaction between all the components in solution is complex, and it is not easy to compute the exact pH at any given time (Ishida and Maekawa, 2000). As concrete carbonates, the reaction is fast enough relative to dispersion that three distinct zones can be assumed to form within the concrete (Houst and Wittman, 2002). One is the fully carbonated layer into which CO₂ has penetrated and reacted (complete reaction of Ca(OH)₂ and CSH, pH \leq 8.3). The second is a noncarbonated layer into which CO₂ has not yet penetrated (no reaction of Ca(OH)₂ or CSH, pH \geq 12). CO₂ diffuses through the carbonated layer towards the non-carbonated layer. The third zone is an intermediate transition layer where there is partial consumption of Ca(OH)₂ and CSH, and pH decreases through this layer from \geq 12 to \leq 8.3. Therefore, concrete carbonation can therefore be thought of as a process by which a carbonation front progresses from the outer edges of a specimen inwards, with the carbonated concrete having a lower pH. This is graphically illustrated in Figure 3.1.



Figure 3.1: Progression of carbonation front in a specimen

The standard test to determine the location of the carbonation front is the phenolphthalein test in which a section of the carbonating specimen is split or sawcut and then sprayed with a solution of 1% phenolphthalein in 70% ethyl alcohol. The areas which have carbonated remain clear in color (pH < 9), whereas uncarbonated areas turn purple (pH > 9). The depth of carbonation can then be determined by averaging the depth along the perimeter of the carbonation front at 12 different locations (3 measurements on each side of the section). In all experiments for this thesis, specimens were sawcut, and not split, as the specimens needed to be cut on a fairly regular basis.

The problem with this test is that the actual location of the carbonation front is in fact deeper than that as indicated by the phenolphthalein spray (Thiery et al, 2007). Pacheco Torgal et al (2012) reported that the use of phenolphthalein indicator may underestimate real carbonation depths by as much as 100%. The phenolphthalein test indicates a position within the transition zone where pH is = 9, and not the actual start of the transition zone. The actual length of the transition zone is a subject of debate. McPolin et al (2009) report it to be as much as 8 mm. The area in front of this location has already started to carbonate to a pH between 12 and 9. For this reason, it has been found that the location of the carbonation front as determined by the phenolphthalein test does not in fact need to be exactly at the depth of the rebar, but only within about 5 mm of the embedded rebar to induce corrosion (Yoon et al, 2007). Chang and Chen (2006) determined that the location of the carbonation front determined by the phenolphthalein test corresponds to a location where approximately $\frac{1}{2}$ of the initial Ca(OH)₂ has been consumed. Therefore, for modelling purposes, it is permissible to divide the concrete into two zones determine where $\frac{1}{2}$ of the Ca(OH)₂ is consumed (pH=9), and then assume that the transition zone begins 5 mm in front of this location.

3.1.1 Fickian Diffusion

Uni-directional diffusion of CO₂ is usually determined for steady state diffusion in a homogenous medium by analogy with Fick's first law:

$$J_x = -D\left(\frac{\partial c}{\partial x}\right) \tag{3.3}$$

where:

 $-J_x$ is the diffusion flux of CO_2 in the x-direction

-D is the diffusion coefficient for CO₂ in the medium of interest

-x is a coordinate normal to the surface of the medium of interest

- c is the CO₂ concentration in the concrete specimen

When there are time variations, one-dimensional diffusion of CO_2 into concrete should be modeled assuming non steady state diffusion by analogy with Ficks second law:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial c}{\partial x} \right) \tag{3.4}$$

where:

-t is time

For the carbonation reaction, the effective diffusivity of the porous concrete medium decreases, as $CaCO_3$, produced by the reaction, gradually blocks the pores in the concrete.

Equations 3.3 and 3.4 generally form the basis for models developed to predict carbonation rates/depths (Yoon et al, 2007, Sisomphon and Franke, 2007, Roy et al, 1999, Papadakis et al, 1992).

Liang and Lin (2003) prepared a comprehensive review of the equations for modeling concrete carbonation, and catalogued the different one-dimensional linear diffusion equations applicable. Depending on the complexity of the model being considered, the equations can be modified to include properties such as reaction rate of CO₂ and pore water conductivity.

3.1.2 Porosity Dependence

The diffusion rate at which molecules are transported in concrete depends on the size and connectivity of the pore system. As the water/cement (w/c) ratio is lowered, the pore system becomes finer and less connected, leading to lower and lower transport rates and a lower effective diffusivity.

Gas diffusion through porous media is often divided into two independent modes or mechanisms, each with a distinct diffusion coefficient. These two modes are Knudsen diffusion and molecular diffusion. In Knudsen diffusion, the gas molecules collide more frequently with the pore walls than with other gas molecules, while molecular diffusion defines the mechanism by which the different species of a mixture move relative to each other under the influence of concentration gradients, with molecule-molecule interactions dominating over molecule-pore wall collisions (Figure 3.2).

Knudsen diffusion	:•	1. 1919	0 0
Molecular diffusion	•• 1	11 383	° ₀ ° 0

Figure 3.2: Knudsen and molecular diffusion mechanisms (Sercombe et al, 2007)

The equations from which the Knudsen diffusion and molecular diffusion coefficients can be calculated are given by Zalc et al (2004). Both Knudsen and molecular diffusion coefficients are temperature dependant, and they can be combined to estimate the overall effective diffusion coefficient (Sercombe et al, 2007):

$$D = \frac{s}{\tau} \left(\frac{1}{D_m} + \frac{1}{D_k} \right)^{-1}$$
(3.5)

where:

-D_m is the molecular diffusion coefficient

-D_k is the Knudsen diffusion coefficient

 $-\epsilon$ is the porosity of the porous medium

 $-\tau$ is the tortuosity of the porous medium

In practice, it is very difficult to accurately predict the ultimate tortuosity and average pore diameter of carbonated concrete. Strong efforts have been made (Wardeh and Perrin, 2006, Maekawa et al, 2003) to model concrete on a microscale and to determine the tortuosity functions of cement paste, but the complexity and uncertainties of this approach are not warranted in the current context.

Papadikas et al (1991) proposed an empirical expression to estimate the effective diffusivity of CO_2 in concrete based on its porosity:

$$D_{CO_2} = A \left(\frac{V_p}{\frac{C}{\rho_c} + \frac{W}{\rho_w}} \right)^{\alpha}$$
(3.6)

where:

-A and α are empirical parameters determined experimentally with suggested values of A=1.64x10⁻⁶ m²/s and α =1.8 (Papadikas et al, 1991)

```
-V_p is the pore volume of cement paste (m<sup>3</sup>)
```

-C is the cement content (kg)

-w is the water content (kg)

 $-\rho_c$ is the absolute density of cement (3120 kg/m³)

 $-\rho_w$ is the density of water (1000 kg/m³)

Additionally, CO_2 diffusing through the concrete is diffusing through concrete which will have had a further reduction in porosity due to carbonation. The expression to calculate V_p along with the further reduction in porosity due to carbonation is found in Papadikas et al (1991). Equation 3.6 is used here to estimate the effective diffusivity, subject to modification by other factors, as discussed below.

3.1.3 Temperature Effects

As temperature increases, the diffusivity of CO_2 increases due to increased molecular activity. The temperature dependence of the diffusion coefficient is commonly assumed (Saetta et al, 1993, Song et al, 2006, Saeki et al, 1991) to follow an Arrhenius relationship:

$$D(T) = D_{ref} e^{\left[\frac{Q}{R}\left(\frac{1}{T_{ref}} - \frac{1}{T}\right)\right]}$$
(3.7)

where:

-Q is the diffusion activation energy. The activation energy for CO_2 diffusing in concrete was experimentally determined (Saeki et al, 1991) to be approximately 39000 J/mol K

-T_{ref} is a reference temperature (298K)

-T is the temperature of interest (K)

It is also important to determine the rate at which CO_2 reacts with $Ca(OH)_2$ to form $CaCO_3$, as this is also temperature-dependant. Numerous studies have been carried out to determine the reaction rate of CO_2 with $Ca(OH)_2$. Studies (Park, 2008, Papadakis et al, 1991, Van Balen and Van Gemert, 1994, Ishida and Maekawa, 2000) have resulted in a wide range of values. Khunthongkeaw and Tangtermsirikul (2005) proposed a second order relationship with a rate constant of:

$$k_c = \beta e^{\left(\frac{-U}{RT}\right)} \tag{3.8}$$

where:

 $-k_c$ is the reaction rate constant for reaction between CO_2 and $Ca(OH)_2$ at the temperature of interest (m³/mol/s)

-U is the reaction activation energy (40000 J/mol K) (Khunthongkeaw and Tangtermsirikul, 2005)

 $-\beta$ is the pre-exponential factor (1390 m³/mol/s) (Khunthongkeaw and Tangtermsirikul, 2005)

It should be noted that an attempt was made by the author to experimentally measure the value for U and β using low temperature Thermographic Analysis (TGA). Results from this experiment were unsuccessful, and a discussion is presented in Chapter 6 of this thesis. Therefore, the values given by Khunthongkeaw and Tangtermsirikul (2005) were utilised in the simulations which follow.

3.1.4 Relative Humidity Dependence

The moisture content in concrete is of major importance. As CO₂ diffusion controls the carbonation process, the reaction slows down when the pores are water-saturated. In that case, CO₂ hardly reacts with the concrete because of the low rate of diffusion of CO₂ in water. The higher the humidity, the slower the transport of gaseous CO₂. Diffusion also slows down if the concrete is too dry, since, although CO₂ diffuses into the capillary pores, there would be no thin layer of water covering the pores for the CO₂ to then dissolve into. The environmental conditions that affect the moisture content in concrete therefore strongly affect carbonation. It has been reported (Marie-Victoire et al, 2006) that the optimum climatic conditions for carbonation are a relative humidity between 50% and 70%, with wetting and drying cycles enhancing the reaction.

Papadikas et al (1991), and Saetta et al (1995) expressed the effective diffusivity of CO_2 in concrete taking into consideration humidity, by a function of the form:

 $D \propto (1 - RH)^m$

(3.9)

where:

-D is the effective diffusivity of CO₂ in concrete

-RH is the ambient relative humidity expressed as a fraction

-m is a humidity constant, suggested to be m= 2.2 (Papadikas et al, 1991)

While many researchers agree that the humidity dependence is of this form, different values of m have been proposed, ranging from 0.6-2.8 (Bahador and Cahyadi, 2009, Ceukelaire and Van Nieuwenburg, 1993). Note that Equation 3.9 is only valid for values of RH > 0.5 (50%) as below this value, the pores become too dry, and the reaction is not able to proceed.

3.1.5 Diffusion of Ca(OH)₂

Another factor to consider is the diffusion of dissolved $Ca(OH)_2$ within concrete. However, previous literature indicates that the diffusion of $Ca(OH)_2$ is not as critical as the diffusion of CO_2 , as it is orders of magnitude smaller than gaseous diffusion. In fact, Papadikas et al (1991) contend that the former may be ignored as it is negligibly small. Park (2008) found that the diffusion coefficient of $Ca(OH)_2$ could be maintained at 1 x 10^{-12} m²/s, and the reaction rate coefficient could be higher by a thousandfold with negligible change in carbonation depth. Therefore, the diffusion coefficient of $Ca(OH)_2$ in this model is taken as 1×10^{-12} m²/s.

3.1.6 Final Formulation of Carbonation Model

Atmospheric CO_2 diffuses into the concrete primarily through the air space in the pores. The rate of diffusion of CO_2 through the water in the pores is much smaller in magnitude (Saetta et al, 1993), and is therefore ignored.

Upon reaching a given point, gaseous CO_2 dissolves into the water and forms aqueous CO_2 at that location at a concentration governed by Henry's Law:

$$CO_{2(aq)} = HRTCO_{2(g)} \tag{3.10}$$

where:

- H is Henry's constant (mol/m³ atm)
- R is the gas constant $(8.2 \times 10^{-5} \text{ m}^3 \text{ atm}/\text{ K mol})$

Henry's Constant itself varies with temperature (Fogg and Sangster, 2003):

$$H(T) = H_{ref} e^{\left[\Delta \left(\frac{1}{T_{ref}} - \frac{1}{T}\right)\right]}$$
(3.11)

where:

- H_{ref} is the reference Henry's Constant (34.2 mol/m³ atm)

- Δ is an enthalpy constant (2400 K)

 CO_2 which has dissolved into the concrete porewater at a given time also reacts with dissolved aqueous $Ca(OH)_2$, to form $CaCO_3$, thereby lowering the overall concentration of CO_2 at that location and time. This is a second order irreversible reaction (Khunthongkeaw and Tangtermsirikul, 2005), with its rate given by:

$$r_{CO_2} = k \left[CO_{2(aq)} \right] \left[Ca(OH)_{2(aq)} \right]$$

where:

- k is the reaction rate constant determined by Equation 3.8

- $CO_{2(aq)}$ and $Ca(OH)_{2(aq)}$ are the aqueous concentrations of carbon dioxide and calcium hydroxide respectively

There is an upper limit to how much $Ca(OH)_2$ can react, related to the solubility of $Ca(OH)_2$ which can dissolve in the pore water. Unfortunately, there is very limited information on the solubility of $Ca(OH)_2$ in the pores of cement paste/concrete. The only applicable equation for the solubility of $Ca(OH)_2$ in concrete at a given temperature was given (Nakarai et al, 2006) as:

$$K_{sp} = (0.0125 \times 10^9) e^{-0.019T}$$
(3.13)

where:

- K_{sp} is the solubility product of calcium hydroxide in mmol³/l³.

Assuming $Ca(OH)_2$ is the predominant alkaline component to dissolve in the pore water, the maximum concentration of $Ca(OH)_{2(aq)}$ in the solution can then be estimated from a basic solubility equilibrium formula (Zumdahl, 1998):

$$[Ca(OH)_{2(aq)}] = \left(\frac{K_{sp}}{4}\right)^{\frac{1}{s}}$$
(3.14)

Finally, the overall mole balance for CO_2 in concrete pore water at a given location and time is given by the amount of gaseous CO_2 which diffuses into the concrete and then dissolves into the pore water to form $CO_{2(aq)}$ minus the amount of CO_2 which reacts with $Ca(OH)_2$ at that point. If the diffusivity is independent of position, this can be expressed as,

$$\frac{\partial}{\partial t} [CO_{2(aq)}] = D \frac{\partial^2}{\partial x^2} [CO_{2(g)}] HRT - k [CO_{2(aq)}] [Ca(OH)_{2(aq)}]$$
(3.15)

for the domain:

$$CO_{2(g)}(x,t)$$
 $0 \le x \le L \text{ and } 0 \le t < \infty$

with initial and boundary conditions:

CO _{2(g)} (x,0)=0	for x>0
$CO_{2(g)}(0,t)=CO_{2(atm)}(t)$	for t>0
d	

 $\frac{d}{dx}CO_{2(g)}(L,t) = 0 \qquad \qquad \text{zero-flux boundary}$

Note that the second condition is a time-dependent boundary condition. Similar to Equation 3.15, the mole balance for the overall concentration of $Ca(OH)_2$ in a pore at a given time and location is:

$$\frac{\partial}{\partial t} \left[Ca(OH)_{2(aq)} \right] = D \frac{\partial^2}{\partial x^2} \left[Ca(OH)_{2(aq)} \right] - k \left[CO_{2(aq)} \right] \left[Ca(OH)_{2(aq)} \right]$$
(3.16)

for the domain:

 $\mathsf{Ca}(\mathsf{OH})_{2(\mathsf{aq})}(\mathsf{x},\mathsf{t}) \qquad \qquad 0 \leq \mathsf{x} \leq \mathsf{L} \text{ and } 0 \leq \mathsf{t} < \infty$

with initial and boundary conditions:

$$\begin{split} & Ca(OH)_{2(aq)}(x,0) = Ca(OH)_{2(aq)i} & \text{for } x > 0 \\ & \frac{d}{dx}Ca(OH)_{2(aq)}(0,t) = 0 & \text{zero-flux boundary} \\ & \frac{d}{dx}Ca(OH)_{2(aq)}(L,t) = 0 & \text{zero-flux boundary} \end{split}$$

For concrete, the thermal diffusivity is much greater than the mass diffusivity. Therefore, the temperature of the concrete is assumed to be uniform at any time so that there is no need to also solve the energy equation or to account for the heat of reaction.

A flowchart to illustrate how Equations 3.15 and 3.16 are formulated is shown in Figure 3.3. A sample iteration for the process is given in Appendix A. Equations 3.15 and 3.16 are solved in MATLAB to determine the concentrations of CO₂ and Ca(OH)₂ at a given time and location within a concrete specimen using the "Method of Lines" (Cutlip and Shacham, 2007). They were numerically solved using nodes spaced 5 mm apart in the simulated specimen. The solution turned out to be stiff, and therefore, the 'ODE23s' (2nd/3rd order Runge-Kutta) function was utilized to solve the simultaneous equations, rather than 'ODE45' (4th/5th order Runge-Kutta), the more common solver.



Figure 3.3: Flowchart for the determination of CO₂ and Ca(OH)₂ concentrations as functions of time

3.2 Model Verification: Uncracked Concrete

In order to compare the carbonation model described in the previous section with experimental data, specimens were cast, cured, and subjected to accelerated testing in an ESPEC PR4-KPH carbonation chamber. The carbonation chamber was able to control CO_2 concentration (0%-20%, +/- 0.1%) temperature (-5 °C - 80 °C, +/- 0.1 ° C), and relative humidity (5%-98%, +/- 1%). Concrete blocks of dimensions 100 mm x 100 mm x 350 mm were cast, allowed to cure in a 20° C water bath for 28 days, removed from the bath and then preconditioned at laboratory conditions (20° C, 60% RH) over a further 28 days before being placed in the carbonation chamber.

Two types of concrete were tested. One was a virgin, uncontaminated mix (Mix A), while the other was a chloride-contaminated mix (0.5% /wt of cement) (Mix B) with the same basic design as Mix A. The

contaminated mix was selected to determine whether the presence of chlorides would affect the carbonation progress. For each of the mixes, the slump was maintained at 200 mm +/- 25 mm and the air content was maintained between 4%-8%. Slump and air content were measured as per CSA A23.2 (CSA, 2009). A chemical analysis of the cement used is provided in Appendix A. The mix design is given in Table 3.1:

Type 10 Ordinary Portland	
Cement	380 kg/m ³
Water	190 kg/m ³
20 mm Coarse Aggregate	800 kg/m ³
Fine Aggregate	850 kg/m ³
Air Entrainment Admixture	150 mL/m ³

Table 3.1: Mix A, uncontaminated mix design (w/c=0.5)

Samples were subjected to four different laboratory scenarios, with each scenario running for 8 weeks. The scenarios were selected in such a way as to evaluate the effect of time for each individual atmospheric variable (CO₂ concentration, temperature and humidity) on carbonation progress, by linearly incrementing each with time. For each type of mix, and for each scenario, five blocks of concrete were cast. This made for a total of 40 blocks cast and subjected to carbonation testing over the course of the study. The scenarios are described in Figure 3.4:



Figure 3.4: Laboratory scenario descriptions

At 7-day intervals, the specimens were removed from the chamber, and sections 30 mm thick were sawcut from each block. Each section was then sprayed with phenolphthalein solution, and 12 measurements were taken and averaged to determine the carbonation depth. A sample section is shown in Figure 3.5:



Figure 3.5: Carbonated concrete section

The results from all four laboratory scenarios are compared with the predictions of the carbonation model in Figures 3.6-3.13.



Figure 3.6: Comparison of experimental results vs model predictions for Scenario A, uncontaminated concrete, (air

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content=5.2%)
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Figure 3.7: Comparison of experimental results vs model predictions for Scenario B, uncontaminated concrete, (air content=5.0%)



Figure 3.8: Comparison of experimental results vs model predictions for Scenario C, uncontaminated concrete, (air content=4.0%)



Figure 3.9: Comparison of experimental results vs model predictions for Scenario D, uncontaminated concrete, (air

content=4.0%)



Figure 3.10: Comparison of experimental results vs model predictions for Scenario A, chloride-contaminated

concrete, (air content=5.4%)



Figure 3.11: Comparison of experimental results vs model predictions for Scenario B, chloride-contaminated concrete, (air content=7.0%)



Figure 3.12: Comparison of experimental results vs model predictions for Scenario C, chloride-contaminated concrete, (air content=8.0%)



Figure 3.13: Comparison of experimental results vs model predictions for Scenario D, chloride-contaminated

concrete, (air content=5.5%)

It can be seen from Figures 3.6-3.13 that with manual fitting, the model matches the experimental results quite well. In order to manually fit the model to the experimental data from all experiments, in Equation 3.6 A was adjusted to $4x10^{-5}$ m²/s rather than $1.64x10^{-6}$ m²/s as originally proposed (Papadakis et al, 1991). The effect of the presence of chloride ions in the contaminated mixes seems to be inconclusive, as differences in the rates of carbonation between contaminated and non-contaminated concrete may be attributable more to differences in air contents. However, while the presence of chloride ions may not affect carbonation rates, in cases where concrete contains significant levels of chloride contamination, carbonation causes bound chloride ions to be released from the cement hydration products and the resistivity decreases, so high rates of corrosion may be sustained even when the humidity of the surrounding air is kept at moderate levels. Therefore the joint effects of chlorides and carbonation should be taken into account when assessing risk of damage to aging concrete buildings (Page, 2012).

Most carbonation related studies use the empirical formulation in Equation 3.6 to estimate the effective diffusivity of CO₂ in concrete. However, some studies have questioned the value of A originally suggested (Wang and Lee, 2009), (Bahador and Cahyadi, 2009). Closer examination of Equation 3.6 is needed with respect to the value of A proposed in this thesis. Logic dictates that as the concrete porosity approaches unity, the diffusivity of CO₂ should approach that of the diffusivity of CO₂ in air. A very porous concrete would have a very high water content, and a low cement content. Therefore, in Equation 3.6, as c decreases and w increases, V_p, as well as the denominator, approach 1, so that D_{co2} approaches the value for A. This assertion can be numerically verified using any theoretical mix design for a mix design with an extremely high w/c ratio. Therefore, A should be close to the value for the diffusivity of CO₂ in air. The diffusivity of CO₂ in air at 298K has been measured to be $1.65 \times 10^{-5} \text{ m}^2/\text{s}$ (Marrero and Mason, 1972), which is much closer to the proposed value of A of $4 \times 10^{-5} \text{ m}^2/\text{s}$ imposing an upper limit on D_{co2} of $1.65 \times 10^{-5} \text{ m}^2/\text{s}$ (diffusivity in air). Alternatively, it may also be possible to set A as $1.65 \times 10^{-5} \text{ m}^2/\text{s}$, and adjust the value of α as an alternate way of correcting Equation 3.6.

In order to further verify the uncracked model when multiple atmospheric conditions were simultaneously varied, a number of sound concrete specimens were cast, water cured for 28 days, allowed to come to equilibrium with laboratory conditions (20° C, 60% RH) over a further 28 days then subjected to accelerated testing in the carbonation chamber. Two additional concrete mixes (C+D) were designed, and details are specified in Tables 3.2 and 3.3. Slump was maintained at 225 mm +/- 25 mm and an air content of 6% +/- 1%. Five 100 mm x 100 mm x 350 mm prismatic block specimens were prepared per batch, and each batch of specimens was placed in the chamber for a slightly longer duration of 12 weeks. For Mixes C and D, as CO₂ concentrations were linearly increased from 4%-10%, temperature was concurrently raised from 24 to 60° C, while the RH was held constant at 60%.

Type 10 Ordinary Portland	
Cement	290 kg/m ³
Water	188.5 kg/m ³
20 mm Coarse Aggregate	990 kg/m ³
Fine Aggregate	740 kg/m ³
Air Entrainment Admixture	150 mL/m ³

Table 3.2: Mix C (w/c=0.65)

Type 10 Ordinary Portland	
Cement	380 kg/m ³
Water	228 kg/m ³
20 mm Coarse Aggregate	770 kg/m ³
Fine Aggregate	820 kg/m ³
Air Entrainment Admixture	150 mL/m ³



Figure 3.14: Comparison of experimental results vs model predictions for Mix C, (air content=4.0%)

Table 3.3: Mix D (w/c=0.60)



Figure 3.15: Comparison of experimental results vs model predictions for Mix D, (air content=6.5%)

Clearly from Figures 3.14 and 3.15, the model predictions match the measured experimental values very well. These results provide additional evidence that the original model holds for sound, uncracked concrete when being subjected to multiple changes in ambient conditions. This makes it suitable to be able to predict carbonation depths under conditions of climate change. It would also be prudent to verify the model against data from naturally carbonated concrete where it may be available.

It has been established that there is a time lag in reaching equilibrium conditions between external and internal relative humidity (Russell et al, 2001, Franzen and Mirwald, 2004, Ryu, 2011), when the external relative humidity is fluctuating. The lag time increases with the depth of concrete, and therefore, the humidity profile is not uniform. For Scenario C where humidity is increased by 40% over 8 weeks, the actual internal relative humidity would likely be less than the external humidity. To rectify this, this scenario could be run over a longer time period to allow internal and external humidities to equilibrate at the carbonation front.

It should be noted that previous studies have found that for natural carbonation of average quality concrete, the measured diffusion coefficient is around $5x10^{-8}$ to $50x10^{-8}$ m²/s (Sanjuan and del Olmo,

2001). As expected, for accelerated tests where environmental conditions would be highly conducive to promote carbonation, simulations calculate a value for the diffusion coefficient up to 65 times greater than that those under natural atmospheric conditions $(1.1x10^{-2}-3.4x10^{-2} \text{ cm}^2/\text{s})$. The same code gives diffusion coefficients in the same range as found in (Sanjuan and del Olmo, 2001) for simulations under natural atmospheric conditions. Therefore, while it is entirely possible that the microstructure of carbonated concrete formed in accelerated conditions may not be the same as that under natural conditions, considering how well the simulation matches the experimental data, and the reasonable values for the diffusion coefficient obtained under natural conditions, we believe that the results can be applied to simulate natural carbonation as well. The issue was further considered, and carbonation products of concrete subjected to natural and accelerated Carbonation conditions were tested by X-ray diffraction (XRD) Analysis, and the results are presented in Chapter 7 of this thesis.

3.3 Model Development: Corrosion Propagation

When developing a model to determine the time to end of servicable life for a specimen due to corrosion, the time frame can be split into two parts: The time to initiation of corrosion (t_0), and the propagation time (t_{cr}) (Figure 3.16). t_0 can now be calculated using the model developed in previous sections. We focus on calculation of t_{cr} in this section.



Figure 3.16: Corrosion initiation and propagation diagram (El Maaddawy and Soudki, 2007)

Numerous models have been developed to predict the time from the onset of corrosion propagation to cracking and spalling of the concrete cover. Chernin and Val (2011) thoroughly summarized the development of all existing empirical and analytical models for prediction of corrosion induced cover cracking. In particular the recently developed model by El Maaddawy and Soudki (2007) has been widely utilized. Essentially, the model uses an analytical thick-walled uniform cylinder which assumes that the generation of a volume of corrosion products around the corroding steel causes an expansion in the diameter of the steel. The expansion exerts a uniform pressure on the concrete surrounding the rebar, and the concrete cracks when the average tensile stress is equal to the tensile strength of the concrete. They also assume the presence of a porous zone (approximately 10 μ m thick) around the rebar which must first be filled by corrosion products before they can start exerting pressure on the surrounding concrete. A schematic for crack propagation is given in Figure 3.17.



Figure 3.17: Crack propagation schematic (El Maaddawy and Soudki, 2007)

The rigorous mathematical derivation for this model can be found in El Maaddawy and Soudki (2007). A simplified description is as follows:

The expansion of the diameter of the embedded corroding rebar is given by Equation 3.17 (Chernin and Val, 2011):

$$\Delta d = \frac{2W_{rust}}{\pi d} \left(\frac{1}{\rho_{rust}} - \frac{\gamma}{\rho_{steel}} \right) - 2\delta \tag{3.17}$$

where:

 $-\Delta d$ is the increase in bar diameter (mm)

-d is the initial bar diameter (mm)

 $-\rho_{rust}$ is the density of rust (g/mm³)

 $-\rho_{steel}$ is the density of steel (g/mm³)

 $-\delta$ is the thickness of the porous zone (10 μ m)

 $-\gamma$ is the ratio of the mass of steel to rust (0.622)

W_{rust} is the mass of corrosion product formed per unit length of reinforcing bar (g/mm)

A relation between the expansion of the rebar and the pressure caused by it on a thick-walled uniform cylinder is given by Equation 3.18 (Chernin and Val, 2011):

$$\Delta d = \frac{d}{E_{eff}} \left(1 + \vartheta - \frac{d^2}{4b(b+d)} \right) \frac{2bf_{ct}}{d}$$
(3.18)

where:

-E_{eff} is the effective modulus of elasticity of concrete (MPa)

-v is the Poissons Ratio of concrete (0.18)

-b is the concrete cover (mm)

 $-f_{ct}$ is the tensile strength of concrete (MPa)

Expressions for the modulus of elasticity of concrete (E) and the tensile strength of concrete (f_{ct}) can be found in ACI 318 (2008), and the formula for the effective modulus of elasticity (E_{eff}) is found in Chernin and Val (2011).

Faraday's Law is used to calculate the rate of rust production:

where:

-t is time (s)

-I(t) is the corrosion current density with respect to time (A/mm²)

-M is the molar mass of iron (55.85 g/mol)

-z is the valence of the reaction (2)

-F is Faraday's Constant (96458 C/mol)

A number of studies have looked at the effect of temperature on the corrosion of steel in concrete (Pour-Ghaz et al, 2009, Hussain and Ishida, 2011, Otsuki et al, 2009, Jaggi, 2001). They all have concluded that the temperature dependency of steel corrosion in concrete follows an Arrhenius relation.

$$I(t) = I_o^{-\alpha(\frac{1}{T(t)} - \frac{1}{T_0})}$$
(3.20)

where:

 $-I_{o}$ is the current flow density at the reference temperature (A/mm²)

-T(t) is the temperature at a given time (K)

-T_o is the reference temperature (K)

 $-\alpha$ is the activation energy constant (K)

Parameters such as activation energy, and the reference current flow are generally not constant and may depend on interactions between concrete resistivity, saturation level, and the cover depth. Resistivity and saturation levels vary according to concrete cover, and also change as corrosion cracks propagate. An analysis of previous literature shows the relations between depth, resistivity, saturation, and current for a corrosion microcell are wide ranging and difficult to relate (Ostvik, 2005).

It was identified that the corrosion current flowing through rebar is influenced mainly by temperature, concrete saturation, concrete resistivity, and cover depth. For concrete in service, these values tend to change with time, and therefore, generally, the corrosion current in the rebar also tends to vary with time. In order to obtain a reference current flow for Equation 3.20, a constant value for concrete resistivity and cover were assumed during the propagation phase and inserted into El Maaddawy and Soudki's (2007) corrosion model, to describe the time to cover cracking. Review of literature indicates no clear consensus exists on what the reference corrosion current density should be. The value is highly dependent on cover and concrete resistivity. Even within a particular geographical area, the corrosion rate within a structure can vary heavily depending on its exposure conditions, which in turn affect the microclimate around the embedded rebar. The European standard EN 206 (2000) tries to consider this by assigning a reference corrosion current as per the exposure class, with a particular exposure class corresponding to a set of local environmental and exposure conditions a given part of the concrete structure is exposed to. Pour-Ghaz et al (2009) found that for concrete with resistivity of 1250 Ω m and 60 mm cover depth, w/c=0.5, the reference corrosion density (I_0) at 20 C was approximately 0.1 μ A/cm². The reference corrosion current density is that which is considered to correspond to a low level of corrosion in rebar (Andrade and Alonso, 1996), or a XC1- dry exposure class in EN 206-1.

Therefore, the model can predict the change in the current flow density for a time dependent temperature in Equation 3.20. Equation 3.20 can be substituted into Equation 3.19 and then integrated to find the mass of rust produced over a certain time. This time-dependent expression for rust formation may then be substituted into Equation 3.17, and finally Equation 3.18 may be equated with

Equation 3.17 to solve for the time taken for enough rust to be generated to develop a pressure which cracks the cover concrete. The formulation is represented graphically in Figure 3.18.



Figure 3.18: Time to crack formulation

The extension of the uncracked model to consider the propagation phase of corrosion has not been experimentally verified, as it was developed and verified based on research and empirical data from previous researchers. Therefore, in Chapter 4, it has been combined with the initiation model for uncracked concrete, and the unified model was used to determine what the effects of climate change would be on the ultimate lifespan of carbonation induced corrosion of virgin, uncracked concrete right from casting to failure.

3.4 Effective Diffusion Model Development: Cracked Concrete

During its service life, the durability of concrete is often controlled by its ability to impede ion and fluid transport. During its lifespan, the transport properties of concrete are likely to be modified by the

formation of cracks. Therefore, it is important to extend any numerical model to consider how the presence of cracks in concrete may affect rates of carbonation.

Cracks may be either structural or non-structural. Structural cracks tend to be wider in width (> 0.1 mm) while non-structural cracks are generally finer (< 0.1 mm). Structural cracks usually are a result of one, or a combination of the following factors:

- Low strength of concrete
- Insufficient reinforcement
- Excessive loading
- Impact loading
- Movement of subgrade

Non-structural cracks may occur due to:

- Thermal expansion/contraction
- Plastic shrinkage
- Drying shrinkage
- External chemical attack
- Aggregate/cement interactions
- Weathering

Cracks are inevitable in most concrete members due to the weakness of concrete in tension. These cracks influence the diffusivity of the medium. However, current transport models often do not cover the effect of cracks, voids and defects in concrete on corrosion initiation, rendering them less robust than desired (Pacheco and Polder, 2010).

There have been numerous studies which have looked at diffusion properties of deleterious substances through cracked concrete (Gerard and Marchand, 2000, Alahmad et al, 2009, Song et al, 2006, Jang et al, 2011, Odeh et al, 2006). All these studies have come to the conclusion that cracks increase the total molar flux of gases/fluids through concrete.

In a world of climate change, conditions are not steady state. Atmospheric CO₂ concentrations and temperatures are expected to increase with time. However, the rate of change of CO₂, as well as temperature, will be relatively very slow, even for the worst case climate change scenarios. Therefore, it is permissible to model the process as pseudo steady state. Secondly, we assume that once the concrete has carbonated, there are no further chemical interactions between the diffusing CO₂ and the concrete. Under such pseudo steady state conditions, Fick's First Law states:

$$J = D(\nabla c) \tag{3.21}$$

where:

-J is the diffusion flux of CO₂

-D is the diffusion coefficient for CO₂ in the medium of interest

- c is the CO₂ concentration in the concrete specimen

Under steady-state conditions, cracked concrete has been depicted by many researchers (Jang et al, 2011, Odeh et al, 2006, Song et al, 2006, Gerard and Marchand, 2000) as a two regime parallel model where the deleterious substance diffuses through the sound matrix and the cracks separately:

$$J_{tot} = \frac{A_{ucr}J_{ucr} + A_{cr}J_{cr}}{A_{tot}}$$

where:

-J is the diffusion flux of CO₂

-D is the diffusion coefficient for CO₂ in the medium of interest

-A_tot, A_cr and A_ucr are the total, cracked and uncracked surface areas of concrete respectively

 $-J_{\text{tot}},\,J_{\text{cr}}$ and J_{ucr} are the total, cracked and uncracked surface areas of concrete respectively

Wilke (1950) established the concept of the 'effective diffusion coefficient', which can be used to estimate rates of diffusion in multicomponent systems such as cracked concrete. Substituting Equation 3.21 into Equation 3.22 yields:

$$D_{tot}(\nabla c) = \frac{A_{ucr}D_{ucr}(\nabla c) + A_{cr}D_{cr}(\nabla c)}{A_{tot}}$$
(3.23)

Recognizing that D_{tot} is the effective diffusion coefficient, this simplifies to:

$$D_{eff} = \frac{A_{ucr}D_{ucr} + A_{cr}D_{cr}}{A_{tot}}$$
(3.24)

An empirical formula for diffusivity of CO_2 in sound/uncracked concrete is given in Section 3.3. Considering that cracks in concrete are ideally simply void spaces filled with air, the diffusion coefficient of CO_2 in cracks should be equivalent to that of CO_2 in air. However, we recognize that the correlation is not entirely valid, as tortuosity, connectivity and constrictivity of the crack path would slow the diffusion
rate down. Therefore, a 'crack geometry factor' β (Jang et al, 2011) can be incorporated to account for these factors, and Equation 3.24 is rewritten as:

$$D_{eff} = \frac{A_{ucr}D_{ucr} + A_{cr}\beta D_0}{A_{tot}}$$
(3.25)

where:

- β is a crack geometry factor to account for tortuosity, connectivity and constrictivity of a crack

 $-D_0$ is the diffusion coefficient of CO₂ in air =1.65x10⁻⁵ m²/s @25°C (Marrero and Mason, 1972)

If we can measure/estimate the cracked area of a deteriorating concrete surface, we can calculate the effective diffusion coefficient of the cracked concrete using Equation 3.25, and substitute it into the model for sound concrete given earlier. We could then predict the increased rates of carbonation due to the presence of damage/cracks at the surface.

3.5 Effective Diffusion Model Verification: Cracked Concrete

In order to verify whether or not the effective diffusion coefficient concept can be used to predict carbonation depths in structurally cracked concrete, several batches of specimens were cast, and then cracked using a manual loading device.

To begin with, two different mixes were investigated, one batch having a w/c=0.5 and the other having w/c=0.65 (Tables 3.4 and 3.5):

Type 10 Ordinary Portland	
Cement	380 kg/m ³
Water	190 kg/m ³
20 mm Coarse Aggregate	800 kg/m ³
Fine Aggregate	850 kg/m ³
Air Entrainment Admixture	150 mL/m ³

Table 3.4: Mix E (w/c=0.5)

Table 3.5: Mix F (w/c=0.65)

Type 10 Ordinary Portland	
Cement	290 kg/m ³
Water	188.5 kg/m ³
20 mm Coarse Aggregate	990 kg/m ³
Fine Aggregate	740 kg/m ³
Air Entrainment Admixture	150 mL/m ³

For each batch, a total of 12 100 mm x 100 mm x 350 mm prismatic block specimens were cast with each block containing a piece of 10M rebar with 15 mm of cover. The specimens were loaded into 4 point loading devices and cracked (Figure 3.19 + 3.20). The specimens remained loaded so that the cracks were kept open over the course of the experiment. Each week, one of these specimens was removed from the carbonation chamber, saw cut, and had its carbonation depth measured by spraying the cut surface with phenolphthalein and noting the color change. Saw cuts were taken at three different locations on the blocks in order to examine the variation in diffusion rates depending on distance to the vicinity of a crack (Figure 3.21).



Figure 3.19: Concrete specimen under 4 point loading



Figure 3.20: Typical cracked concrete specimen



Figure 3.21: Sawcut locations

Cracks tended to traverse along the tension face of the concrete. The crack width varied between 0.1-0.3 mm to simulate structural cracking. In general, 1 or 2 cracks would form of varying depths. Cracks traversed in the middle 1/3 section of the concrete.

In all cases, the depth of carbonation on the cracked side was significantly greater than on the uncracked sides. This clearly shows that carbonation progresses faster through a damaged interface than through a sound interface. Therefore, when measuring the average carbonation depth, measurements were taken on the cracked side only. Taking measurements on the uncracked sides would provide unrepresentative results for a cracked interface. The carbonation depth provided in Tables 4 and 5 is the average depth of carbonation on the cracked side, at the three sawcut locations for each specimen.

The predicted carbonation depths presented in Tables 3.5 and 3.6 are calculated using the effective diffusion coefficient from Equation 3.25. Theoretically, the upper limit on the value of β in Equation 3.25 is 1.0, as the purpose of this factor is to account for diffusion retardation due to tortuosity, connectivity and constrictivity. The actual value should be less than 1.0. However, initially a value of 1.0 was used, and it was expected that the factor could then be adjusted to < 1.0 based on the actual crack depths.

Week	Surface Crack Area (mm²)	Carbonation Depth (mm)	Max Crack Depth (mm)	Predicted Carbonation Depth (mm)
1	10	0	70	2.5
2	20	8.2	70	5.0
3	20	11.9	50	8.0
4	10	16.0	60	11.1
5	12	24.5	55	14.5
6	20	24.9	50	18.0
7	22	33.9	55	21.8
8	22	28.2	40	26.3
9	4	26.1	60	30.9
10	15	38.3	50	36.1
11	19	39.3	50	41.9
12	10	50.0	50	48.3

Table 3.5: Crack and carbonation data, mix E, (air content=6.5%)

Table 3.6: Crack and carbonation data, mix F, (air content=5.0%)

Week	Surface Crack Area (mm ²)	Carbonation Depth (mm)	Max Crack Depth (mm)	Predicted Carbonation Depth (mm)
1	18	6.4	10	2.3
2	22	14.2	30	4.4
3	27	19.5	10	7.0
4	12	8.1	10	9.5
5	80	40.4	65	12.5
6	15	14.5	10	15.4
7	23	18.8	55	19.1
8	35	26.9	10	22.7
9	8	15.1	40	26.9
10	25	17.1	45	31.6
11	16	13.4	45	36.8
12	13	20.4	15	42.0

Results indicate that the presence of cracks severely affects the carbonation depth, causing it to vary significantly from specimen to specimen, depending on the actual cracks. Based on these findings, the effective diffusion coefficient concept cannot be used to accurately predict carbonation depths in

concrete containing discrete structural cracks. Rather, it is postulated that the presence, of deep, wide structural cracks allows for rapid penetration through the crack, followed by diffusion orthogonally through the concrete (Figures 3.22, 3.23). This can be verified, as it was found that usually, for early stages of carbonation, wherever crack depths exceeded the predicted carbonation depth, the actual measured depth would also exceed the predicted depth (Tables 3.5 + 3.6). Therefore, the presence of a deep structural crack in a concrete specimen greatly increased the initial rate of carbonation, and may lead to premature, localized corrosion within the specimen.



Figure 3.22: CO₂ diffusion into cracked concrete



Figure 3.23: Depassivation Front in cracked concrete (Pacheco and Polder, 2010)

3.6 Series Diffusion Model: Cracked Concrete

It was recognized that there was a need to further investigate the nature of carbonation in the vicinity of the crack. Therefore, a final batch of 11 additional specimens, having the same mix design as Mix E was cast. The specimens were again cracked using the same 4 point loading device as earlier (Figure 3.19). This time, however, the specimen was sawcut forming a plane orthogonal to the direction of crack propagation (Figure 3.24).



Figure 3.24: Orthogonal sawcut section of cracked specimen

Cutting the specimens in this manner allowed for closer examination of the carbonation front in the vicinity of the crack itself, and to verify whether or not diffusion through the crack was relatively instantaneous compared to diffusion through sound concrete. The length of the carbonation front in a direction orthogonal to crack propagation could also be measured.

Surface crack width, crack depth, and carbonation depths were measured at select locations as shown in Figure 3.25 and are presented in Table 3.7. Note that x is the orthogonal penetration depth at the end of the crack, y is the orthogonal penetration depth at the start of the crack, z is the distance from the surface to the carbonation front away from the vicinity of the crack and w is the depth from the surface to where orthogonal penetration is 0. The measurement locations have been illustrated by superimposing arrows onto the specimens in Figures 3.26-3.28.



Figure 3.25: Measurement locations

Table 3.7: Crack data

Week	Specimen	Surface Crack	Surface Crack	z (mm)	w (mm)	y (mm)	x (mm)
		Width (mm)	Depth (mm)				
1	1	0	0	6.5	6.5	0	0
2	2	0.1	85	11.0	19.7	11.7	0
	3	0	0	9.7	9.7	0	0
3	4	1.5	95	11.8	72.7	15.7	0
	5	0.04	40	7.5	14.0	9.8	0
4	6	0.05	10	15.3	15.3	0	0
	7	1.5	120	15.0	77.9	18.9	0
5	8	0.02	10	14.0	14.0	0	0
	9	0.5	90	11.9	90	9.2	9.2
6	10	0.3	90	15.9	70.2	20.2	7.8
	11	0.3	90	14.4	59.1	19.1	0



Figure 3.26: Carbonation profile of specimen 2 around crack



Figure 3.27: Carbonation profile of specimen 4 around crack



Figure 3.28: Carbonation profile of specimen 5 around crack

In Figures 3.26-3.28, the crack depth is indicated by the black arrow, the length w by the yellow arrow, the length y by the green arrow, and the length z by the red arrow.

One interesting finding was that the length of y was consistently greater than that of z. As the surface concentrations of CO_2 at both these locations should be similar, it was expected that these two values should be approximately equal. However, a review of literature indicates that this is consistent with previous findings, and can be explained as a 'corner effect' as was noted by Saetta et al (1995).

Visual inspection of the carbonated specimens, along with analysis of the data in Table 3.7 reveals that the mechanism of diffusion in the vicinity of a crack was as postulated earlier. CO₂ penetrates rapidly along the crack, followed by orthogonal diffusion outwards into the specimen. However, the transport of CO₂ through the crack is not instantaneous, and is not the same as the rate of diffusion of CO₂ through air. Rather, the rate at which CO₂ penetrates through the crack is a function of the crack width, constrictivity, and tortuosity, along with time. This causes the formation of carbonation profiles which can be seen in Figures 3.26-3.28. Orthogonal carbonation depths are much greater at the start of the crack than at the end. In some cases, orthogonal penetration becomes zero at a depth much less than the total crack depth which was measured at the surface. If CO₂ penetration through the crack had been instantaneous, then the penetration depth profile would be uniform along its entire length.

Crack width, constrictivity, and tortuosity are clearly the most important factors when determining the rate at which CO_2 is able to penetrate through the crack. Considering Figures 3.26-3.28, we note that the wider the crack (Specimen 5 = 0.05mm, Specimen 2 = 0.1mm, Specimen 4 = 1.5mm), the greater the penetration depth (w). Thereafter, the orthogonal penetration depth depends on time, as well as on the concentration profile at that location (Figure 3.29).



Figure 3.29: Neutralization depth in cracked concrete

Based on these observations, a new conceptual model for diffusion in cracked concrete is proposed. It may be possible to think of diffusion through a crack and then orthogonally into the concrete similar to a multilayer diffusion process, where the diffusion through the crack can be considered as diffusion through one particular medium, and then orthogonal penetration outwards as diffusion through a second medium.

The mathematical formulation for diffusion in a multilayer system with N layers (Liu et al, 2009) is:

$$\frac{\partial c_i}{\partial t} = \frac{\partial}{\partial x} \left(D_i \frac{\partial c_i}{\partial x} \right) \tag{3.26}$$

for:

i=1,2,3,...,N

We consider penetration and diffusion through a crack as a 2 layer system (N=2). This is conceptually shown in Figure 3.30:



Figure 3.30: Cracked concrete as a multilayer system schematic

For N=1 (the 'cracked' layer), the coefficient of Diffusion, D_1 will be dependent on crack width and tortuosity. Unfortunately, estimation of this coefficient is outside the scope of the thesis. However, if enough data were to be collected, it should be possible to obtain an empirical relation between crack width, tortuosity, and this coefficient.

Therefore, for N= 1, we have:

$$\frac{\partial}{\partial t} \left[CO_{2(g)} \right] = D_1 \frac{\partial^2}{\partial x^2} \left[CO_{2(g)} \right] \tag{3.27}$$

for the domain:

 $CO_{2(g)}(x,t)$

a \leq x \leq b and 0 \leq t $< \infty$

with initial and boundary conditions:

CO_{2(g)}(x,0)=0 for x>0

 $CO_{2(g)}(a,t)=CO_{2(atm)}(t)$ for t>0

For N=2, Equations 3.28 and 3.29 are very similar to Equations 3.15 and 3.16:

$$\frac{\partial}{\partial t} \left[CO_{2(aq)} \right] = D_2 \frac{\partial^2}{\partial x^2} \left[CO_{2(g)} \right] HRT - k \left[CO_{2(aq)} \right] \left[Ca(OH)_{2(aq)} \right]$$
(3.28)

for the domain:

$$CO_{2(g)}(x,t)$$

with initial and boundary conditions:

CO_{2(g)}(x,0)=0

for x>0

 $\frac{d}{dx}CO_{2(g)}(d,t) = 0$

zero-flux boundary

 $D_2 = D_{CO2}$ as per Equation 3.6.

$$\frac{\partial}{\partial t} \left[Ca(OH)_{2(aq)} \right] = D_3 \frac{\partial^2}{\partial x^2} \left[Ca(OH)_{2(aq)} \right] - k \left[CO_{2(aq)} \right] \left[Ca(OH)_{2(aq)} \right]$$
(3.29)

for the domain:

$$Ca(OH)_{2(aq)}(x,t) b \le x \le d \text{ and } 0 \le t < \infty$$

with initial and boundary conditions:

$$Ca(OH)_{2(aq)}(x,0) = Ca(OH)_{2(aq)i} \qquad for x>0$$

 $\frac{d}{dx}Ca(OH)_{2(aq)}(b,t)=0 \hspace{1cm} \text{zero-flux boundary}$

where:

 $D_3 = 1 \times 10^{-12} \text{ m}^2/\text{s}$ (diffusion coefficient of Ca(OH)₂ in concrete) (Park, 2008)

Theoretically, it is possible to simultaneously solve Equations 3.27-3.29 numerically to determine the total depth of penetration AC, and then simply subtract the distance AB to determine the orthogonal diffusion depth.

While this series model is theoretically sound, it needs to be verified experimentally. Unfortunately, at present, there is no data on estimation of D_1 for CO_2 diffusing through a crack. A database needs to be developed to be able to estimate the crack diffusion coefficient based on measured widths and tortuosities before this model could be used to measure orthogonal carbonation depths for cracked concrete.

3.7 Final Remarks

A new carbonation model based on Fick's Second Law was developed to predict the depth of carbonation in non-pozzolanic, unloaded concrete specimens, in accelerated carbonation tests, taking into account for the first time, time-varying concentrations of CO₂, temperature and humidity. The model accurately predicts scenarios where concrete is not only subjected to single changes in ambient conditions, but also when subjected to multiple changes in conditions. This makes it ideal to be able to predict carbonation depths in concrete structures under conditions of global climate change.

The model was extended based on work by El Maddawy and Soudki (2007) to consider not only the initiation phase of corrosion, but also the propagation phase, thereby providing a service life estimate for the structure. In Chapter 4, this model is used to predict service lives of concrete structures subject to climate change around the world.

Finally, an attempt was made to see if the model could be modified to consider cracked concrete structures. It was found that using the effective diffusion coefficient concept was not permissible for concrete containing discrete structural cracks. Rather, it seems that the presence of deep, wide structural cracks allows for rapid transport of CO₂ through the crack, and then orthogonal diffusion through the concrete. Therefore, the presence of a structural crack with a width exceeding a minimum threshold width, and extending to the depth of rebar may be considered sufficient to induce localized depassivation at its surface. Thereafter, a theoretical 'Series Diffusion Model' was proposed which could be used to measure orthogonal carbonation depths in structurally cracked concrete.

Chapter 4: Global Service Life Analysis

In this chapter, the unified service life model developed in Chapter 3 is applied to simulate the effects of climate change on carbonation induced corrosion of concrete structures in cities at different parts of the world.

Six cities were selected:

- Mumbai, India
- London, UK
- New York City, USA
- Sydney, Australia
- Toronto, Canada
- Vancouver, Canada

Carbonation progress was modelled for an element of a typical non-pozzoloanic concrete structure in each city, having w/c of 0.5, a compressive strength of 40 MPa and an air content of 6% were modeled. Each city is from a different region in the world, with different local climates. All are considered to be major urban centers.

4.1 Climate Scenarios

In developing the simplified climate model for this study, ambient temperature changes, CO₂ concentrations, and relative humidity levels were accounted for, as these are likely to have the most direct effect on concrete deterioration. Rainfall amounts would affect erosion/abrasion of concrete surfaces, as well as diffusion of pollutants into the subsurface. However, the actual effects of rainfall on a concrete structure are highly site specific, as the rainfall, surface temperatures, and surface impact depend on the orientation of the site, as well as any shelter provided to the surface. Therefore, for simplicity, this aspect is ignored in the weather model of these simulations.

4.1.1 CO₂ Concentrations

The locations being considered, are all urban centers, and would have higher than average CO_2 concentrations. Idso et al (2002) reported urban CO_2 concentrations of approximately 67% higher in the urban city center of Phoenix, Arizona, USA compared to the outlying rural areas, and noted the presence of an urban CO_2 dome. George et al (2007) also reported atmospheric CO_2 as being consistently and significantly increased on average by 66 ppm (approximately 15%), from rural to urban areas in and around the city of Baltimore, Maryland, USA. George et al (2007) also reported on a variety of urban centers, where the average concentration was 5-30% higher than in nearby rural environments. Therefore, in their weather model, they employed an 'Urban Environment Factor' of 1.15, thereby increasing concentrations in urban centers by 15%. Based on CO_2 concentration data provided by the SRES report (storylines A1F, A2, B1, B2) (IPCC, 2000), as well as the original IPCC data (for IS92a) (IPCC, 1992), projected CO_2 increases based on the data after applying the Urban Environment Factor of 1.15 are provided in Figure 4.1 for the BERN carbon cycle model starting from the year 2000:



Figure 4.1: Projected global CO₂ concentrations

The worst case scenario to consider, therefore, is Scenario A1FI (Scenario α) which shows the highest projected increase in CO₂ concentrations over 100 years. The best case scenario is Scenario B1 (Scenario β) which projects the lowest increase in CO₂ concentrations over 100 years. In addition, we will consider a third control scenario in which CO₂ concentrations are held constant at present day concentrations (Scenario γ). Concentrations in PPM can be converted into molar concentrations considering ambient temperatures assuming ideal gas behavior. Equations can then be developed via regression to describe how CO₂ levels will increase over time.

4.1.2 Temperature Predictions

Originally, temperatures were to be predicted using data from various national climate models However, this approach was abandoned, as the surface resolution for these models are generally insufficient, and the results would not be representative for a specific city. Sufficient resolution is important, as carbonation is highly dependent on site conditions. Rather, the change of temperature produced by global warming for the upcoming years is modeled using a simplified model which considers changes in mean global temperature and seasonal variations of weather parameters localized to a particular city through a linear time-variant function based on the work by Bastidas-Arteaga et al (2010). The mean yearly temperature is expected to increase due to global warming, while the seasonal temperature fluctuates yearly around the mean, with a peak during the annual hot season, and a trough during the annual cold season. In addition, it is recognized that over time, the duration of the hot season is expected to increase, while the duration of the cold season decreases.

To begin, based on weather data from local national weather centers, equations were developed to predict the mean yearly temperature for each of the cities, starting from the year 2000 over the next 100 years. The projected annual mean temperature for Vancouver is shown in Figure 4.2.



Figure 4.2: Projected mean temperature increases for Vancouver

A third order polynomial equation was found to best fit the projected mean temperatures. Therefore, we define the equations for mean yearly temperatures in each city by the functions:

T(t)

Mumbai:

Scenario
$$\alpha$$
 (°K) T(t) = -5E-06t³ + 0.0009t² + 0.0045t + 300.53 (4.1)

Scenario β (°K) T(t)= -7E-07t³ + 2E-05t² + 0.0248t + 300.49 (4.2)

Scenario γ (°K) T(t)=300.45 (4.3)

London :

Scenario α (°K) T(t) = -5E-06t³ + 0.0009t² + 0.0045t + 283.83 (4.4)

Scenario β (°K) T(t) = -7E-07t ³ + 2E-05t ² + 0.0248t + 283.79	(4.5)
Scenario γ (°K) T(t)= 283.75	(4.6)
New York City :	
Scenario α (°K) T(t) = -5E-06t ³ + 0.0009t ² + 0.0045t + 285.23	(4.7)
Scenario β (°K) T(t) = -7E-07t ³ + 2E-05t ² + 0.0248t + 285.19	(4.8)
Scenario γ (°K) T(t)= 285.15	(4.9)

Sydney :

Scenario
$$\alpha$$
 (°K) T(t) = -5E-06t³ + 0.0009t² + 0.0045t + 290.73 (4.10)

Scenario
$$\beta$$
 (°K) T(t) = -7E-07t³ + 2E-05t² + 0.0248t + 290.69 (4.11)

Vancouver:

Scenario α (°K) T(t)=-5E-06t ³ + 0.0009t ² + 0.0045t + 283.33	(4.13)

Scenario β (°K) T(t)= -7E-07t³ + 2E-05t² + 0.0248t + 283.29 (4.14)

Scenario γ (°K) T(t)= 283.25	(4.15)
------------------------------	--------

Toronto:

Scenario α (°K) T(t) = -4E-06t³ + 0.0008t² - 0.0066t + 282.42 (4.16)

Scenario β (°K) T(t) = -1E-06t ³ + 0.0002t ² + 0.0132t + 282.35	(4.17)

(4.18)

where:

- t is time in years

To model seasonal fluctuations, a sinusoidal function can be used with an amplitude ϕ corresponding to the yearly deviation of the maximum and minimum temperature from the mean. Based on historical data for each city, the following yearly amplitudes were determined:

Mumbai:	$\phi = 6^{\circ}$	(4.19)
London:	$\phi = 7^{\circ}$	(4.20)
New York City:	φ= 12.4°	(4.21)
Sydney:	$\phi = 5^{\circ}$	(4.22)
Vancouver:	φ= 7.2°	(4.23)
Toronto:	φ= 13.2°	(4.24)

where:

- φ is the temperature amplitude in $^{\circ}K$

The corresponding weather model is represented graphically in Figure 4.3:



Figure 4.3: Projected temperature variations

Additionally, the change in the duration of the seasons is assumed to be linear (Bastidas Arteaga et al, 2010), which is represented in Equation 4.25:

$$R(t) = R_o + \left(\frac{\Delta R}{t_a}\right) [t]$$
(4.25)

Where:

-R(t) is the fractional duration of the hot season

 $-R_{\circ}$ is the fractional duration of the hot season in 2000 (0.5)

 $-\Delta R$ is the fractional change in duration of the hot season over 100 years

-t_a is the time over which climate change is considered (100 years)

-[t] is the floor function of time

The change in duration is illustrated graphically in Figure 4.4. Notice that towards the end of the time duration, the length of the cold season has decreased, while that of the hot season has increased.



Figure 4.4: Change in seasonal duration over time (Bastidas Arteaga et al, 2010)

For the worst case scenario, the expected change in duration of the hot season (ΔR) was an increase between 0.16-0.22 (Bastidas Arteaga et al, 2010) while for the best case scenario, the expected change was between 0.06-0.14 (Bastidas Arteaga et al, 2010). Based on these values, the expected change in the duration of the hot season to be used in this model for the worst case scenario was taken as 0.2 while that for the best case scenario was assumed to be 0.1. For the control, there will be no change in durations.

Finally, the equations for the temperature of each of the cities taking into account seasonal fluctuations varying around a mean yearly temperature, with a linear decrease in the length of the cold season over time can be represented by (Bastidas Arteaga et al, 2010):

$$K(t) = T(t) + \varphi \sin(\frac{t - |t|}{1 - R(t)}\pi)$$
(4.26)

where:

- K is in $^{\circ}$ K

The final equations K(t) for the A1FI (α) and Control (γ) scenario for Vancouver are shown in Figure 4.5 and 4.6:



Figure 4.5 : Vancouver temperatures, scenario $\boldsymbol{\alpha}$

 $T(t)=-5E-06t^{3} + 0.0009t^{2} + 0.0045t + 283.3, \phi= 7.2$ °, $\Delta R=0.2$





T(t)= 283.3, ϕ = 7.2 °, Δ R=0

Figure 4.5 clearly shows that as yearly temperatures fluctuate around the mean, the mean yearly temperature gradually increases over the course of the century. The same result occurs for all cities.

4.1.3 Relative Humidity Predictions

Trends in relative humidity over the next hundred years have been a source of contention amongst climate researchers for many years. Global warming increases the evaporation from the ocean and from many land areas, leading to an increase in atmospheric water vapor content. As the global climate has warmed during the last several decades, constant global relative humidity has been observed, so within global climate modeling of future scenarios of climate change, constant relative humidity is generally assumed (IPCC 2001), (IPCC, 2007). However, not all researchers agree with this assumption. Vuille et al (2003) and Sperling et al (2004) have predicted increases in relative humidity of between 0% and 2.5% per decade. An analysis of historical trends in relative humidity in Canada, however, shows that between 1950 and 2000 there was an overall decrease in average relative humidity across the country of 6% (Van Wijngaarden and Vincent, 2005).

Ultimately, given that the current generation of climate model projections assume constant relative humidity, and that they are used as the basis for all major climate change studies including the IPCC Assessment Reports (IPCC 2001), (IPCC, 2007), we have adopted this assumption for our study, with the relative humidity remaining constant at the mean values from the year 2000. We define the equations for mean relative humidity in each city by the functions (Equations 4.27-4.32):

H(t)

Mumbai:

H(t)= 79.6%

London:

(4.27)

H(t)= 74.0%	(4.28)
New York City:	
H(t)= 58.3 %	(4.29)
Sydney:	
H(t)= 61.3 %	(4.30)
Vancouver:	
H(t)= 78.5%	(4.31)
Ioronto:	(4.22)
11(1) - 73.270	(4.52)

4.2 Year 2000

Carbonation progress was modelled for an element of a typical non-pozzoloanic concrete structure in each city, having w/c of 0.5, a compressive strength of 40 MPa and an air content of 6% were modeled. Depending on national code requirements, cover requirements will vary. Generally, codes require covers ranging from 20 mm to 75 mm depending on the grade of concrete, and the exposure class. For example, as per ACI 318 (2008), concrete slabs, joists and walls exposed to earth or weather require a minimum cover of 25 mm (+/- 10 mm). For a normal strength concrete for a similar exposure class, this is a typical value of concrete cover used throughout the world. Therefore, in this study, rebar in the reinforced concrete is assumed to have 25 mm of cover, meaning that carbonation induced corrosion would begin when the carbonation front had reached 20 mm of depth.

Assuming the structure goes into service in the year 2000, the carbonation depth is shown for each city for the three scenarios in Figures 4.7-4.12.



Figure 4.7: Mumbai carbonation depths, constructed in 2000



Figure 4.8: London carbonation depths, constructed in 2000



Figure 4.9: NYC carbonation depths, constructed in 2000



Figure 4.10: Sydney carbonation depths, constructed in 2000



Figure 4.11: Toronto carbonation depths, constructed in 2000



Figure 4.12: Vancouver carbonation depths, constructed in 2000

From the figures, four initial observations are made. First, we note an increase in the ultimate carbonation depths of between 27%-45% when comparing the control carbonation depth against the A1FI carbonation depth for the cities in question (Table 4.1). Second, carbonation is a highly site dependent phenomenon. Coastal cities (Mumbai, NYC, Sydney) which exhibit moderate humidity, and higher temperatures are more prone to corrosion than cooler, wetter cities (London, Toronto, Vancouver). Although % increases for Mumbai, NYC and Sydney were lower than that of London, Toronto or Vancouver, ultimate carbonation depths of Mumbai, NYC and Sydney were significantly higher than that of London, Toronto, and Vancouver (Table 4.2). Third, we notice that climate change does not begin to seriously affect the rate of carbonation until about 30 years into the future (in these simulations, the year 2030). It is only after 30 years that we start to see the carbonation depth curves for the A1FI and B1 scenarios begin to seriously divert from the control curves for all six of the cities. Finally, we notice that over 100 years, for all cities, there is clearly a noticeable effect of climate change on carbonation depths.

London	27%
NYC	32%
Mumbai	27%
Sydney	31%
Toronto	44%
Vancouver	45%

Table 4.1: Increase in ultimate carbonation depths, Control vs A1FI

However, it is also important to consider the actual effects of climate change on the service life of a structure. Inputting climate change data into the propagation model described in Section 3.3, the times to initiation and cracking due to carbonation induced corrosion for each of the cities are given in Table 4.2.

For simplicity, we have considered 0.1 μ A/cm² as the reference corrosion density in Equation 3.20. It is recognized that the value is speculative and considering that concrete cover depths are often < 60 mm, would somewhat overestimate propogation times. In fact, concrete cover depths can often be as low as 20 mm, and resistivity values are greatly affected by cover moisture contents. Stewart and Ping (2010) used higher values of I_o in an empirical model (0.1-0.431 μ A/cm² at 20 C). These values are reported by DuraCrete (1998) and based on the different concrete exposure classes in EN 206-1 (2000). A justification of using 0.1 μ A/cm² as the value for the reference corrosion density, and an analysis of what may happen when exposure classes are varied for a city is given in Section 4.2.1. The activation energy constant (α) used in Equation 4 is 7500K for a corrosion microcell as per Otsuki et al (2009).

London	Time to Initiation (yrs)	Time to Cracking (yrs)	Ultimate Carbonation Depth (mm)	
Control	>100	>100	11	
B1	>100	>100	13	
A1FI	>100	>100	14	
NYC	Time to Initiation (yrs)	Time to Cracking (yrs)	Ultimate Carbonation Depth (mm)	
Control	70.6	80.1	25	
B1	58.9	66.4	30	
A1FI	57.1	63.4	33	
Mumbai	Time to Initiation (yrs)	Time to Cracking (yrs)	Ultimate Carbonation Depth (mm)	
Control	62.8	65.8	26	
B1	56.6	59.2	30	
A1FI	55.3	57.4	33	
Svdnev	Time to Initiation (vrs)	Time to Cracking (vrs)	Ultimate Carbonation Depth (mm)	
Control	65.0	72.1	26	
B1	55.3	61.3	31	
A1FI				
	54.5	60.1	34	
Toronto	54.5 Time to Initiation (yrs)	60.1 Time to Cracking (yrs)	34 Ultimate Carbonation Depth (mm)	
Toronto Control	54.5 Time to Initiation (yrs) >100	60.1 Time to Cracking (yrs) >100	34 Ultimate Carbonation Depth (mm) 16	
Toronto Control B1	54.5 Time to Initiation (yrs) >100 >100	60.1 Time to Cracking (yrs) >100 >100	34 Ultimate Carbonation Depth (mm) 16 18	
Toronto Control B1 A1FI	54.5 Time to Initiation (yrs) >100 >100 88.2	60.1 Time to Cracking (yrs) >100 >100 94.4	34 Ultimate Carbonation Depth (mm) 16 18 23	
Toronto Control B1 A1FI Vancouver	54.5 Time to Initiation (yrs) >100 >100 88.2 Time to Initiation (yrs)	60.1 Time to Cracking (yrs) >100 >100 94.4 Time to Cracking (yrs)	34 Ultimate Carbonation Depth (mm) 16 18 23 Ultimate Carbonation Depth (mm)	
Toronto Control B1 A1FI Vancouver Control	54.5 Time to Initiation (yrs) >100 ≥100 88.2 Time to Initiation (yrs) ≥100	60.1 Time to Cracking (yrs) >100 >100 94.4 Time to Cracking (yrs) >100	34 Ultimate Carbonation Depth (mm) 16 18 23 Ultimate Carbonation Depth (mm) 11	
Toronto Control B1 A1FI Vancouver Control B1	54.5 Time to Initiation (yrs) >100 >100 88.2 Time to Initiation (yrs) >100 >100	60.1 Time to Cracking (yrs) >100 >100 94.4 Time to Cracking (yrs) >100 >100	34 Ultimate Carbonation Depth (mm) 16 18 23 Ultimate Carbonation Depth (mm) 11 14	

Table 4.2: Time to corrosion initiation – constructed in 2000

Note that for all the combinations considered, the time to end of service life exceeds 55 years. Considering that the structures in question would likely be subjected to deterioration by means other than carbonation during the same time, the reduction in initiation time caused by climate change would be one of many factors affecting service life. Secondly, we also note that there is a minimal reduction in propagation time (difference between time to initiation and time to failure) between the control cases, and the climate change cases, for each city.

Therefore, in the short term, it is reasonable to conclude that climate change will not significantly affect the durability of our concrete infrastructure. However, it was noted earlier that the effects of climate change become significant in fact after approximately 30 years. Therefore, in Section 4.2.2, we consider the next 'generation' of concrete structures which may be built, using the year 2030 as the time of construction.

4.2.1 Effect of Varying I₀

Stewart and Ping (2010) recommend the following mean values for I_o based on different exposure classes for concrete defined in EN206-1 (2000) and the DuraCrete Report (1998) (Table 4.3).

Exposure Class	Mean I_o (μ A/cm²)
XC1-Dry, permanently wet	0.1
XC2-Wet, rarely dry	0.345
XC3-Moderate humidity	0.172
XC4-Cyclic wet-dry	0.431

Table 4.3: Mean corrosion densities

Each exposure class corresponds to a different microclimate for the rebar embedded within the concrete, and therefore, each exposure class has a different reference corrosion density. For example,

under dry conditions, corrosion density is far lower as an insufficient amount of moisture is available for the current to flow. Even within a city, it is entirely possible that concrete could be subjected to a different exposure class from site to site. All the simulations presented in this paper assume a XC1-dry indoor exposure class, with indoor humidity equal to outdoor humidity, right from initiation, through to propagation and failure. This would in fact provide conservative estimates by overestimating values for the time to cracking. Both for carbonation progress, and corrosion propagation, a cyclic wet-dry condition would accelerate the processes. However, exposure is highly site specific, and it is currently impossible to predict moisture conditions to that level of accuracy over the next 100 years. Therefore, rather than comparing different exposure classes in different cities, to maintain uniformity, the dry exposure class was assumed for all simulations.

However, to try and quantify by how much propagation times may have been underestimated in the simulations, a single set of simulations was run for a concrete structure in the city of Sydney, Australia in 2000, where a larger difference in propagation times was noted for the worst case scenario (A1FI) for each different exposure class. The results are presented in Table 4.4:

Exposure Class	Time to Initiation (yrs)	Time to Cracking (yrs)	Propagation Time (yrs)	% Reduction in Propagation Time
XC1-Dry or				
permanently wet	54.5	60.1	5.6	-
XC2-Wet, rarely dry	54.5	56.2	1.7	69.4%
XC3-Moderate				
humidity	54.5	57.8	3.3	40.9%
XC4-Cyclic wet-dry	54.5	55.9	1.4	74.7%

Table 4.4: Propagation times, Sydney, year 2000 construction, A1FI

Clearly, the exposure class has a huge effect on the propagation time for a given city and scenario. In this case, the % Reduction in propagation time was as high as 74.7% for the C4 exposure case. It can be inferred that there would be significant reductions in propagation time for concrete subjected to more severe exposure conditions in the other cities in this study as well. However, overall, it is important to note that in this case, the propagation time was only about 10% of the initiation time, and therefore, the overall % reduction in time to cracking would not be too significant. While the values presented in this thesis are still valid, as the methodology is still sound, it may be worthwhile to do a probabilistic analysis for the different exposure classes for the different cities, and determine what is the predominant exposure class within each city as the data become available, to determine just how much faster the time to cracking is under harsher exposure conditions.

4.3 Year 2030

The scenarios were repeated for structures to be constructed in 2030. However, in this instance we consider only two climate change scenarios, schematically represented in Figure 4.13. In the control scenario, CO₂ emissions and temperature increases continue as per an A1FI scenario until the year 2030 where they stabilize. The structures would then be subjected to these stabilized, but elevated levels. The justification for this is that analysis of data over the past decade indicates that the A1FI scenario is actually the one being followed and possibly exceeded throughout the world (Schneider, 2009), and therefore, we assume that it will take until at least the year 2030 before any sort of mitigation/stabilization takes effect. In the other 'Worst Case' scenario we assume that climate change continues unabated past 2030, all the way to 2100, as per the A1FI scenario, and consider the results (Figures 4.14-4.19) (Table 4.5).


Figure 4.13: Control and A1FI scenarios for 2030



Figure 4.14: Mumbai carbonation depths, constructed in 2030



Figure 4.15: London carbonation depths, constructed in 2030



Figure 4.16: NYC carbonation depths, constructed in 2030



Figure 4.17: Sydney carbonation depths, constructed in 2030



Figure 4.18: Toronto carbonation depths, constructed in 2030



Figure 4.19: Vancouver carbonation depths, constructed in 2030

	Time to Initiation	Time to Cracking	Ultimate Carbonation Depth
London	(yrs)	(yrs)	(mm)
Control	>70	N/A	9
A1FI	>70	N/A	13
	Time to Initiation	Time to Cracking	Ultimate Carbonation Depth
NYC	(yrs)	(yrs)	(mm)
Control	57.2	65.4	23
A1FI	42.4	48.8	31
	Time to Initiation	Time to Cracking	Ultimate Carbonation Depth
Mumbai	(yrs)	(yrs)	(mm)
Control	53.9	56.6	24
A1FI	41.5	43.8	31
	Time to Initiation	Time to Cracking	Ultimate Carbonation Depth
Sydney	Time to Initiation (yrs)	Time to Cracking (yrs)	Ultimate Carbonation Depth (mm)
Sydney Control	Time to Initiation (yrs) 52.7	Time to Cracking (yrs) 59.2	Ultimate Carbonation Depth (mm) 25
Sydney Control A1FI	Time to Initiation (yrs) 52.7 40.4	Time to Cracking (yrs) 59.2 45.4	Ultimate Carbonation Depth (mm) 25 32
Sydney Control A1Fl	Time to Initiation (yrs) 52.7 40.4 Time to Initiation	Time to Cracking (yrs) 59.2 45.4 Time to Cracking	Ultimate Carbonation Depth (mm) 25 32 Ultimate Carbonation Depth
Sydney Control A1Fl Toronto	Time to Initiation (yrs) 52.7 40.4 Time to Initiation (yrs)	Time to Cracking (yrs) 59.2 45.4 Time to Cracking (yrs)	Ultimate Carbonation Depth (mm) 25 32 Ultimate Carbonation Depth (mm)
Sydney Control A1FI Toronto Control	Time to Initiation (yrs) 52.7 40.4 Time to Initiation (yrs) >70	Time to Cracking (yrs) 59.2 45.4 Time to Cracking (yrs) N/A	Ultimate Carbonation Depth (mm) 25 32 Ultimate Carbonation Depth (mm) 14
Sydney Control A1FI Toronto Control A1FI	Time to Initiation (yrs)52.740.4Time to Initiation (yrs)>70>70	Time to Cracking (yrs) 59.2 45.4 Time to Cracking (yrs) N/A N/A	Ultimate Carbonation Depth (mm) 25 32 Ultimate Carbonation Depth (mm) 14 19
Sydney Control A1FI Toronto Control A1FI	Time to Initiation (yrs) 52.7 40.4 Time to Initiation (yrs) >70 >70 Time to Initiation	Time to Cracking (yrs) 59.2 45.4 Time to Cracking (yrs) N/A N/A Time to Cracking	Ultimate Carbonation Depth (mm) 25 32 Ultimate Carbonation Depth (mm) 14 19 Ultimate Carbonation Depth
Sydney Control A1FI Toronto Control A1FI Vancouver	Time to Initiation (yrs)52.740.4Time to Initiation (yrs)>70>70Time to Initiation (yrs)	Time to Cracking (yrs) 59.2 45.4 Time to Cracking (yrs) N/A N/A Time to Cracking (yrs)	Ultimate Carbonation Depth (mm) 25 32 Ultimate Carbonation Depth (mm) 14 19 Ultimate Carbonation Depth (mm)
Sydney Control A1FI Toronto Control A1FI Vancouver Control	Time to Initiation (yrs)52.740.4Time to Initiation (yrs)>70>70Time to Initiation (yrs)>70	Time to Cracking (yrs) 59.2 45.4 Time to Cracking (yrs) N/A Time to Cracking (yrs) N/A	Ultimate Carbonation Depth (mm) 25 32 Ultimate Carbonation Depth (mm) 14 19 Ultimate Carbonation Depth (mm) 10

Table 4.5: Time to corrosion initiation – constructed in 2030

Analysis of the forecasts for structures built in 2030 reveal two important points. First, Figure 4.20 shows that when comparing each scenario, structures built in 2030 carbonate almost the same amount in 70 years as a structure built in 2000 carbonates in 100 years. This confirms that the majority of



carbonation occurring is projected to propagate after the year 2030. Second, there is a noticeable decrease in the time to cracking for the control scenario vs the A1FI scenario (Figure 4.21):

Figure 4.20: Carbonation depths for various cities in 2100

Control

A1FI

Vancouver: Year of Construction

Control

A1FI

Toronto: Year of Construction



Figure 4.21: Time to cracking for various cities

Results of the simulations for structures constructed in 2030 may cause concern. When comparing the results for NYC, Mumbai and Sydney, it is noticeable that the corrosion initiation times for the Control and A1FI scenarios in 2030 are worse than even the A1FI scenario in the year 2000. Furthermore, the worst case climate change scenario for the 2030 cases causes the time to cracking to decrease to under 45 years. In cities susceptible to carbonation damage (Mumbai, NYC, Sydney), the average reduction in life span appears to be approximately 15-20 years due to climate change. This reduction would need to be accounted for at the time of design/construction, as it would cause an earlier time to repair, which would occur within the design lifespan of the structure.

4.4 Final Remarks

Global Climate Change will affect the progression of carbonation induced corrosion in our concrete infrastructure. We will see much higher ultimate carbonation depths in the long term.

Although Climate Change will have minimal effects in the near future on durability of concrete structures, the real effects of climate change will become evident after approximately 30 years. Therefore, structures constructed in 2020-2030 may have to begin taking into account degradation due to climate change when they are designed. For the worst case scenario, for concrete structures constructed in the year 2030, in areas where carbonation induced corrosion would be a concern (moderate humidity, higher temperatures), simulations indicate that we can expect structures to begin to show a reduction in serviceable lifespan due to climate change of approximately 15-20 years, with signs of damage being apparent within 40-45 years of construction.

Concrete exposure conditions have a significant effect on corrosion propagation times in concrete. The results for time to cracking presented in this paper are for concrete only subjected to a dry exposure class, and therefore, times to cracking are somewhat overestimated, meaning the effects of climate change on time to crack initiation may be being underestimated. For harsher exposure classes, propagation times will be shorter. For one scenario, the propagation time was overestimated by approximately 75%. It may be worth conducting a probabilistic analysis for different cities, and different exposure classes to estimate the overall further reduction in times to cracking due to carbonation induced corrosion. One other consideration is that in the simulations run, a single concrete mix design was applied to all the cities under investigated. Different cities will have different design specifications based on local exposure conditions. Therefore, it may be useful to investigate the appropriateness of a local code to resistance against carbonation induced corrosion by inputting mix design values for the city being investigated and analyzing the results.

In general, throughout North America, the state of our infrastructure is quite poor. Even before considering the effects of climate change, our infrastructure is not being designed and maintained properly, and is generally not able to achieve its design life as prescribed by building codes. In this

chapter, it has been shown that climate change would play a role in decreasing the service life of an idealized structure due to carbonation induced corrosion. If we were to consider factors such as cracking due to weathering, overloading, along with the presence of chlorides in marine environments, or environments where deicers are regularly used, it is safe to conclude that in the future, climate change effects would reduce service lives even further. Therefore, it is recommended that focus be placed on designing and maintaining durable infrastructure, so that infrastructure service lives are increased sufficiently to be able to meet their prescribed service lives, and ensure that they are durable enough to deal with the longer term effects of climate change. Engineers must consider durability, and not just strength when designing concrete structures. Potential ways of increasing durability and mitigating carbonation related corrosion damage are discussed in detail in Chapter 9.

Finally, Stewart and Ping (2010) developed probabilistic models and conducted a reliability-based life cycle analysis to determine what the probabilities of climate-change related damage were to structures in several cities throughout Australia. A similar approach could be used in combination with the model developed in Chapter 3 of this thesis to determine the optimal maintenance schedule to lower costs associated with increased carbonation induced damage due to global climate change for cities throughout the world.

Chapter 5: Non-Destructive Testing of Carbonated Concrete

It is often necessary to test concrete structures after they have been in service to determine whether the structure is still sound and safe. Ideally such testing should be done without damaging the concrete. The tests available for concrete range from the completely non-destructive, where there is no damage to the concrete, through those where the concrete surface is slightly damaged, to partially destructive tests, such as core tests and pullout and pull off tests, where the surface has to be repaired after the test. The range of properties that can be assessed using non-destructive tests and partially destructive tests is quite large and includes such fundamental parameters as density, elastic modulus and strength as well as surface hardness and surface absorption, and reinforcement location, size and distance from the surface. In some cases it is also possible to check the quality of workmanship and structural integrity by the ability to detect voids, cracks and delamination.

Although it is well known that carbonation alters the properties of concrete which would influence the results of non-destructive tests (NDT) on concrete, a comprehensive study on the topic has not yet been conducted. Beyond simply modelling and forecasting carbonation depths due to climate change, it is also important to know what kind of mechanical and chemical response to expect from NDTs in order to assess damage levels within a structure in the future. Therefore, a thorough study was carried out, and in this chapter the results of a variety of NDTs on carbonated concrete are presented.

5.1 Specimen Preparation

Two types of mixes were cast:

- A. Virgin, undamaged concrete
- B. Concrete which has been contaminated with Cl ions

Mix A was meant to simulate freshly poured, idealized concrete which would have the highest resistance to any of the potential deterioration mechanisms.

Mix B simulated a special, but common case, where concrete has been subjected to, and become contaminated with chloride ions, leading to increased risk of corrosion. The amount of chloride added was 0.5% by weight of cement (Sappakittipakorn, 2010). Mix designs for Mix A and B are identical to those of Mix A and B in Chapter 3 of this thesis (Table 3.1).

Concrete specimens cast have a w/c ratio of 0.5, with no pozzolanic materials. An air entrainment agent was used to reach the target air content, and superplasticizers were not used. Slump was consistently maintained in the range of 200 mm +/- 25 mm and air content was maintained in the range of 5%-7%. Specimens were prepared as per ASTM C192 (2008). All specimens were cured in a 20 $^{\circ}$ C water bath.

For each type of mix, ten 100 mm x 100 mm x350 mm prismatic beams were cast, along with twenty seven 100 mm x 200 mm cylinders. Five of the prismatic specimens in each batch have a piece of 10M rebar embedded in it, with 25 mm of concrete cover (Figure 5.1).



Figure 5.1: Specimen types for testing

5.2 Testing Schedule

Specimens were carbonated in an ESPEC PR-4KPH Accelerated Carbonation Tester for Concrete (Figure 5.2). The chamber properties were provided in detail in Chapter 3 of this thesis. Each specimen was subjected to one of four different testing scenarios (Figure 5.3):



Figure 5.2: Carbonation chamber





Scenarios B, C and D are intended to discover what effect incrementing each of the three variables has on NDT Response of carbonating concrete. Scenario A is a baseline against which the variables can be compared.

Specimens from Mix A and B were tested simultaneously for each scenario. Each scenario took 8 weeks to complete. Therefore, it would take 32 weeks to run all of the scenarios. Each week, for each mix, 5 prismatic specimens were removed and tested for mechanical properties, and 5 were removed to determine changes in corrosion potential. Additionally 3 test cylinders were removed and subjected to compressive strength tests. The test details are explained in the following section.

5.3 Testing

As the specimens carbonated, changes in their mechanical response were monitored, as well as the corrosion potential of the rebar embedded within. As the mechanical response of the specimen deteriorates, it is likely that corrosion potential would increase as CO₂ and Cl is more easily able to diffuse in. Furthermore, once the propagation phase of corrosion begins, the mechanical response is drastically affected as corrosion products form, and the concrete begins to crack and spall.

5.3.1 Mechanical Response: Tests

The change in mechanical response with time can be determined by measuring the resonant frequency of the specimen, as per ASTM C215 (2008). Damage levels can also be judged by ultrasonic pulse velocity (UPV) tests, as per ASTM C597 (2008). Five of the ten prismatic specimens in a given batch were thus used exclusively for non-destructive mechanical response tests.

An important dynamic property of any elastic system is the natural frequency of vibration. For a vibrating beam of given dimensions, the natural frequency of vibration is mainly related to the dynamic

modulus of elasticity and density. Hence the dynamic modulus of elasticity of a material can be determined from the measurement of the natural frequency of vibration of prismatic bars and the mathematical relationships between the two. Thus the resonant frequency of vibration of a concrete specimen or structure directly is related to its dynamic modulus of elasticity and hence, its mechanical integrity (Malhotra and Carino, 2004).

The UPV technique involves determining the velocity of an ultrasonic high frequency pulse traveling through a solid material. The velocity at which the pulse propagates through the material depends on the density and elastic properties of the material. The quality of a material is often related to its elastic properties, and therefore, UPV can be used to determine the extent of decay of a given specimen. For example, a RC member which has undergone corrosion and subsurface delamination will have cracked and will be more flexible, thus having a lower elastic modulus than when the concrete was originally poured (Malhotra and Carino, 2004). UPV values were taken with the transmitter and receiver 350 mm apart at each end of each specimen.

Strength of specimens can also be directly measured via a destructive cylindrical compression test as per ASTM C39 (2008). Cylindrical concrete specimens (100 mm x 200 mm) were cast for this test. Of the 27 cylindrical specimens cast, 3 were removed on a weekly basis and destroyed in compression tests to monitor their change in strength over time. Compression tests were done on a 2.6 MN Forney FX600 compression testing unit (Figure 5.4).



Figure 5.4: Forney testing machine

5.3.2 Mechanical Response: Results

The results of resonant frequency tests on the concrete specimens as they carbonate are shown in Figures 5.5 and 5.6:



Figure 5.5: Resonant frequency vs time, uncontaminated concrete



Figure 5.6: Resonant frequency vs time, contaminated concrete

Based on Figures 5.5 and 5.6 it seems that concrete carbonation has no observable effect on the resonant frequency of a specimen. Looking at both the uncontaminated, and chloride contaminated mixes, as carbonation depth increases, no particular trend developed for the corresponding frequency measurements. As there does not seem to be any sort of correlation, monitoring resonant frequency is not a good way of monitoring carbonation development within a concrete specimen.

The UPV tests results proved to be quite interesting and unexpected (Figures 5.7-5.10). As a specimen carbonates, its density tends to increase slightly, due to the replacement of Ca(OH)₂ by CaCO₃. Since ultrasonic pulses tend to travel faster through dense media than through porous media, as carbonation depth progresses, one would expect UPV values to increase.



Figure 5.7: UPV results vs time, uncontaminated concrete



Figure 5.8: UPV results vs time, contaminated concrete



Figure 5.9: UPV vs carbonation depth, uncontaminated concrete



Figure 5.10: UPV vs carbonation depth, contaminated concrete

On the contrary, it was found that the UPV values tended to decrease with time (Figures 5.7-5.8). When UPV values are plotted against carbonation depths, we confirm the trend (Figures 5.9-5.10). As the

specimens carbonated from the outside inwards, velocities decreased. This was true in all scenarios for both types of concrete. For Scenario C, the decrease was the lowest in magnitude, which leads to speculation that the decrease in UPV may not be due to an increase in carbonation depth, but rather a loss in pore water. With time, specimens tend to dry out in the chamber, making them more porous and decreasing UPV readings. The exception was for Scenario C where humidity increased with time. Increasing humidity could prevent drying out of the pore space, and could provide an explanation as to why the magnitude of the decrease was lowest for this scenario. Moreover, the probability of damage due to carbonation shrinkage would be nearly at a maximum at relative humidities of 65% as they were in Scenarios A,B, and D. Relative humidities under 50% or near saturation mimimize carbonation shrinkage. Therefore, the humidity conditions are believed to be affecting UPV readings, both by a loss of pore water, and damage due to carbonation shrinkage. The data warrants further research to confirm this as being the mechanism of decrease in UPV.

The results of compressive strength tests are shown in Figures 5.11 and 5.12:



Figure 5.11: Compressive strength vs time, uncontaminated concrete



Figure 5.12: Compressive strength vs time, contaminated concrete

As with UPV, a slight increase in compressive strength was expected as specimens carbonate. While at the end of 6 weeks, there tended to be a slight overall increase in compressive strength, there was no exact measureable trend which could be used to correlate the rate of increase of strength with time.

5.3.3 Corrosion Potential: Tests

The change in corrosion potential of the system can be determined by measuring the linear polarization resistance (LPR), as per ASTM G59 (2009) and G102 (2010). Five of the ten prismatic specimens had a piece of 10M rebar embedded in them with 20 mm of cover, and thus could be used for non-destructive corrosion potential tests.

A simplistic summary of the method is that the test measures the amount of outside electrical current necessary to displace the corrosion potential of the reinforcing steel by a small, but known voltage. By measuring a series of offset voltages and the corresponding current within a short range of the equilibrium potential, a linear relation can be established between corrosion potential and corrosion current, called the polarization resistance. The corrosion resistance is inversely related to the

polarization resistance. A specimen which requires a large amount of voltage applied to it to induce a minimal amount of corrosion current has a high resistivity, and will not corrode as easily (Malhotra and Carino, 2004).

5.3.4 Corrosion Potential: Results

For LPR tests, corrosion is considered to be in progress once a minimum threshold current density of 0.1μ A/cm² (0.0012 mm/yr) has been reached. A moderate corrosion risk has been reached at 0.5 μ A/cm² (0.006 mm/yr). Therefore, we consider this as the threshold value beyond which an active corrosion cell has formed in the concrete and there is a real threat of failure due to carbonation-induced corrosion. Corrosion rates vs time for each mix are given in Figures 5.13 and 5.14:



Figure 5.13: Corrosion rate vs time, Mix A uncontaminated concrete



Figure 5.14: Corrosion rate vs time, Mix B contaminated concrete

Over the course of the accelerated tests, the corrosion threshold was far from being breached. However, closer examination of corrosion rate vs carbonation depth provides a possible explanation (Figures 5.15 + 5.16):



Figure 5.15: Corrosion rate vs carbonation depth, Mix A uncontaminated concrete



Figure 5.16: Corrosion rate vs carbonation depth, Mix B contaminated concrete

It has been found that carbonation induced corrosion does not initiate until the carbonation front has reached to within 5 mm of the depth of the rebar (Yoon et al, 2007). This means that for the specimens in question having a cover of 25 mm, the carbonation front must progress at least 20 mm from the outer edge of the specimens in order to measure a notable corrosion current density. Since carbonation depths never reached 20 mm, it was not surprising that corrosion current densities remained well below the threshold.

In order to test this hypothesis, two more mixes were prepared (Mixes C + D) having w/c ratios of 0.5 and 0.65 with mix designs corresponding to those provided in Tables 3.4 and 3.5. This time, rebar cover was decreased to only 15 mm, and the tests ran for 12 weeks, rather than 8, to ensure that the carbonation front reached the depth of the rebar. Over the 12 weeks, Relative Humidity was held constant at 60%, while temperature was linearly incremented from 24° C to 60° C and CO_2 concentrations were linearly incremented from 4% to 10%. Results for these tests are shown in Figures 5.17 and 5.18:



Figure 5.17: Corrosion rate vs time, Mix C (w/c=0.5)



Figure 5.18: Corrosion rate vs time, Mix D (w/c=0.65)

For Mixes C and D, with time, it was found that the corrosion current density for all specimens was extremely low, generally < 0.006 mm/yr. Even more astonishing was that while the initial LPR-derived

corrosion rates were sometimes close to 0.006 mm/yr, as carbonation depth increased to well beyond the depth of the rebar, the corrosion rate decreased. This was completely contrary to expectations. Yoon et al (2007) reported that carbonation induced corrosion typically initiated when carbonation depths reached to within 5 mm of the expected rebar. However, no such increase in corrosion rate was noticed at such carbonation depths, and in fact, it seems that corrosion rates actually decreased with increasing carbonation depth.

A review of the literature regarding corrosion current showed that corrosion current is heavily dependent on ambient relative humidity. Jung et al (2003) state that little corrosion is able to occur when the relative humidity is less than 60% in concrete. Enevoldsen et al (1994) contend that the minimum relative humidity required is even higher (>80%). Millard et al (2001) showed that environmental conditions such as temperature and humidity can significantly influence LPR results. Specimens subjected to LPR testing were tested immediately after being removed from the carbonation chamber, in which the ambient relative humidity had been held constant at 60%. Therefore, when the specimens were being tested, the relative humidity in the vicinity of the rebar was not high enough for a significant corrosion current to develop. To test this hypothesis, a number of specimens which had initially shown low levels of corrosion as per LPR results, were left outside, exposed to natural atmospheric conditions, where they would be subjected to fluctuating levels of relative humidity, often in excess of 80%. Under such conditions, within a matter of weeks, it was visually apparent that corrosion product had developed (Figure 5.19). Therefore, while LPR can still be used as a valuable tool to assess corrosion progression within a specimen, it was not appropriate to assess corrosion rates in this study, as relative humidity values in the accelerated tests were far too low to allow a current to develop. Rather, before running LPR tests, the specimens should be allowed to come to equilibrium with a higher ambient humidity before testing for the corrosion current. Looking at the LPR results at face value immediately after removal from the testing chamber would lead to the erroneous conclusion that the carbonated specimens were not susceptible to corrosion.



Figure 5.19: Formation of corrosion product on corroded rebar

5.4 Final Remarks

Two general conclusions can be made regarding the different types of tests described in this chapter:

1) Concrete carbonation has no observable effect on the resonant frequency of a specimen. Monitoring resonant frequency is therefore not a good way of monitoring carbonation development within a concrete specimen.

2) Humidity and internal moisture conditions inside concrete can heavily affect NDT readings. Humidity may be one of the reasons that the results of UPV tests on carbonated specimens were so unanticipated, and insufficient humidity and moisture was identified as the reason that LPR results were erroneous. While these two types of tests hold promise to monitor carbonation progress, ambient test conditions must be considered. Before comparing results between multiple NDTs it is important to ensure that humidity and moisture conditions are uniform, and that the NDT itself is not being affected by humidity levels.

Chapter 6: Thermogravimetric Analysis

Thermogravimetric analysis (TGA) is a technique in which the weight of a substance is monitored as a function of temperature or time as the sample specimen is subjected to a controlled temperature program in a controlled atmosphere. Measurements are primarily used to determine the composition of materials. The technique may also be used to determine reaction rate coefficients between certain compounds. In this chapter, results are presented from an attempt to use TGA to determine the reaction rate coefficient between CO₂ and Ca(OH)₂.

6.1 Theoretical Basis

As mentioned in Chapter 3, the carbonation reaction between CO_2 and $Ca(OH)_2$ is assumed to be second order, with a rate given by:

$$r_{CO_2} = k_c [CO_{2(aq)}] [Ca(OH)_{2(aq)}]$$
(6.1)

where:

 $-CO_{2(aq)}$ is the concentration of carbon dioxide which has dissolved into the pore water (mol/L)

-Ca(OH)_{2(aq)} is the concentration of calcium hydroxide which has dissolved into the pore water (mol/L)

 $-k_c$ is the reaction rate constant for reaction between CO_2 and $Ca(OH)_2$ at the temperature of interest(L/mol s)

 $-r_{CO2}$ is the CO₂ reaction rate (mol/L s)

The rate constant k has a temperature dependence generally calculated using the Arrhenius equation (Keuleers et al, 2002):

$$k_c = \beta e^{\left(\frac{-U}{RT}\right)}$$

where:

-U is the reaction activation energy (J/mol)
-β is the pre-exponential factor (mol/L s)
-R is the universal gas constant (8.314 J/mol K)

Often, studies which try to predict the rate of carbonation within a concrete structure require knowledge of the carbonation rate (Papadakas et al, 1991, Park, 2008). Therefore, it is imperative that the rate constant be accurately known. In all these studies, a reaction rate constant was used independent of temperature. Studies which consider temperature dependency of the reaction rate constant between CO_2 and $Ca(OH)_2$ require knowledge of the values of β and Q in Equation 6.2. Khunthongkeaw and Tangtermsirikul (2005), propose the same temperature dependency (Equation 6.2), however, their values for U and β were obtained by trial and error to achieve the best accuracy in predicted carbonation depths for data generated in their study.

Kinetic analysis of heterogeneous reactions generally starts with a general formula for reaction rate (Keuleers et al, 2002):

$$\frac{d\alpha}{dt} = k_c f(\alpha) \tag{6.3}$$

where:

(6.2)

- α is the degree of conversion

 $-f(\alpha)$ is a mathematical function whose form depends on the reaction

When nucleation is facile across all surfaces, large numbers of growth nuclei are formed immediately on establishment of reaction conditions. A comprehensive interface forms rapidly initially and advances inwards thereafter from the original particle outer boundaries towards each particle centre. This is referred to as the "contracting cube equation" (Equation 6.4) (Craig and Galwey, 2007, Sun et al, 2008, Sun et al, 2007):

$$f(\alpha) = 3(1-\alpha)^{\frac{2}{5}}$$
(6.4)

Substituting Equation 6.4 into Equation 6.3 and integrating with respect to time allows one to solve for the rate constant k_c :

$$k_c = \left[\frac{1 - (1 - \alpha)^{\frac{1}{8}}}{t}\right] \tag{6.5}$$

Finally, the degree of conversion can be determined through weight measurement as per Equation 6.6 (Sun et al, 2008):

$$\alpha = \left(\frac{\Delta W}{W_{\rm i}}\right) \left(\frac{M_{\rm i}}{(M_{\rm 2} - M_{\rm i})}\right) \tag{6.6}$$

where:

-W is the weight increase due to reaction (g)
-W_i is the initial weight of specimen (g)
-M₁ is the molecular weight of Ca(OH)₂(g/mol)
-M₂ is the molecular weight of CaCO₃ (g/mol)

Therefore, conducting thermogravimetric analysis under isothermal conditions over a range of temperatures gives us different values of α and k and subsequently allow us to determine β and Q in Equation 6.2. Rather than using empirical values proposed by other researchers, determination of these values would be extremely useful to generate accurate modeling results.

Several TGA studies have been carried out on concrete in the past. Chang and Chen (2006) used temperatures increasing from 20°C to 1000°C in their investigation on concrete carbonation depths. Parrott and Killoch (1989) used temperatures increasing from 20°C to 750°C in their study on in-situ carbonated concrete. However, it is important to remember that at temperatures above 300°C the constituents of cement begin to breakdown and it begins to lose strength. Therefore, mass changes at higher temperatures are unlikely to be representative of the carbonation reaction only. Secondly, in practise, atmospheric temperatures rarely exceed 50°C. Therefore, in order to better correlate with real world conditions, and to ensure that the concrete itself remains thermally stable, three temperatures of 60°C, 80°C and 100°C were tested in the analysis.

6.2 Experimental Procedure

A number of prismatic cement specimens (w/c=0.5) were cast (Figure 6.1), water cured for 28 days, then dried out and allowed to come to 60% humidity at room temperature, before being subjected to thermogravimetric analysis. The specimens had approximate dimensions of 10 mm x 10 mm x 10 mm and masses between 1000-2000 mg.



Figure 6.1: Cement specimens

The analysis was conducted on a custom designed atmospheric TGA system built by the University of British Columbia Chemical and Biological Engineering Department (Figure 6.2). The system allows for ultra-pure grade CO₂ and N₂ to be mixed at the inlet of the reactor. Mass flow controllers were used to control the gas flow rates to obtain the desired concentrations. The gas was then allowed to flow through the suspended sample basket. A balance with 1 µg sensitivity was used to measure the mass of the specimens. Additionally, there were two heaters which control the temperature inside the reactor. A data acquisition system continuously records temperature, mass, and gas concentrations. Further details on the system, along with schematics, can be found in Sun et al (2007).



Figure 6.2: Thermogravimetric analyzer

In Equation 6.1, the reaction between $Ca(OH)_2$ and CO_2 only occurs at the water covered surface of $Ca(OH)_2$ which is not occupied by $CaCO_3$ particles (Shih et al, 1999, Thiery et al, 2007). Therefore, to drive the reaction, a minimum humidity > 60% (Marie-Victoire et al, 2006) (using steam) was maintained inside the thermogravimetric chamber. Shih et al (1999) noted no difference in the effect of CO_2 concentration on the carbonation of $Ca(OH)_2$ from 3.15-12%. For this experiment, a CO_2 concentration of 5% CO_2 in N₂ was supplied to the reactor.

6.3 Results

Results from the five trial runs are shown in Figures 6.3-6.7. Initially, the trial temperature used was 100° C. It was expected that with time, there should be an increase in the mass of the specimen, as the fraction of Ca(OH)₂ (74 g/mol) reacts, and is replaced by CaCO₃ (100 g/mol).



Figure 6.3: Thermogravimetry trial 1 Results (100°C, 5% CO₂)



Figure 6.4: Thermogravimetry trial 2 Results (100°C, 5% CO₂)



Figure 6.5: Thermogravimetry trial 3 Results (100°C, 5% CO₂)



Figure 6.6: Thermogravimetry trial 4 Results (100°C, 5% CO₂)



Figure 6.7: Thermogravimetry trial 5 Results (100°C, 5% CO₂)

Figures 6.3-6.7 show that as per the trial runs there was no clear correlation between specimen weight and time. First, as mentioned earlier, a slight increase in mass would be expected rather than an overall decrease, which occurred for some of the specimens. This result is clearly erroneous, as at such a low temperatures, the constituents of concrete cannot break down. Secondly, the data appears to vary randomly, and cannot be described by functions such as that described by Equation 6.3.

Two reasons are postulated for the inexplicable/erroneous results. First, it is likely that there was a buildup of condensation on the specimen while it is in the reaction chamber. As the load cell is ultra sensitive, the buildup, and subsequent loss of even the slightest amount of condensation from the surface of the specimens will heavily influence the results. This may explain why the load seems to fluctuate in all the tests. At such low temperatures, it is difficult to control the buildup of condensation, as water vapour is prone to condense rather than remain in the air. Secondly, it is possible that electrostatic forces may have built up within the chamber over time, thereby affecting the load cell values. In either case, the results given by the TGA would clearly be flawed.

6.4 Final Remarks

It was found to be impossible to conduct TGA analysis on concrete specimens at low temperatures, and it had already been determined that it would be redundant to conduct the analysis at higher temperatures. Until a TGA unit can be constructed which is able to protect the surface of the specimen from condensation buildup, and is able to very accurately control temperature and gas flows, it would not be possible to conduct this experiment at lower temperatures. Therefore, considering that the values given by Khunthongkeaw and Tangtermsirikul (2005) in Equation 6.2 to calculate the reaction rate coefficient gave good results when predicting carbonation depths under accelerated test conditions (Chapter 3), they were also considered accurate and reliable enough for the global simulations in Chapter 4.

Chapter 7: X-Ray Diffraction Analysis

Powder X-ray diffraction analysis (XRDA) is one of the primary techniques used to examine the physiochemical make-up of unknown solids. In this chapter, the results of XRD tests to identify the composition of specimens subjected to natural and accelerated carbonation are presented and discussed.

7.1 Theoretical Basis

Carbonation rates in natural atmospheres are too slow for laboratory testing, and therefore, testing is usually accelerated by using higher CO₂ concentrations. While no general correlation exists on how to extrapolate these testing conditions to real performance, a study by Sanjuan et al (2003) indicates that 7-15 days of accelerated carbonation at 4-5% CO₂ is roughly equivalent to one year of carbonation at natural atmospheric conditions. Their study concluded that accelerated testing may alter concrete resistance towards carbonation by the formation of different reaction products which modify the diffusion coefficient.

CaCO₃ exists in the form of three polymorphs: calcite, aragonite and vaterite. Calcite has a trigonal crystalline structure, whereas aragonite has an orthorhombic structure, and vaterite has a hexagonal structure. It is believed that at CO₂ concentrations higher than atmospheric levels, the CaCO₃ formed is not in the form of calcite, as in natural carbonation, but instead in the form of aragonite which has a much more crystalline structure (Cizer et al, 2008). Aragonite crystals are smaller than calcite, and the density of calcite (specific gravity = 2.71) is less than that of aragonite (specific gravity = 2.95). Vaterite has a slightly lower density than calcite (specific gravity =2.54). Therefore, if calcite is replaced with aragonite, we can expect slightly higher diffusion coefficients due a small increase in the volume of pores space. Consequently, there is some debate as to whether carbonation studies performed at CO₂ concentrations >> 1% are valid and are even representative of atmospheric carbonation.

A comprehensive list of the CO_2 levels used in experiments related to carbonation in concrete was presented by da Silva et al (2009). Currently the primary European standard for resistance to
carbonation, EN 13295 (2004), suggests a testing concentration of 1%. The other older standard, RILEM CPC-18 (1988) does not specify an exact CO₂ concentration for accelerated tests. However, data from da Silva et al (2009) shows that the vast majority of studies used levels above 5%. Many researchers specifically state that diffusion coefficients based on accelerated CO₂ tests should not be used as the diffusion coefficients for concrete under regular atmospheric carbonation. Although the exact diffusion coefficients at higher concentrations may not be the same, it should still be possible to draw valid comparisons as to what would happen when atmospheric CO₂ concentrations increase with time through accelerated carbonation tests with increasing CO₂ concentrations. Finally, considering that the vast majority of research has been conducted at levels > 1%, there has been some discussion advocating increasing the testing concentration up to 5% (da Silva et al, 2009). Secondly, some research has been done on the influence of CO₂ levels, and it was found that diffusion coefficients measured at 5 and 20% are quite similar (Sanjuan and del Olmo, 2001).

Powder X-ray diffraction analysis (XRDA) is one of the primary techniques used by mineralogists and solid state chemists to examine the physico-chemical make-up of unknown solids. The data are represented in a collection of single-phase X-ray powder diffraction patterns for the three most intense D values in the form of tables of interplanar spacings (D), relative intensities (I/I_o), and mineral name. The XRD technique takes a sample of the material and places a powdered sample in a holder. Then the sample is illuminated with X-rays of a fixed wave-length and the intensity of the reflected radiation is recorded using a goniometer. These data are then analyzed for the reflection angle to calculate the inter-atomic spacing (D value in Angstrom units - 10⁻⁸ cm). The intensity (I) is measured to discriminate (using I ratios) the various D spacings, and the results are examined to identify possible matches.

XRD can be used to identify some of the constituents of concrete and hydrated cement paste, and to differentiate between the crystalline phases of $CaCO_3$ (Ni and Ratner, 2008), (Kontoyannis and Vagenas, 2000). Therefore, by taking samples of cement paste carbonated at 0.04% (atmospheric), 2% and 10% CO_2 concentrations, it would be possible to determine the difference between the types of $CaCO_3$ formed under different CO_2 concentrations.

7.2 Experimental Procedure

All samples were cement paste specimens having a w/c ratio of 0.5. They were water cured for 28 days, and then kept in an indoor environment of 20°C and 65% relative humidity (RH) for a further 28 days to condition the samples and allow them to come to equilibrium with the environment prior to being placed in the carbonation chamber. There is currently no consensus specifying the drying/conditioning period for carbonation tests. In a study by Neves et al (2012), specimens were preconditioned for 3 weeks at 65% relative humidity and 20°C. Furthermore, based on a review of other experimental setups of previous researchers (Russell et al, 2001, Franzen and Mirwald, 2004, Ryu et al, 2011), it is believed that the conditioning time employed is sufficient to achieve a uniform humidity profile in the first 10-20 mm of concrete depth. Accelerated carbonation testing was carried out in the ESPEC PR4-KPH carbonation chamber described in Section 3.2.

The three cement paste samples were subjected to carbonation as per the regime in Table 7.1:

Sample	Туре	CO ₂ Concentration
1	Cement Paste	0.04%
2	Cement Paste	2%
3	Cement Paste	10%

Table 7.1: Sample types

After being carbonated at the desired CO₂ concentration, each specimen was reduced into fine powder to the optimum grain-size range for X-ray analysis (<10μm) by grinding under ethanol in a vibratory McCrone Micronising Mill for 7 minutes. Step-scan X-ray powder-diffraction data were collected over a 2θ range between 3-80° with CoKa radiation on a Bruker D8 Focus Bragg-Brentano diffractometer equipped with an Fe monochromator foil, 0.6 mm (0.3°) divergence slit, incident- and diffracted-beam Soller slits and a LynxEye detector. The long fine-focus Co X-ray tube was operated at 35 kV and 40 mA, using a take-off angle of 6°. The X-ray diffractograms were analyzed using the International Centre for Diffraction Database PDF-4 using Search-Match software by Bruker. X-ray powder-diffraction data of the samples were refined with the Rietveld program Topas 4.2 (Bruker AXS).

7.3 Results

Results from the XRD analysis (crystalline phases only) for Samples 1-3 are shown in Table 7.2:

Mineral		Sample 1 (0.04%	Sample 2 (2%	Sample 3 (10%
wineral	ideal Formula	CO ₂)	CO ₂)	CO ₂₎
Quartz	SiO ₂	1	1.5	1.3
Calcite	CaCO ₃	48.3	48	68.5
Aragonite	CaCO ₃	1.5	20.1	6
Vaterite	CaCO ₃	3.7	10.2	8.6
Belite	Ca ₂ SiO ₄	18.4	7.5	5.9
Portlandite	Ca(OH) ₂	3.2	0	0
Ettringite	Ca ₆ Al ₂ (SO ₄) ₃ (OH) ₁₂ ·26H ₂ O	10.8	4.2	2.1
Brownmillerite	$Ca_2(AI,Fe^{3+})_2O_5$	7.1	6.4	5.6
Gypsum	CaSO ₄ ·2H ₂ O	1	0	0
Magnesite	MgCO ₃	2.1	2.1	1.3
Hexahydrite	MgSO₄·6H₂O	1.4	0	0
Aluninate	3CaO·Al ₂ O ₃	1.5	0	0.7
Totals		100	100	100

Table 7.2: XRD analysis results (by % mass composition)

7.4 Discussion

Comparing the results from Samples 1 and 2, we see there is a significant change in the nature of the products formed at higher CO₂ concentrations. For Sample 1, the higher concentrations of Belite, Ettringite, and Portlandite indicate that this sample may not have fully cured before being placed in the carbonation chamber, and that there was the potential for formation of additional calcite to form in this sample over time. Therefore, if we were to compare Samples 1 and 2, the results are as expected, with calcite concentrations dropping with an increase in the CO₂ concentration, and an increase in aragonite and vaterite concentrations.

However, it is interesting to note that compared to Sample 2, calcite concentrations were higher for Sample 3, while aragonite and vaterite concentrations were lower. This result was not expected. For Samples 2 and 3, while the formation of higher aragonite and vaterite concentrations compared to Sample 1 were expected, it was also expected that calcite concentrations would remain the same, or perhaps be slightly lower. Therefore, at higher concentrations of CO₂ it seems that not only are aragonite and vaterite concentrations higher, but calcite concentrations may increase as well.

Results from this study show that carbonation products formed under accelerated carbonation test conditions are different from those under natural carbonation conditions. Under accelerated tests, significantly higher concentrations of $CaCO_3$ in the form of aragonite and vaterite are present. Therefore, while accelerated tests are useful to determine the general resistance of a specimen to carbonation, the exact CO_2 diffusion coefficient measured in an accelerated test will likely not be the same as that under natural conditions due to the change in the morphology of $CaCO_3$.

In Chapter 3 of this thesis, it was found that it was possible to accurately predict carbonation depths using a modified empirical formulation for the diffusion coefficient (Equation 3.6) originally proposed by Papadikas et al (1991), The empirical formulation assumed that the value of the diffusion coefficient was

dependent only on porosity, temperature and relative humidity of the test specimens. It was found that it was possible to accurately predict the carbonation depth in accelerated tests for concrete specimens with w/c=0.5, where the temperature and relative humidity remain constant, and only the CO_2 concentration was incremented over time at a constant rate from 6%-10%. Therefore, it is possible to infer that since it was possible to accurately estimate the diffusion coefficients in this range of CO_2 concentrations, there was likely little variation in the pore structure of the concrete within this range of CO_2 concentrations. The same model was verified for concrete specimens with w/c=0.6 and w/c=0.65, for conditions where relative humidity remained constant, but CO2 concentrations were constantly incremented from 4%-10% and temperature was incremented from 24°C-60°C. Again, it was possible to conclude that the change in the diffusion coefficient over time was attributable to the variation in temperature, irrespective of the test concentrations.

In light of these findings, along with those from Sanjuan and del Olmo (2001) it is possible that the test concentration of CO₂ for accelerated carbonation tests recommended by EN 13295 (2004) may need to be revisited. The majority of laboratory tests conducted are at CO₂ concentrations higher than 1%, and considering that the purpose of the accelerated test is to reduce test times, the use of a higher concentration should be permitted in order to do so. Considering that the morphology of CaCO₃ is going to be different regardless of the exact CO₂ concentration under accelerated conditions, and empirical data seems to suggest that there will be little difference in the pore structure at concentrations between 4% and 10%. Therefore, it makes sense to determine at what range of concentrations diffusion coefficients are similar, and then set an upper limit within this range.

In general, there is little acknowledgement of the importance of preconditioning of specimens prior to testing. Specimens to be tested need to be given ample time to come to equilibrium with the atmosphere prior to testing preferably at temperatures and relative humidities equivalent to those in the test chamber. Failure to do so will lead to erroneous results, as during the initial stages of the accelerated test, the specimen will still be equilibrating to the conditions in the chamber. Optimal humidity conditions for carbonation are suggested to be between 50%-70% (Marie Victoire et al, 2006), along with higher temperatures leading to higher carbonation rates. However, excessively high

temperatures can damage the pore structure of the concrete at the surface. Bahador and Jong (2006) reported that even temperatures as low as 40°C may damage the pore structure at the surface of the specimen. We also consider that in most indoor environments, to maintain occupant comfort, humidities are typically around 65% +/- 5% and temperatures are at 20°C +/- °2 C. Therefore, to optimize the test, it is suggested that test conditions and preconditioning conditions be specified with humidity at 65% and temperature at 20°C, unless the specimens being tested are for concrete which will be subjected to significantly different environmental conditions. This corresponds with existing RILEM CPC-18 (1988) recommendations for preconditioning. It is also close to EN 13295 (2004) which suggests a humidity of 60%. However, a minimum condition period should also be specified. Parrot (1994) contends that several months of drying at 55-60% relative humidity at 20°C are required to achieve approximate moisture equilibrium in specimens only a few centimeters thick. At present no consensus exists on how long this period should be, with EN 13295 (2004) recommending a minimum preconditioning time of 14 days. However, further research needs to be conducted to definitively establish an optimal preconditioning time for specimens to be subjected to accelerated tests.

7.5 Final Remarks

Carbonation in Portland cement paste samples was examined for three regimes of CO₂ concentration ranging from 0.04-10%. The carbonated paste was analysed using XRDA to estimate the mass fraction of various crystalline products through the Rietveld refinement process.

It was found that carbonation products formed under accelerated carbonation test conditions differed from those under natural carbonation conditions. Whereas the predominant carbonated product under natural carbonation is calcite, under accelerated tests, significantly higher concentrations of aragonite and vaterite were present.

Therefore, while accelerated tests are useful to determine the general resistance of a specimen to carbonation, the exact CO_2 diffusion coefficient measured in an accelerated test will likely not be the same as that under natural conditions due to the change in the morphology of CaCO₃. This assertion

needs to be verified by devising a test method to measure CO_2 diffusion coefficients of samples carbonated at different CO_2 concentrations.

Since the purpose of an accelerated carbonation test is to reduce test times, it is possible that a higher concentration of CO₂ should be permitted. Considering that the morphology of CaCO₃ will differ regardless of the exact concentration under accelerated conditions, it makes sense to determine at what range of concentrations diffusion coefficients are similar, and then set an upper limit within this range, along with the specification of an optimal testing temperature and humidity. Empirical results suggest there would likely be little difference in the diffusion coefficient for concentrations between 4%-10%. Further research needs to be conducted to determine an optimal preconditioning time, setting precondition conditions as similar as possible to the accelerated test conditions.

Chapter 8: pH Sensing

As described in Section 3.1, determining the relationship between pH and carbonation depth is complex. As concrete carbonates, three distinct zones can be assumed to form within the concrete. The most common method of determining the location of the carbonation front is by phenolphthalein spray. However, this method is not entirely accurate, as the spray provides a location where the pH of the specimen is ≤ 9 , within the transition zone from carbonated to uncarbonated concrete, and not the actual location of the start of the transition zone.

Much of the research done on pH sensors used in concrete structures has centered around the use of Fibre Optic Chemical Sensor Systems (Basheer et al, 2004); (Grattan et al, 2009); (McPolin et al, 2009). However, there are other types of sensors available which could possibly be used. The nanosystems research group at the University of Manitoba Department of Electrical and Computer Engineering has developed a combination electrode sensor which can be used to detect pH in aqueous electrolytic media to an accuracy of +/- 0.1. Theoretically, these sensors could also be used as part of a structural health monitoring (SHM) system to detect changes in pH of concrete as it carbonates. To test their applicability, and to try to develop a relation between pH and carbonation depth as determined by phenolphthalein spray, several of these sensors were mounted inside hardened cement paste blocks, and then allowed to carbonate. The change in potential difference in the combination electrode was measured in order to monitor the change in pH as the carbonation front advanced in the specimen.

8.1 Experimental Procedure

The pH combination electrode, consisting of a sensing electrode and a reference electrode, is amongst the most common types of pH sensor. The sensing electrode provides a potential proportional to the pH of the sample and the reference electrode ideally provides a stable and consistent potential independent of the sample. When pH is being sensed with electrodes, H⁺ ions in the electrolyte are actually being sensed. The H⁺ ion in the cement paste reacts with the sensing electrode and changes the potential of the sensing electrode. The reference electrode does not react with hydrogen ion and gives a contact potential. Therefore, by measuring the potential difference of the combination electrode we can measure the pH of the sample. Generally, it is connected to a high impedance voltmeter to measure the potential difference (Bhadra et al, 2011).

Combination electrodes were embedded at several depths inside a hardened cement paste specimen. The specimen was then placed inside a carbonation chamber, and as the specimen carbonated, H⁺ concentration in the cement paste pore solution (electrolyte) changed. The change in potential between the reference and sensing electrode was continuously measured and correlated with pH. At the same time, sections were saw cut from one end of the specimen, and the corresponding carbonation front was measured using phenolphthalein spray. In this way, it would theoretically be possible to correlate carbonation depth as measured by phenolphthalein, pH as measured by the combination electrode, and potential difference between the reference and sensing electrode.

The reference and sensing electrodes were prepared by Ms. Sharmistha Bhadra, a PhD candidate at the University of Manitoba, Department of Electrical and Computer Engineering. Each sensor was approximately 40 mm long and 2.5 mm in diameter (Figure 8.1).



Figure 8.1: Sensor photograph and dimensions

The iridium/iridium oxide (Ir/IrOx) sensing electrode was prepared by the direct oxidation method, and the silver/silver chloride (Ag/AgCl) reference electrode was prepared from silver wire via the electroplating method. They were used in combination to form the pH sensor. Full details on the fabrication process can be found in Bhadra et al (2011).

After fabrication, the sensors had to be mounted onto tabs so that they would be held in place when fresh cement paste was poured around them. They were mounted onto inert plexiglass tabs using fast drying epoxy, which was allowed to harden for approximately 12 hours (Figure 8.2).



Figure 8.2: Mounted sensors

The plexiglass tabs were then screwed onto wooden carriages which sat on top of the specimen moulds (Figure 8.3). In this way, the combination electrodes were held in place within the concrete specimen, at the specific depths indicated in Figure 8.4.



Figure 8.3: Tabs mounted to carriage



Figure 8.4: Electrode depths

Finally, fresh cement paste having a w/c ratio of 0.5 was poured into the concrete moulds around the electrodes (Figure 8.5). The moulds had dimensions of 100 mm x 100 mm x 350 mm. After 24 hours, the specimens were demoulded and placed into water tanks to cure for 28 days.



Figure 8.5: Fresh cement paste poured into moulds

After being removed from the water tanks, the specimens were preconditioned in a controlled atmosphere of 65% RH at 20°C for an additional 28 days. After this the samples were ready to be placed inside the carbonation chamber. However, prior to being placed in the chamber, it was necessary to cover all but the top side of each specimen with a barrier. This was necessary as 2D carbonation effects needed to be avoided. Sensor readings could potentially become compromised if carbonation fronts were to advance towards them from different directions. Rather, the effects of a single front advancing from the top of each specimen were to be measured by the sensors. The barriers were provided by 2 mm thick PVC sheets which were epoxied onto all but one of the surfaces (Figure 8.6).



Figure 8.6: Sample specimens with PVC barriers

8.2 **Results**

After preconditioning, and application of the barriers, the individual specimens were placed into the carbonation chamber, and allowed to carbonate. Two specimens to be tested, were placed in the chamber while two others were left outside as control specimens. At specific intervals, the test specimens were removed from the chamber, and the potential difference across the four combination electrodes in each specimen were measured. At the same time, a section 15 mm thick was sawcut from one end of the specimen, and the carbonation depth was noted by a phenolphthalein test (Figure 8.7).



Figure 8.7: Test specimen schematic

The specimen was then returned to the chamber, and the reaction was allowed to continue. Note that at all times, in the chamber, CO₂ concentration was maintained at 10% and relative humidity at 65% so as to accelerate front progression as quickly as possible. With time, as the carbonation front progressed, the relationship between the potential difference at each of the electrodes, along with progression of the carbonation front, was analysed. For the type of sensors used, an empirical correlation had been previously developed between potential difference measured at the sensor, and pH (Bhadra et al, 2011). As the value of the potential difference measured increased, the pH of the specimen decreased. Therefore, theoretically, carbonation should cause an increase in the potential difference measured at a sensor, once the carbonation front has reached its location. The relation is shown in Figure 8.8. The potential differences measured for the specimens are presented in Figures 8.9-8.12:



Figure 8.8: Typical potential difference vs pH relationship for sensor (Bhadra et al, 2011)



Figure 8.9: Specimen 1, Potential difference vs time (CO₂=10%, relative humidity=65%)



Figure 8.10: Specimen 2, Potential difference vs time (CO₂=10%, relative humidity=65%)



Figure 8.11: Specimen 3 (control), Potential difference vs time (CO₂=10%, relative humidity=65%)



Figure 8.12: Specimen 4 (control), Potential difference vs time ($CO_2=10\%$, relative humidity=65%)

It was expected that for the first 28 days, the potential differences measured would be quite unstable and fluctuate due to formation of various hydration products. This was indeed noted for all four specimens. However, after 28 days, the potential difference, and therefore pH, were expected to stabilize, as the majority of hydration reactions would have occurred. In all specimens it was noticed that while the amount of perturbation decreased, potential difference values did not fully stabilize. It was only after 56 days that sensor readings fully stabilized, as can be seen for the control specimens in Figures 8.11 and 8.12. For Specimens 1 and 2 on the other hand, after 56 days there was an overall trend of increasing potential difference, thereby indicating that, as expected, as the carbonation front progressed in these specimens, the embedded sensors were reading a decrease in pH.

Originally, it was expected that all electrodes should have the same measured value of potential difference at a specific baseline value at 56 days, since theoretically, each specimen should have uniform pH throughout, regardless of the sensor location. However, this was clearly not the case, as baseline values tended to vary not only from specimen to specimen, but from sensor to sensor. Only for Specimen 4 did the baseline potential difference stabilize at around 35 mV. It is postulated that the reason for the different baseline values could be because of differing moisture contents among the

specimens, as well as differing moisture contents at various depths. In the same way that moisture/humidity has an effect on NDT results, it may also influence sensor readings. Electrode potential depends on the conductivity of the medium it is placed in, and conductivity will be dependent on moisture content. Therefore, it is possible to get a different values of potential for the same pH due to the varying conductivity of the sensor locations. An alternate approach was suggested by McPolin et al (2009) where fibre optic sensors where found to be able to accurately detect a carbonation front when they were embedded into drilled holes AFTER casting to avoid damaging the sensors when fresh mortar is poured around them.

Next, partially as a consequence of non-uniform baseline sensor potential differences, it seems that the relation suggested by Bhadra et al (2011) cannot be used for sensors embedded in concrete. As per Figure 8.8, for concrete to have a pH > 12, as it would at 56 days, the potential difference measured at all sensors should be < -150 mV. In fact, values of baseline potential differences fluctuated greatly between 20-100 mV. The discrepancies could be due to differences in treatment of the electrodes during fabrication, or some sort of interaction between the electrodes and some hydration product present in the concrete other than H^+ ion. It is important to ensure that the sensors are properly calibrated initially. McCarter and Vennesland (2004) suggest pH sensors should be calibrated against a standard pH glass electrode in three solutions of different alkalinity containing only calcium hydroxide and sodium hydroxicde.

We first examine the results of Specimen 2 in Figures 8.13 and 8.14:



Figure 8.13: Specimen 2, Potential difference vs time from the onset of accelerated testing



Figure 8.14: Specimen 2, Potential difference vs carbonation depth from the onset of accelerated testing

In Figure 8.13, we can clearly see that with time, as the carbonation front progresses, the sensors are increasing in potential difference, indicating a decrease in pH. Considering that at the same time, potential difference remained constant in the control specimens, the sensors seem to have been reacting to the formation of carbonation products. However, it is curious that there was a decrease in pH in Sensors 1, 2 and 3 simultaneously. Plotting the linear trendlines for these sensors gave us slopes of +0.971, +0.527, and +1.068 respectively, while the slope for Sensor 4 was -0.230. This can be confirmed by examining Figure 8.14. The formation of a transition zone within the carbonation front was described in Chapter 3, the length of which is assumed to be 5 mm (Yoon et al, 2007). Therefore, it was expected that when the carbonation front measured by the phenolphthalein test was within approximately 5 mm of the sensor depth the potential difference at the sensor should start to increase. Figure 8.14 clearly shows that all four sensors suddenly spiked when the carbonation front reached a depth of approximately 11 mm. This is likely due to the sensor embedded at 13 mm (Sensor 1) reacting to the detection of the carbonation front. It was expected that sensor only, and then stabilized once the carbonation front had passed by it. The reason for the simultaneous changes is unknown.

While the sensors embedded in Specimen 1 did not stabilize before 56 days as they did in Specimen 2, the sensor readings and general trends were closer to what was expected. As the carbonation front progressed, all 4 sensors showed increases in potential difference, with the greatest increase being in Sensor 1 (Figure 8.15).



Figure 8.15: Specimen 1, Potential difference vs carbonation depth from the onset of accelerated testing

The spike in potential difference noticed in Specimen 2 as the carbonation front approached a sensor was again noticed in Specimen 1. Again, there was a spike in potential difference at Sensor 1 once the carbonation front reached a depth of approximately 11 mm (Figure 8.16). After the spike, the values seem to have stabilized. The spike was only noticed in Sensor 1, and not in sensors 2, 3 or 4. Therefore, for this specimen, it seems that there was minimal cross-interaction between the electrodes, and the observed trends in potential difference were closer to what was expected. In retrospect the specimens should have been allowed to carbonate further so that response of sensors 2, 3 and 4 could have been noted when the carbonation front approached them.



Figure 8.16: Specimen 1, Potential difference vs time from the onset of accelerated testing

8.3 Final Remarks

The way forward in concrete durability monitoring lies in instrumentation of structures at the time of construction thereby allowing collection of data from commissioning. Such instrumentation would form an important component in a design for durability philosophy. Routine monitoring would then allow a database to be built-up for the particular structure and enable a more informed prediction of likely long-term performance (McCarter, 2001). The use of pH sensors to detect the progression of a carbonation front in concrete is an area of research which is showing promise. For the control specimens, the potential difference remained constant in the embedded sensors, while for the test specimens, the embedded sensors responded to the progression in the carbonation front by reading a decrease in pH levels as expected. The sensors appeared to detect the approach of the carbonation front, by a sudden spike in potential difference readings. This confirms the presence of a transition zone within the carbonation front which appears to be approximately 2-3 mm in front of the carbonation front as measured by a phenolphthalein test.

While the use of these sensors shows promise, there are still many problems which need to be dealt with before they can be used regularly. Most importantly, the absolute value of pH for a sensor embedded in concrete has to be correlated with a measured potential difference. At this point, while the sensors were able to detect general trends in pH as a specimen carbonates, the readings varied greatly, not only from specimen to specimen, but from sensor to sensor, and therefore, could not be correlated to determine the exact value of pH. Further tests need to be conducted to generate enough data to be able to develop such a correlation. Moreover, there appeared to be cross-interaction between some sensors which caused readings measured in one sensor to be affected by readings in an adjacent sensor. This problem needs to be dealt with before this kind of sensor could be used regularly in practice.

Chapter 9: Conclusions and Recommendations

9.1 Conclusions

A new model based on Fick's Second Law was developed to predict the depth of carbonation in nonpozzolanic, unloaded concrete specimens, in accelerated carbonation tests, taking into account for the first time, time-varying concentrations of CO₂, temperature and humidity. The model accurately predicts scenarios where concrete is not only subjected to single changes in ambient conditions, but also when subjected to multiple changes in conditions. This makes it ideal to be able to predict carbonation depths in concrete structures under conditions of global climate change.

Using this model, and inputting forecasts for increases in future atmospheric CO₂ concentrations and weather conditions, it was shown that global climate change will affect the progression of carbonation induced corrosion in our concrete infrastructure. It is expected that we will see much higher ultimate carbonation depths in the long term. Although Climate change will have minimal effects in the near future on durability of concrete structures, the real effects of climate change will become evident after approximately 30 years. Therefore, in geographic areas where carbonation induced corrosion is a concern, structures being constructed in 2020-2030 may have to begin taking into account degradation due to climate change when they are being designed.

For the worst case scenario, for concrete structures constructed in 2030, in areas where carbonation induced corrosion would be a concern (moderate humidity, higher temperatures), we can expect structures to begin to show a reduction in serviceable lifespan due to climate change of approximately 15-20 years, with signs of damage being apparent within 40-45 years of construction.

Concrete exposure conditions have a significant effect on corrosion propagation times in concrete. The results for time to cracking presented in this thesis are for concrete which is only subjected to a dry exposure class, and therefore, times to cracking are somewhat overestimated, meaning that the effects

of climate change on time to crack initiation may be being underestimated. For harsher exposure classes, propagation times are shorter. For one scenario described, the propagation time was overestimated by approximately 75%.

Finally, an attempt was made to see whether the model could be modified to consider cracked concrete structures. It was found that using the effective diffusion coefficient concept was not permissible for concrete containing discretized structural cracks. Rather, it seems the presence of deep, wide structural cracks allows for rapid transport of CO₂ through the crack, and then orthogonal diffusion through the concrete. The presence of a structural crack with a wide enough width, which extends to the depth of rebar may be considered sufficient to induce localized depassivation at its surface. Thereafter, a new theoretical 'series diffusion model' was proposed which could be used to measure orthogonal carbonation depths in structurally cracked concrete.

9.2 **Recommendations**

In general, throughout North America, the state of infrastructure is considered to be quite poor. Even before considering the effects of climate change, infrastructure is not being designed and maintained properly, and is generally not able to achieve its design life as prescribed by building codes. In this thesis, it has been shown that climate change could play a role in decreasing the service life of an idealized structure due to carbonation induced corrosion. If we were to consider factors such as cracking due to weathering, improper placement, or overloading, along with the presence of chlorides in marine environments, or environments where deicers are regularly used, it is safe to conclude that in the future, climate change effects would reduce service lives even further than what they are today.

Therefore, it is recommended that focus be placed on designing and maintaining durable infrastructure, so that infrastructure service lives are increased sufficiently to be able to meet their prescribed service lives, and ensure that they are durable enough to deal with longer term effects of climate change. It may be wise to emphasize durability, not just strength, when designing concrete structures. As a remedial measure, the impact of enhanced corrosion risk in new structures due to climate change can be countered at the design stage, through the development of new technologies and materials. Monteiro et al (2012) reported that many structures displaying symptoms of corrosion had concrete covers less than their specified values. It is imperative that during construction, prescribed concrete covers be maintained. Durability could also be enhanced by conventional techniques, including surface coating barriers, further increasing cover where required, and increasing strength (Wang et al, 2010). One can also contemplate the use of active cathodic protection in structures, and last but not least, noncorroding reinforcement based on fiber reinforced polymers.

The use of NDT methods, and SHM techniques could be invaluable in monitoring the progress of carbonation in a structure, but the data generated must be analyzed carefully before drawing any conclusions. For the NDT methods and carbonation sensors evaluated in this study, it was found that ambient test conditions had a major impact on results. Therefore, while these areas show promise, they need to be developed further so that they can be actively used in industry.

9.3 Suggestions for Further Research

There is great uncertainty associated with not only the science of climate change, but also, the properties of concrete infrastructure. It is impossible to predict the exact values of temperature and CO₂ concentrations in the future, and impossible to describe with absolute certainty, the properties of concrete as a material, not just from one structure to another, but even within a given structure itself. Rather, it is easier to make future climate predictions with an associated likelihood of a particular scenario, as well as describe the vulnerability of a structure to carbonation induced corrosion damage in probabilistic terms. Therefore, a major suggestion to build upon on the results of this thesis would be to develop probabilistic models and conduct a reliability-based life cycle analysis to determine what the probabilities of climate-change related damage were to structures throughout the world. Stewart and Ping (2010) have done such work for cities in Australia, and a similar approach could be used in combination with the model developed in Chapter 3 of this thesis to determine the optimal maintenance schedule to lower costs associated with increased carbonation-induced damage due to global climate change for cities throughout the world. It may be worth conducting a probabilistic analysis, not only for different cities, but for structures subjected to different exposure classes, to

estimate the overall further reduction in times to cracking due to carbonation-induced corrosion.

It should be noted that the model developed was validated for non-pozzolanic concretes having w/c=0.5-0.65. This would describe the range of concretes classified as low, or medium strength. The addition of pozzolans into the mix, or lowering the w/c ratio would obviously modify transport properties in the concrete, and so such mixes should be investigated with modifications made to the model as necessary.

The climate data used in thesis were based on that from the IPCC Special Report on Emissions (SRES). They were published in 2000, and were subsequently used in the IPCC 3rd and 4th Assessment Reports. However, for the 5th Assessment Report which is to be released in 2013, the SRES scenarios are to be superseded by RCP (Representative Concentration Pathways). At the time of publication of this thesis, use of RCP data was not in widespread use. However, use of the new data coupled with newer generation climate models allows for the generation of temperature distribution maps with a greater resolution. This would be likely be an improvement on the climate model which was used in this thesis, and is an advancement future researchers should consider.

This thesis primarily focused on the effects of climate change on carbonation induced corrosion. In Section 2.1.4, all the potential effects of climate change were described. Climate change will not only increase the risk of carbonation-induced corrosion, but also, there is increased potential of damage due to extreme weather events, as well as chloride induced corrosion of structures. Therefore, a further suggestion would be to not only consider the effects of carbonation induced corrosion, but a combination of all the potential effects of climate change.

In Chapter 3, a theoretical series diffusion model for carbonation of cracked concrete was proposed. This model needs to be verified by first determining what the diffusion coefficient of CO_2 in a structural crack, which could be empirically done by measuring diffusion rates in cracks of varying widths, tortuosity, and constrictivity. In general, the area of carbonation in cracked concrete is poorly understood and needs to be investigated further.

In Chapter 6, it was found to be impossible to conduct thermographic analysis on concrete specimens at low temperatures. A suggestion would be to develop a TGA unit which is able to protect the surface of the specimen from condensation buildup, and able to very accurately control temperature and gas flows, so that it may be possible to conduct this experiment at lower temperatures.

In Chapter 7, it was found that carbonation products formed under accelerated carbonation test conditions differ from those under natural carbonation conditions. Whereas the predominant carbonated product under natural carbonation is calcite, for accelerated tests, significantly higher concentrations of aragonite and vaterite were present. Therefore, the exact CO₂ diffusion coefficient measured in an accelerated test will likely not be the same as that under natural conditions due to the change in the morphology of $CaCO_3$. This assertion needs to be verified by devising a test method to measure CO_2 diffusion coefficients of samples carbonated at different CO_2 concentrations. If the diffusion coefficient was significantly different, then the model described in Chapter 3 would need to be modified to take into account the discrepancy between accelerated and natural carbonation. In general, it is also felt that since the purpose of an accelerated carbonation test is to reduce test times, it is possible that the use of a higher CO_2 concentration should be permitted. Considering that the morphology of CaCO₃ is different regardless of the exact concentration under accelerated conditions, it makes sense to determine at what range of concentrations diffusion coefficients are similar, and then set an upper limit within this range, along with the specification of an optimal testing temperature and humidity. Further research needs to be conducted to determine an optimal preconditioning time, with precondition conditions being as similar as possible to the accelerated test conditions.

Chapter 8 described the potential application of a structural health monitoring system via the use of pH sensors to detect the progression of a carbonation front in concrete. While this area of research shows promise, there are still many problems which need to be dealt with before they can be used regularly. Most importantly, it was found that the absolute value of pH for a sensor embedded in concrete has to be correlated with a measured potential difference. At this point, while the sensors were able to detect general trends in pH as a specimen carbonates, the readings varied greatly, not only from specimen to

specimen, but from sensor to sensor, and therefore, could not be correlated to determine what the exact pH. A number of further tests need to be conducted to generate enough data to be able to develop such a correlation. In addition, there appeared to be cross-interaction between some sensors which caused readings in one sensor to be affected by readings in an adjacent sensor. This problem needs to be dealt with before this sort of sensors could be used regularly in practice.

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Appendix A: Sample Iteration

In this appendix a sample iteration to calculate the CO_2 concentration at a node 5 mm deep for a sample in Vancouver, in the year 2000 is presented.

City: Vancouver

Scenario: Control, Year 2000

Concrete Properties:

Cement Content: 380 kg/m³

Water Content: 190 kg/m³

Air Content: 6%

First Iteration:

Time: t=0 sec

Temperature:

Temperature (T) = 283.25 K

Reaction rate coefficient between $CO_{2(aq)}$ and $Ca(OH)_{2(aq)}$ (Equation 3.8) :

$$k_{c} = \beta e^{\left(\frac{-U}{RT}\right)}$$
$$k_{c} = 1390e^{\left(\frac{-40000}{8.314 \times 283.25}\right)}$$

$$k_c = 5.87 \text{ x } 10^{-5} \text{ m}^3/\text{mol/s}$$

where,

 $-k_c$ is the reaction rate constant for reaction between CO_2 and $Ca(OH)_2$ at the temperature of interest(m³/mol/s)

-U is the reaction activation energy (40000 J/mol K) (Khunthongkeaw and Tangtermsirikul, 2005) -β is the pre-exponential factor (1390 m³/mol/s) (Khunthongkeaw and Tangtermsirikul, 2005)

Calculation of concentration of $Ca(OH)_{2(aq)}$ (Equations 3.13, 3.14):

$$K_{sp} = (0.0125 \times 10^9)e^{-0.019T}$$

 $K_{sp} = (0.0125 \times 10^9)e^{-0.019 \times 283.25}$
 $K_{sp} = 57497.066$

$$[\operatorname{Ca}(\operatorname{OH})_{2(aq)}] = \left(\frac{K_{sp}}{4}\right)^{\frac{1}{3}}$$

 $[Ca(OH)_{2(aq)}] = 24.314 \text{ mol/m}^3$

Concentration of $CO_{2(g)}$ (for the scenario in question):

CO_{2(g)}=0.787 mol/m³

Determination of Henrys Constant (Equation 3.11) :

$$H(T) = H_{ref} e^{\left[\Delta \left(\frac{1}{T_{ref}} - \frac{1}{T}\right)\right]}$$
$$H(0) = 34.2e^{\left[2400\left(\frac{1}{298.5} - \frac{1}{T}\right)\right]}$$

 $H(0) = 22.18 \text{ mol/m}^3 \text{ atm}$

where,

- H_{ref} is the reference Henry's Constant (34.2 mol/m³ atm)
- Δ is an enthalpy constant (2400 K)

Determination of effective diffusion coefficient:

As concrete carbonates, we assume that two distinct layers form within the concrete. One is the carbonated layer into which CO_2 has penetrated, and one is the non-carbonated layer into which CO_2 has not penetrated. CO_2 diffuses through the carbonated layer towards the non-carbonated layer. The carbonation reaction occurs at the interface between these two layers.

The porosity of the carbonated layer is also less than that of the uncarbonated layer, as the volume products are carbonation are less than that of non-carbonated concrete.

The porosity of the concrete, ε is defined as the ratio of pore volume to the total volume of concrete decreases with time due to the processes of cement hydration and carbonation. This is mathematically shown as (Papadakis, 1999a), (Papadikas, 1999b), (Papadikas, 2000), (Papadakis et al, 1991):

$$\boldsymbol{\epsilon}_{O} := \boldsymbol{\epsilon}_{air} + \frac{w}{\rho_{W}}$$

where,

 ϵ_{air} = air content of fresh concrete (m³)

w = initial water content of fresh concrete (kg)

$$\rho_{\rm W}$$
 = water density (kg/m³)

$$\varepsilon := \varepsilon_0 - \Delta \varepsilon H - \Delta \varepsilon C$$

where,

 ε_0 = porosity of fresh concrete (m³)

 $\Delta \varepsilon_{\rm H}$ = reduction in porosity due to hydration (m³)

 $\Delta \varepsilon_{\rm C}$ = reduction in porosity due to carbonation (m³)

Using Bogues Formulas (Hewlitt, 1998), we find that:

 $C_2S := [2.864F_{SiO2} - 0.754(C_3S)] \cdot C$

$$C_{3}A := (2.6F_{Al2O3} - 1.69F_{Fe2O3}) \cdot C$$

$$C_{4}AF := 3.043F_{Fe2O3}C$$

$$C_{3}S := (4.071F_{CaO} - 7.6F_{SiO2} - 6.718F_{Al2O3} - 1.43F_{Fe2O3} - 2.852F_{SO3}) \cdot C$$
where

where,

c = cement (kg)

Furthermore, using the stoichiometry of the hydration reactions, and the molar weights of the reactants and products, the amounts of the finally produced compounds can be estimated (Papadakis, 1999a):

$$CSH:= 2.85 F_{SiO2}C$$

$$CaOH_{2}:= \left[1.321 \left(F_{CaO} - 0.7F_{SO3}\right) - 1.851 F_{SiO2} - 2.18F_{Al2O3} - 1.39F_{Fe2O3}\right] \cdot C$$

$$\Delta \varepsilon_{\mathrm{H}} := (\mathbf{C}_{3} \mathrm{S}) \cdot \Delta \mathrm{V}_{\mathrm{C3S}} + (\mathbf{C}_{2} \mathrm{S}) \cdot \Delta \mathrm{V}_{\mathrm{C2S}} + (\mathbf{C}_{3} \mathrm{A}) \cdot \Delta \mathrm{V}_{\mathrm{C3A}} + (\mathbf{C}_{4} \mathrm{AF}) \cdot \Delta \mathrm{V}_{\mathrm{C4AF}}$$

The four products of cement hydration are: C_3S, C_2S, C_3A, C_4AF, therefore:

 $\Delta \varepsilon_{C} := (CaOH_2) \cdot \Delta V_{CaOH2} + (CSH) \cdot \Delta V_{CSH}$

According to the reaction stoichiometry, and using the molar volumes of the solid reactants and products, the molar volume difference for the reactions are (Papadikas, 1999a), (Papadikas et al, 1991):

$$\Delta V_{C3A} := 0.576910^{-3} \cdot \frac{m^3}{kg}$$
$$\Delta V_{CaOH2} := 5.20310^{-5} \frac{m^3}{kg}$$
$$\Delta V_{C3S} := 0.233410^{-3} \frac{m^3}{kg}$$

$$\Delta V_{C2S} := 0.228510^{-3} \frac{m^3}{kg}$$
$$\Delta V_{C4AF} := 0.232110^{-3} \frac{m^3}{kg}$$
$$\Delta V_{CSH} := 4.49510^{-5} \frac{m^3}{kg}$$

For the cement used in all experiments, chemical analysis shows that the % fractions of the compounds within the cement are:

silica dioxide: SiO₂: 19.8% aluminium dioxide: Al₂O₃: 4.4%

ferric oxide: Fe₂O₃: 3.3%

calcium oxide: CaO: 64.6%

magnesium oxide: MgO: 0.8%

sulphur trioxide: SO3: 2.7%

$$F_{Al2O3} = 0.04 F_{SO3} = 0.02 F_{Fe2O3} = 0.03 F_{CaO} = 0.64 F_{MgO} = 0.00 F_{SiO2} = 0.198$$

Thereafter, we can solve for porosity and substitute into Equation 3.6:

$$D_{CO_2} = A \left(\frac{V_p}{\frac{c}{\rho_c} + \frac{w}{\rho_w}} \right)^{\alpha}$$

-A and α are empirical parameters determined experimentally with suggested values of A=4.0x10⁻⁵ m²/s and α =1.8 (Papadikas et al, 1991)

-V_p is the pore volume of cement paste (m³)

 $-\rho_c$ is the absolute density of cement (3120 kg/m³)

 $-\rho_w$ is the density of water (1000 kg/m³)

Running the first iteration in MATLAB gives:

 $D_{CO_2} = 1.0238 \times 10^{-5} \text{ m}^2/\text{s}$

Subject to a temperature correction (Equation 3.7) and a humidity correction (Equation 3.9):

$$D_{CO2}(T,RH) = D_{ref} e^{\left[\frac{Q}{R}\left(\frac{1}{T_{ref}} - \frac{1}{T}\right)\right]} \times (1 - RH)^{2.2}$$

With T=283.25K, RH=78.5%,

 $D_{CO2}(T,RH) = 1.52 \times 10^{-7} \text{ m}^2/\text{s}$

The diffusion coefficient of calcium hydroxide is set as (Section 3.1.5):

 $D_{CaOH2} = 1 \times 10^{-12} \text{ m}^2/\text{s}$

Finally, Equations 3.15 and 3.16 can now be simultaneously solved:

$$\frac{\partial}{\partial t} \left[CO_{2(aq)} \right] = D_{CO2} \frac{\partial^2}{\partial x^2} \left[CO_{2(g)} \right] HRT - k \left[CO_{2(aq)} \right] \left[Ca(OH)_{2(aq)} \right]$$
$$\frac{\partial}{\partial t} \left[Ca(OH)_{2(aq)} \right] = D_{CaOH2} \frac{\partial^2}{\partial x^2} \left[Ca(OH)_{2(aq)} \right] - k \left[CO_{2(aq)} \right] \left[Ca(OH)_{2(aq)} \right]$$

Running the first iteration in MATLAB gives a Ca(OH)₂ concentration at the first node as 1643 mol/m³. Thereafter, iterations continue until the concentration has become half this original value. At that point, the time is noted, and the node is considered to have been fully carbonated.