MICROSTRUCTURAL REFINEMENTS IN CONCRETE DUE TO FIBER REINFORCEMENT AND ITS INFLUENCE ON CORROSION INITIATION OF REINFORCING STEEL

by

Manote Sappakittipakorn

B.Eng. King Mongkut’s University of Technology North Bangkok, 1996
M.Eng. Asian Institute of Technology, 1998

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Abstract

Permeability plays an important role in governing the durability of concrete in deleterious environments. Earlier studies indicated that the addition of cellulose fiber is effective in reducing water permeability and thereby making concrete more durable. In this thesis, microstructural refinement and corrosion resistivity performance of fiber reinforced concrete (FRC) were studied. Two fiber types, cellulose and polypropylene, at various dosages, were examined.

Microstructural refinement was studied using thermoporometry (TP) and mercury intrusion porosimetry (MIP) methods. After that, a two-part experiment was performed to investigate corrosion of steel in concrete in the presence of fiber reinforcement. First, diffusion of chloride in concrete was investigated using the bulk diffusion test as well as a silver nitrate spray test. A rapid chloride permeability test was also performed. Secondly, FRC beams were subjected to flexural stress while exposed to a simulated tidal zone of marine environment. Corrosion activity in reinforcing steels was monitored for 56 weeks using three electrochemical methods: half-cell potential, galvanic current and linear polarization resistance.

Results demonstrated that fibers did bring about a refinement in the pore structure by converting part of the permeable porosity to non-permeability porosity. Diffusion results clearly show that while the presence of fibers increased the coefficient of chloride diffusion
based on total chlorides, there was a decrease in the coefficient related to free chlorides. Fibers therefore appear to bind the chlorides and inhibit their transport. Corrosion tests indicated that fibers delayed corrosion in specimens with no load or a lighter load, but were not as effective in specimens carrying a heavier load.

Finally, a long-time performance of fiber reinforcement was illustrated through a service life modeling. Corrosion initiation period was analyzed using a model called LIGHTCON. Empirically based on the test results, it was modified to take the effects of fiber reinforcement and load intensity into consideration. The modified model was then verified in two case studies. In each of the cases, a critical impact of load induced cracks on a service life of structures was emphasized and a promising benefit of fiber reinforcement was demonstrated.
Preface

The content of this thesis comprises four proposed manuscripts (chapters 2, 3, 4 and 5, respectively). For the first manuscript (chapter 2), only the experimental test of mercury intrusion porosimetry method performed by Dr. Zheng-Wu Jiang at Tongji University is presented. In recognition of his contribution, he is included as a co-author. For the remaining manuscripts (chapters 3 to 5), I performed all the laboratory tests myself, including all data analysis. Preparation of all four manuscripts, including the contents, figures and tables, has been solely my responsibility. Dr. Nemkumar Banthia reviewed all the manuscripts, gave feedback on technical content, assisted with the formulation of concepts and made suggestions for clarity of presentation. Accordingly, Dr. Banthia is a co-author on all four manuscripts.
Table of Contents

Abstract ........................................................................................................................................ ii
Preface ........................................................................................................................................ iv
Table of Contents .......................................................................................................................... v
List of Tables ................................................................................................................................ x
List of Figures ........................................................................................................................... xii
Acknowledgements .................................................................................................................. xx
Dedication ...................................................................................................................................... xxi

Chapter 1  Introduction .................................................................................................................. 1
  1.1 Outline of the Thesis ............................................................................................................... 3
  1.2 Objectives and Scope ............................................................................................................ 6
  1.3 Fiber and Concrete Durability .......................................................................................... 7
  1.4 Mechanism of Rebar Corrosion in Concrete ................................................................. 16
    1.4.1 Anode (a site having an anodic reaction) ................................................................. 16
    1.4.2 Cathode (a site having a cathodic reaction) ......................................................... 18
    1.4.3 Conductive medium (a path for electrons) ......................................................... 18
    1.4.4 Electrolyte (a path for ions) ................................................................................. 18
  1.5 Diffusion Process in a Cementitious Medium .............................................................. 20
    1.5.1 Steady-state diffusion ......................................................................................... 21
    1.5.2 Non steady-state diffusion ............................................................................... 22
  1.6 Cracks in Concrete Structures in Relation to Corrosion of Steel Rebar ....................... 25
    1.6.1 Cracks accelerated corrosion ........................................................................... 25
    1.6.2 Corrosion induced cracks ................................................................................. 28
<table>
<thead>
<tr>
<th>Chapter 2</th>
<th>Cryoporometry Based Evidence of Pore Refinement in Cementitious Composites</th>
<th>42</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Outline ..................................................</td>
<td>42</td>
</tr>
<tr>
<td>2.2</td>
<td>Introduction ............................................</td>
<td>43</td>
</tr>
<tr>
<td>2.3</td>
<td>Thermoporometry ......................................</td>
<td>44</td>
</tr>
<tr>
<td>2.4</td>
<td>Mercury Intrusion Porosimetry ....................</td>
<td>49</td>
</tr>
<tr>
<td>2.5</td>
<td>Experimental Protocol ................................</td>
<td>50</td>
</tr>
<tr>
<td>2.6</td>
<td>Results and Discussion ..............................</td>
<td>53</td>
</tr>
<tr>
<td>2.6.1</td>
<td>Thermoporometry with differential scanning calorimeter</td>
<td>53</td>
</tr>
<tr>
<td>2.6.2</td>
<td>Ice formation .........................................</td>
<td>56</td>
</tr>
<tr>
<td>2.6.3</td>
<td>Mercury intrusion porosimetry ....................</td>
<td>58</td>
</tr>
<tr>
<td>2.7</td>
<td>Conclusions ............................................</td>
<td>60</td>
</tr>
<tr>
<td>2.8</td>
<td>Acknowledgements .....................................</td>
<td>61</td>
</tr>
<tr>
<td>2.9</td>
<td>Notation ................................................</td>
<td>61</td>
</tr>
<tr>
<td>2.10</td>
<td>References .............................................</td>
<td>63</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chapter 3</th>
<th>Corrosion of Rebar and Role of Fiber Reinforced Concrete, Part 1: Chloride Transport</th>
<th>65</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>Outline ..................................................</td>
<td>65</td>
</tr>
<tr>
<td>3.2</td>
<td>Introduction ............................................</td>
<td>66</td>
</tr>
<tr>
<td>3.3</td>
<td>Research Significance ...............................</td>
<td>68</td>
</tr>
<tr>
<td>3.4</td>
<td>Experimental Procedures ............................</td>
<td>69</td>
</tr>
<tr>
<td>3.4.1</td>
<td>Materials and specimens .............................</td>
<td>69</td>
</tr>
<tr>
<td>3.4.2</td>
<td>Bulk diffusion test ....................................</td>
<td>71</td>
</tr>
<tr>
<td>3.4.3</td>
<td>Silver nitrate spray test ............................</td>
<td>72</td>
</tr>
<tr>
<td>3.4.4</td>
<td>Chloride profiles and chloride diffusion coefficients ........................................</td>
<td>74</td>
</tr>
<tr>
<td>3.4.5</td>
<td>Rapid chloride permeability test .........................</td>
<td>75</td>
</tr>
<tr>
<td>3.4.6</td>
<td>Chloride binding ........................................</td>
<td>76</td>
</tr>
</tbody>
</table>
3.5 Results and Discussions ................................................................. 77
  3.5.1 Chloride penetration front ......................................................... 77
  3.5.2 Chloride diffusion coefficients ................................................ 79
  3.5.3 Rapid chloride permeability test ............................................. 82
  3.5.4 Chloride binding effect ........................................................... 84
3.6 Conclusions ................................................................................. 86
3.7 References .................................................................................... 89

Chapter 4 Corrosion of Rebar and Role of Fiber Reinforced Concrete,
Part 2: Electrochemical Measurements .............................................. 92
  4.1 Outline ......................................................................................... 92
  4.2 Introduction .................................................................................. 93
  4.3 Research Significance .................................................................. 96
  4.4 Experimental Program ............................................................... 96
    4.4.1 Materials ............................................................................... 96
    4.4.2 Specimens ............................................................................ 98
  4.5 Electrochemical Measurements and Results .............................. 103
    4.5.1 Half-cell potential ............................................................... 103
    4.5.2 Galvanic current ................................................................. 106
    4.5.3 Linear polarization resistance ............................................ 110
    4.5.4 Time to onset of corrosion in reinforcing steel ..................... 114
  4.6 Conclusions ................................................................................ 115
  4.7 References .................................................................................. 117

Chapter 5 Role of Fiber Reinforcement on Service Life of Concrete
Structures in Marine Environments .................................................... 121
  5.1 Outline ....................................................................................... 121
  5.2 Introduction ............................................................................... 122
  5.3 Service Life Models .................................................................... 123
  5.4 The LIGHTCON Model .............................................................. 126
    5.4.1 Modification of the LIGHTCON model for the accelerated
corrosion environment ................................................................. 128
    5.4.2 Influence of fiber reinforcement ......................................... 131
    5.4.3 Influence of applied flexural loadings ................................. 133
5.5 Case Studies .................................................................................................. 134
  5.5.1 Beam specimens of the laboratory corrosion test with a corrosion accelerated environment .................................................... 134
  5.5.2 Reinforced concrete bridge girders incorporating silica fume and fibers located in a splash zone of marine environment ................................................................. 136
5.6 Conclusions .................................................................................................. 140
5.7 References ..................................................................................................... 142

Chapter 6 Conclusions and Recommendations ....................................................... 145
  6.1 Concluding Remarks ..................................................................................... 145
    6.1.1 Pore refinement ................................................................................. 145
    6.1.2 Transport properties .......................................................................... 147
    6.1.3 Electrochemical measurements ......................................................... 155
    6.1.4 Predicting the FRC performance using the modified LIGHTCON model ........................................................................... 157
  6.2 Recommendation for Future Works .............................................................. 160
    6.2.1 Influence of fibers on chloride binding should be investigated further ........................................................................... 160
    6.2.2 Investigating the role of fibers in controlling corrosion induced cracking ........................................................................... 162
    6.2.3 Field studies on the influence of fibers on corrosion in actual structures ........................................................................... 163
    6.2.4 Studies on other fibers and hybridization of fibers in the role of corrosion inhibitors ........................................................................... 164
    6.2.5 Use of chloride binding fibers in repair materials ............................. 165
  6.3 References ..................................................................................................... 166

Appendix A Results of the Thermal Scan on Cellulose Fiber Reinforced Concrete Using Differential Scanning Calorimeter .............................................. 167

Appendix B Profiles of Acid-Soluble and Water-Soluble Chlorides after Bulk Diffusion Test ................................................................. 169

Appendix C Profiles of Acid-Soluble and Water-Soluble Chlorides after Accelerating Corrosion Test ................................................................. 174

Appendix D Details of the Modification of the LIGHTCON Model ...................... 180
### Table of Contents

D.1 The LIGHTCON Model

D.1.1 Input parameters
D.1.2 Assumptions
D.1.3 Mass balance of chloride in concrete
D.1.4 Predicting of chloride diffusion coefficients

D.2 Modification of the LIGHTCON Model for the Accelerating Corrosion Environment

D.3 Influence of Fiber Reinforcement

D.4 Influence of Applied Flexural Loadings

D.5 References

Appendix E Limits of Chloride Content in Concrete
List of Tables

Table 2.1  Mixture proportions
Table 2.2  Average of the heat flow rates and corresponding temperatures
Table 2.3  Porosity from MIP tests
Table 3.1  Concrete mixture proportions
Table 3.2  Properties of fibers investigated
Table 3.3  The chloride contents, the depth of chloride front (d_f) and the diffusion coefficients
Table 4.1  Mixture proportions
Table 4.2  Properties of fibers investigated
Table 4.3  Range of corrosion current density values and expected corrosion level (Andrade and Alonso 2004)
Table 4.4  Time to onset of corrosion in reinforcing steel for various mixtures
Table 5.1  Time to corrosion onset in plain concrete and FRCs
Table 5.2  Chloride diffusion of specimens subjected to wet-dry cyclic exposure in a saline environment
Table 6.1  Coefficients of chloride diffusion of specimens subjected to chloride bulk diffusion exposure
Table 6.2  Coefficients of chloride diffusion of specimens subjected to the wet-dry cyclic exposure in saline environment
Table 6.3  Time to corrosion onset in FRC (weeks)
Table E.1  Allowable chloride ion limits in concrete (% by mass of cement) ............................................................... 192
# List of Figures

| Figure 1.1 | Crack widths versus time for various volume fractions of polypropylene fibers (Grzybowski and Shah 1990) ..........................................10 |
| Figure 1.2 | Deteriorated surfaces of concrete slabs (Al-Tayyib and Al-Zahrani 1990) ..............................................................................................10 |
| Figure 1.3 | Effects of various pozzolans on permeability of plain and fibrous concretes (Soroushian, Mirza, and Alhozaimy 1995) .........................11 |
| Figure 1.4 | Effects of latex polymer on permeability of plain and fibrous composites (Soroushian, Mirza, and Alhozaimy 1995) ............................. 11 |
| Figure 1.5 | Typical flexural load-deflection behavior of cellulose fiber reinforced cement composites in different moisture conditions (Soroushian, Marikunte, and Won 1995) ...................................................12 |
| Figure 1.6 | Interaction of fiber content and moisture condition on flexural performance of cellulose fiber reinforced cement composites: (a) flexural strength and (b) flexural toughness (Soroushian, Marikunte, and Won 1995) .................................................................13 |
| Figure 1.7 | Effects of moisture and aging on the flexural stress of (a) refined and (b) unrefined cellulose fibers (Kim et al. 1999) .........................13 |
| Figure 1.8 | Results of toughness/cross-sectional area of (a) AR-GFRC and (b) E-PGFRC compositions 1 and 2 versus accelerated aging time at 50ºC (Shah et al. 1988) ..........................................................15 |
| Figure 1.9 | Corrosion processes on the surface of steel: (a) reactions at anodic and cathodic sites and electric current loop, (b) flow of |
electrical charge in the electric current loop during the corrosion process. (Bentur, Diamond, and Berke 1997) ....................... 17

Figure 1.10  Fick’s first law of diffusion: the flux of chloride ions is proportional to the chloride concentration gradient normal to the section (Poulsen and Mejlbro 2006) ..................................................... 23

Figure 1.11  Fick’s second law of diffusion: the change in chloride ion content per unit time (on the \( t \)-axis) is equal to the change of flux per unit length (on the \( x \)-axis) ............................................................. 23

Figure 1.12  Schematic of the half-cell potential measurement on reinforcing steel in concrete (ASTM C 876 1998) ................................. 32

Figure 1.13  Electric field around a corrosion area .......................................................... 33

Figure 1.14  Schematic set-up for linear polarization measurements (Bentur, Diamond, and Berke 1997) ................................................................. 33

Figure 1.15  Polarization resistance curve (Bentur, Diamond, and Berke 1997) ................................................................. 35

Figure 1.16  Schematic description of a macrocell test (Bentur, Diamond, and Berke 1997) ................................................................. 36

Figure 2.1  Correlation between freezing and melting point depression of water as a function of pore radii ................................................................. 47

Figure 2.2  Cellulose fiber investigated. The 2.3 mm long fibers are collated in the form of a chip for improved fiber dispersion during mixing ................................................................. 51

Figure 2.3  A cored specimen (left) with a sealable aluminium pan (middle) and a lid (right) ........................................................................ 52

Figure 2.4  Thermograms for multiple specimens: a) plain cement paste; b) 0.1% FRC paste; and c) 0.3% FRC paste (Each specimen has 3 replicates) ........................................................................ 54
| Figure 2.5 | The distributions of pore sizes in plain and fiber reinforced cement pastes as per thermoporometry .............................................................56 |
| Figure 2.6 | Exothermic energy in samples .................................................................57 |
| Figure 2.7 | The pore sizes distributions in plain and fiber reinforced cement pastes based on thermoporometry and mercury intrusion porosimetry ......................................................58 |
| Figure 2.8 | Relationship between porosity and permeability ratio of FRC, noting that permeability data from the study by Banthia and Bhargava (2007) .........................................................................................60 |
| Figure 3.1 | Photographs of fibers investigated (a) cellulose fiber and (b) polypropylene fiber ........................................................................................70 |
| Figure 3.2 | Bulk diffusion test as per ASTM C 1556 ; (a) specimen with epoxy coating and cut in the middle, (b) submersion in NACL solution, and (c) determination of chloride profile ................................................72 |
| Figure 3.3 | The color changes on a concrete sample tested with silver nitrate spray ........................................................................................................73 |
| Figure 3.4 | Rapid chloride permeability test as per ASTM C 1202 ................................75 |
| Figure 3.5 | Chloride penetration fronts as detected by the silver nitrate spray for various mixtures (from left to right, mix #1: plain concrete, mix #2: 0.1% cellulose FRC, mix #3: 0.3% cellulose FRC, mix #4: 0.1% polypropylene FRC, and mix #5: 0.3% polypropylene FRC). ..................................................................................78 |
| Figure 3.6 | Chloride profiles of the average water-soluble (free) and acid-soluble (total) chlorides ......................................................................................81 |
| Figure 3.7 | Influence of surface chloride concentration on coefficient of diffusion (a) free chlorides with effective coefficient and (b) total chlorides with apparent coefficient ................................................81 |
List of Figures

Figure 3.8  Apparent and effective coefficients of chloride diffusion for various volume fractions of fibers .......................... 82

Figure 3.9  Charge passed in rapid chloride ion permeability test (RCPT). The results are listed in the format: average ± standard deviation (coefficient of variation) .................................................. 83

Figure 3.10 Influence of fiber volume fraction on the charge passed in rapid chloride ion permeability test (RCPT) ......................................... 84

Figure 3.11 The changes of the chloride concentration as a function of time due to the chloride binding effect of the cement pastes (5 g) with and without the presence of the cellulose and polypropylene fibers (0.1% and 0.3% volume fractions) .................. 85

Figure 3.12 The bound chloride of the PC and FRC pastes in the NACL solution at various initial chloride concentrations (0.1, 0.3, and 0.6 Molar) after the test duration of 21 days ........................................... 86

Figure 4.1  Photographs of fibers investigated (a) cellulose fiber and (b) polypropylene fiber ................................................................. 98

Figure 4.2  Schematic of a test specimen ......................................................... 99

Figure 4.3  Corrosion test program ................................................................. 100

Figure 4.4  Load–displacement curves for beam specimens in 4-point bending ...................................................................................... 100

Figure 4.5  Steel frame used for applying a steady flexural load on the specimen .................................................................................... 100

Figure 4.6  Relationship between the applied torques and the corresponding bending load for the specimen shown in Figure 4.5 .................................................. 101

Figure 4.7  A schematic of the chamber simulating a corrosive environment .......................................................................................... 103

Figure 4.8  Schematic of half-cell potential measurement .......................... 104
List of Figures

Figure 4.9  Half-cell potentials (with respect to copper/copper sulfate electrode) measured in samples without load ........................................... 105
Figure 4.10 Half-cell potentials (with respect to copper/copper sulfate electrode) measured in samples with 15 kN flexural load ....................... 105
Figure 4.11 Half-cell potentials (with respect to copper/copper sulfate electrode) measured in samples with 30 kN flexural load ....................... 106
Figure 4.12 Schematic of galvanic current measurement ........................................... 107
Figure 4.13 Galvanic current densities measured in specimens without load ............. 108
Figure 4.14 Galvanic current densities measured in specimens with a 15 kN flexural load ........................................................................................ 108
Figure 4.15 Galvanic current densities measured in specimens with a 30 kN flexural load ........................................................................................ 109
Figure 4.16 Schematic of the linear polarization resistance measurement .................. 111
Figure 4.17 Corrosion current densities measured in a linear polarization test in specimens without load ................................................................. 111
Figure 4.18 Corrosion current densities measured in a linear polarization test in specimens with a 15 kN load ................................................................. 112
Figure 4.19 Corrosion current densities measured in a linear polarization test in specimens with a 30 kN load ................................................................. 112
Figure 5.1  Schematic of conceptual model of corrosion of steel reinforcement in concrete (Tuutti 1980) ................................................................. 124
Figure 5.2  The apparent chloride diffusion coefficients as a function of the fiber volume fraction (lines represent the predicted values and markers represent the experimental results) .............................................. 132
Figure 5.3  Time to corrosion initiation of steel in plain concrete and FRC beams subjected to flexural loads – model prediction and experimental data ..................................................................................... 136
Figure 5.4  Predicted time to corrosion onset of reinforcing steel in a concrete bridge girder in a marine splash zone varied with thickness of concrete cover in non-loaded condition ............................... 138

Figure 5.5  Predicted time to corrosion onset of reinforcing steel in a concrete bridge girder in a marine splash zone varied with applied loads (concrete cover = 50 mm) ............................................................................. 140

Figure 6.1  The pore sizes distributions in plain and fiber reinforced cement pastes based on thermoporometry and mercury intrusion porosimetry ............................................................................... 146

Figure 6.2  Relationship between porosity and permeability ratio of FRC, with permeability data from the study by Banthia and Bhargava (2007) .......................................................................................... 146

Figure 6.3  Charge passed in rapid chloride ion permeability test (RCPT). The results are listed in the format: average ± standard deviation (coefficient of variation)............................................................... 148

Figure 6.4  Influence of fiber volume fraction on the charge passed in rapid chloride ion permeability test (RCPT) .......................................................... 148

Figure 6.5  Chloride penetration fronts as detected by the silver nitrate spray for various mixtures (from left to right, mix #1: plain concrete, mix #2: 0.1% cellulose FRC, mix #3: 0.3% cellulose FRC, mix #4: 0.1% polypropylene FRC, and mix #5: 0.3% polypropylene FRC). ................................................................................ 149

Figure 6.6  Penetration depth of chloride in FRC from the silver nitrate spray test .............................................................................................................. 150

Figure 6.7  Coefficients of total and free chloride diffusion of FRC .................. 151

Figure 6.8  The bound chloride of the PC and FRC pastes in the NaCl solution at various initial chloride concentrations (0.1, 0.3, and 0.6 molar) after the test duration of 21 days................................................................. 154
Figure 6.9  Time to corrosion onset in FRC beams subjected to flexural loads (noting that a time to corrosion in 0.3% CL FRC beam in a case of no loading was assumed to represent its superior performance as at the end of the test corrosion was not yet active) ................................................................. 155

Figure 6.10  Time to corrosion initiation of steel in plain concrete and FRC beams subject to flexural loads from the modified model compared to the experimental results .............................................. 158

Figure 6.11  Predicted time to corrosion onset of reinforcing steel in a concrete bridge girder in a marine splash zone varied with thickness of concrete cover in non-loaded condition ....................... 159

Figure 6.12  Predicted time to corrosion onset of reinforcing steel in a concrete bridge girder in a marine splash zone varied with applying loads (concrete cover = 50 mm) ...................................................... 159

Figure A.1  Heat flow of plain concrete samples during the freezing stage in the differential scanning calorimeter .......................................................... 167

Figure A.2  Heat flow of 0.1% cellulose FRC samples during the freezing stage in the differential scanning calorimeter .............................................. 168

Figure A.3  Heat flow of 0.3% cellulose FRC samples during the freezing stage in the differential scanning calorimeter .............................................. 168

Figure B.1  Chloride profiles of plain concrete exposed to the bulk diffusion for 90 days ...................................................................................... 169

Figure B.2  Chloride profiles of 0.1% cellulose FRC exposed to the bulk diffusion for 90 days .............................................................................. 170

Figure B.3  Chloride profiles of 0.3% cellulose FRC exposed to the bulk diffusion for 90 days .............................................................................. 171

Figure B.4  Chloride profiles of 0.1% polypropylene FRC exposed to the bulk diffusion for 90 days ........................................................................... 172
Figure B.5  Chloride profiles of 0.3% polypropylene FRC exposed to the bulk diffusion for 90 days ................................................................. 173

Figure C.1  Profile of acid-soluble chlorides in plain concrete exposed to the accelerating corrosion chamber for 56 weeks ....................... 174

Figure C.2  Profile of acid-soluble chlorides in 0.1% cellulose FRC exposed to the accelerating corrosion chamber for 56 weeks .......... 175

Figure C.3  Profile of acid-soluble chlorides in 0.3% cellulose FRC exposed to the accelerating corrosion chamber for 56 weeks .......... 175

Figure C.4  Profile of acid-soluble chlorides in 0.1% polypropylene FRC exposed to the accelerating corrosion chamber for 56 weeks .......... 176

Figure C.5  Profile of acid-soluble chlorides in 0.3% polypropylene FRC exposed to the accelerating corrosion chamber for 56 weeks .......... 176

Figure C.6  Profile of water-soluble chlorides in plain concrete exposed to the accelerating corrosion chamber for 56 weeks .................... 177

Figure C.7  Profile of water-soluble chlorides in 0.1% cellulose FRC exposed to the accelerating corrosion chamber for 56 weeks .......... 177

Figure C.8  Profile of water-soluble chlorides in 0.3% cellulose FRC exposed to the accelerating corrosion chamber for 56 weeks .......... 178

Figure C.9  Profile of water-soluble chlorides in 0.1% polypropylene FRC exposed to the accelerating corrosion chamber for 56 weeks .......... 178

Figure C.10 Profile of water-soluble chlorides in 0.3% polypropylene FRC exposed to the accelerating corrosion chamber for 56 weeks ............ 179

Figure D.1  Relationship of load intensity and effective depth of the tested beams....................................................................................... 190
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Dedication

To my beloved parents, Sunee and Viroj Sappakittipakorn, and

To my love, Nopmanee Supanam.
Corrosion of steel rebar in concrete has been known as a serious durability problem in reinforced concrete structures for more than half a century (Baker et al. 1957). It has been researched extensively in many aspects such as mechanisms, assessments, consequences, preventions, protections, and remedies (Bentur, Diamond, and Berke 1997; Broomfield 1997; Mietz, Polder, and Elsener 2000; Elsener 2001; Pianca 2003; Bertolini et al. 2004).

A general saying that *rust is a must* does not always mean that rust cannot be controlled. Although corrosion of steel is inevitable in most situations, it is impeded when it is embedded in sound concrete. In reinforced concrete structures, concrete protects steel and thereby produces a durable structural system. Yet, steel corrosion may occur whenever concrete is contaminated or deteriorated. Once corrosion of steel in concrete impairs the performance of reinforced concrete structures as it not only reduces the structural load bearing capacity, but more importantly, it shortens the service life.

In concrete structures exposed to either seawater or deicing salts, chlorides are the major contaminant responsible for corrosion of reinforcing steel. Generally, chlorides need to diffuse through concrete to corrode the reinforcing steel so there are two key factors controlling the time to initiation of the corrosion. One is the rate at which chlorides can
move into concrete. It can be defined as a coefficient of chloride diffusion. Another is the thickness of concrete cover providing a barrier between chloride sources and the steel reinforcement. In most design codes of concrete structures, a minimum concrete cover is specified when corrosion is a concern.

Concrete is weak in tension, and cracking in concrete is mainly due to tensile stresses induced by either service loads or environmental changes. Cracks vary in sizes, inclination, extents, and patterns, depending on the geometry of the structure, loading direction, the causes of cracking, and mechanical properties of the concrete. Through cracks, the rate of chlorides ingress becomes even higher causing a cracked concrete to be less effective in protecting steel. Accordingly, cracked concrete most likely results in more rapid and severe corrosion of steel rebar. Thus, while cracks depreciate the structural integrity they also shorten the service life. To enhance the life of concrete structures, these factors should be addressed.

Fiber addition to concrete alleviates the problem of concrete brittleness. While the fiber performance may not be apparent in stress-free conditions, it becomes prominent when cracks occur under loading. Fibers bridge and capture cracks so that opening a crack is more difficult in fiber reinforced concrete and cracks remain lesser in number and size than in plain concrete. As a secondary benefit, fibers also increase the mechanical properties of the concrete, especially its post cracking tensile strength. Therefore, the fibers do control the crack formation and propagation.

Fibers also improve cracking resistance of concrete under severe environments. In a particular situation, cracks that are noticeable in plain concrete can be lessened and
sometimes eliminated in fiber reinforced concrete. Consequently, fibers would reduce the
effect of cracks on diffusion. In addition, when cracks are small, an effect of self healing
may occur. A chance of healing is increased when the crack size is decreased. The fiber
inclusion thus would also amplify the possibility and the rate of healing.

Previous tests of water permeability (Banthia and Bhargava 2007) indicated that the addition
of cellulose fiber is effective in reducing water permeability both in the presence and
absence of stress, and thereby making concrete more durable. That is a positive indication
leading to a hypothesis that the fiber will delay an initiation of steel rebar corrosion in
concrete. Therefore, in this study, an attempt was made to investigate the role of the fibers in
delaying the initiation of corrosion of reinforcing steel in concrete.

1.1 Outline of the Thesis

A framework of this thesis is presented here. The thesis is comprised of six chapters; 1) Introduction, 2) Thermoporometry-Based Characterization of Pore Structure in Fiber Reinforced Cementitious Composites, 3) Corrosion of Rebar and Role of Fiber Reinforced Concrete, Part 1: Chloride Transport, 4) Corrosion of Rebar and Role of Fiber Reinforced Concrete, Part 2: Electrochemical Measurements, 5) Role of Fiber Reinforcement on Service Life of Concrete Structures in Marine Environment, and 6) Conclusion. The following is a summary of the content of each chapter.
Chapter 1 starts with an introduction providing a literature review, a hypothesis, and a scientific background of this study. The literature was first reviewed to point out how corrosion of steel rebar has extensively deteriorated reinforced concrete structures and how fiber reinforcement could alleviate these problems. Stated next was the main focus of the study, which was to manifest how fiber reinforcement inhibits corrosion of steel rebar in concrete. Correspondingly, objectives and scope of the study were established. At the end, principles of chloride induced corrosion were briefly presented.

In Chapter 2, the influence of fiber reinforcement on the porosity was examined using Thermoporometry (TP) and Mercury Intrusion Porosimetry (MIP) methods. Only the cellulose fiber was examined. TP is a calorimetry-based technique to determine the pore size distribution of porous materials such as glasses and silica gels. It was employed to study cement paste in this study. TP was conducted in a differential scanning calorimeter (DSC) and was processed at the Biomaterials Lab, UBC. The MIP, which is a classical method for a pore size determination, was also used for comparison. The MIP test specimens were prepared at UBC and tested at the Key Laboratory of Advanced Civil Engineering Materials, Tongji University, China. Using both MIP and TP methods, a determination of pore size distribution was achieved. Based on results received from the MIP test, the porosity distribution of pastes was computed. From the test results, a pore refinement was verified in concrete reinforced with cellulose fiber. It conformed to previous findings in an experimental study on water permeability. Further corrosion tests were then conducted in subsequent chapters.
A two-part corrosion experiment was conducted and described in Chapter 3 and 4. In Chapter 3, the influence of fiber reinforcement on a diffusion of chlorides in concrete was examined. Fiber reinforced concrete (FRC) samples were first exposed to chlorides using a bulk diffusion test procedure (i.e. the submersion of the entire sample in NaCl solution). To find the penetration depth of chloride in the samples, a colorimetric test was employed using a silver nitrate spraying test. After that, the chloride profile of the samples (i.e. chloride content vs depth into the concrete sample) was obtained to evaluate the coefficient of chloride diffusion. The profile of free and total chlorides was determined from water-soluble and acid-soluble chloride concentrations, respectively. Additionally, a Rapid Chloride Permeability Test (RCPT) was performed on the FRC samples to corroborate the findings of the diffusion tests.

In Chapter 4, the second part of the corrosion test was carried out to monitor the corrosion initiation of steel rebar in reinforced concrete beams. The monitoring was carried out for 56 weeks using the measurements of half-cell potential, galvanic current, and linear polarization resistance. Corrosion was accelerated using a chamber simulating a tidal zone in a marine environment. Additionally, the beam specimens were subjected to flexural loads to measure the effect of loadings. By analyzing the results from these measurements, a variation of time to corrosion onset was reported.

In Chapter 5, a service life model called LIGHTCON was modified to take into account the influences of fiber reinforcement and flexural loading. Based on the laboratory testing results, several empirically formulated expressions were
developed. The modified model was able to predict the long-term performance of fiber reinforced concrete as a method for corrosion reduction. To validate its applicability, the model was utilized to estimate the initiation of rebar corrosion in two selected applications.

- The last chapter contains conclusions of the study. The effect of fibers on the steel rebar corrosion was summarized and further discussed in various aspects. Its benefit was emphasized. Additionally, some concerns were identified. Recommendations for future researches were also given.

1.2 Objectives and Scope

The main purpose of this study was to study the role of fiber reinforcement on the initiation time of reinforcing steel corrosion in concrete. Two fibers—cellulose and polypropylene—at 0.1% and 0.3% volume fractions were tested. The cellulose fiber is a virgin fiber made of fully purified softwood. It has an average length of about 2.3 mm and is collated in the form of a chip and carrying a surface treatment employed to enhance its alkali tolerance and bond with concrete. The polypropylene fiber was a multifilament fiber treated for alkali-resistance. It has an average length of 16 mm.

Following the experimental scope outlined above, performance of the two fibers was evaluated in many aspects such as characteristic of the pore structure, diffusion of chlorides, and the time to corrosion onset of steel rebar. The FRC samples were compared with plain concrete counterparts. Furthermore, to predict the long-term performance of FRCs in actual
marine environments, an empirical service life model called LIGHTCON was developed using the experimental results.

1.3 Fiber and Concrete Durability

Concrete can be considered a composite material composed of many brittle ingredients such as hydrated cement paste (mostly calcium silicate hydrate and calcium hydroxide) and aggregates (sand and crushed stone). Also, there are many interconnected pores and voids trapped inside the paste making it highly porous. When concrete is subject to load, the voids act as stress concentrators and can trigger internal cracking, which can propagate rapidly resulting in lower strengths as well as a catastrophic failure. Even though researchers have found many ways of improving strength and ductility of concrete (for instance by adjusting the mix proportions, adding supplementary cementitious materials, and by using polymeric admixtures), concrete is still a very brittle material relative to other construction materials. Fortunately, those shortcomings can be overcome by adding fibers into concrete and the resulting material is called fiber reinforced concrete (FRC).

During the past decades, the concept of fiber reinforcement has been researched and applied successfully to enhance concrete ductility. Fibers employed in FRCs are discrete and randomly distributed. They commonly have a high aspect ratio and are relatively tougher than concrete. Depending on the specific property needed in FRC, fibers can vary widely in materials, geometry, and volume fractions. Thus, the use of fibers in FRC is highly versatile.
In earlier studies of FRC, an improvement of the post-cracking mechanical response was of primary interest. Fibers are added to bridge cracks and then provide post-crack stress transfer and ductility. As a consequence, the addition of fibers enhances the toughness of concrete (i.e. its post-peak load carrying capacity). Mechanisms of how a fiber bridges a crack have been widely studied in detail in many papers. In general, fibers do relatively nothing if there are no cracks. Only if a crack is created, can fibers bridging the crack function. They arrest and suppress the crack via an interfacial bond stress developed between fibers and concrete. To achieve a superior ultimate strain while a crack is widening, either yielding or slipping of fibers is preferred but not fracturing. Hence, a well designed fiber can effectively improve toughness of FRC at a wide range of crack openings.

Not only can fibers function well in large cracks but they can effectively bridge small cracks in concrete. Since, in concrete, the loss of internal water in hydrated cement paste causes shrinkage encompassing several mechanisms, tensile strains are developed and accumulated internally. If the strain of the paste exceeds the failure strain level, both surface cracks and internal small cracks are created. As these shrinkage strains are quite small but present extensively throughout the paste, a large number of small (micro) fibers is preferred to contain these cracks. At a given volume fraction, a decrease of fiber diameter will increase the number of fibers. Thus, micro fibers, having very small diameter but high aspect ratios, can be applied effectively to arrest those shrinkage strains (Banthia and Gupta 2006). They also perform outstandingly in controlling the permeability of water in concrete either when subjected to stresses or without (Banthia and Bhargava 2007).

Because cracks are usually adverse to durability of concrete, one can hypothesize that FRCs having less cracks would be more sustainable than ordinary plain concrete. However, more
research and experiments should be carried out to prove such durability performance of FRCs. One research area is the influence of fiber on corrosion of steel rebar, an initiation part of which was investigated in this thesis. Some previous studies on FRC with regard to concrete durability are reviewed below.

Grzybowski and Shah (1990) found that a reduction of shrinkage effect on the matrix (using the ring-type specimens in restrained condition) was achieved with using polypropylene fibers as shown in Figure 1.1. Also, polypropylene fibers enhanced the resistance to deterioration of concrete surfaces subjected to seawater (Al-Tayyib and Al-Zahrani 1990). A sound surface, as shown in Figure 1.2, is clearly seen on the specimens reinforced with fibers. Even though polypropylene fibers can greatly lessen cracks, tests of chloride permeability indicated that polypropylene fibers have no advantage on this property (Soroushian, Mirza, and Alhozaimy 1995). Supplementary pozzolanic materials do improve the permeability as do some polymers, as shown in Figure 1.3 and Figure 1.4. In addition, fibers have no significant effect on the electrical resistivity and water absorption (Soroushian, Mirza, and Alhozaimy 1995).
Figure 1.1 Crack widths versus time for various volume fractions of polypropylene fibers (Grzybowski and Shah 1990)

Figure 1.2 Deteriorated surfaces of concrete slabs (Al-Tayyib and Al-Zahrani 1990)
Figure 1.3  Effects of various pozzolans on permeability of plain and fibrous concretes (Soroushian, Mirza, and Alhozaimy 1995)

Figure 1.4  Effects of latex polymer on permeability of plain and fibrous composites (Soroushian, Mirza, and Alhozaimy 1995)

Generally, cellulose fibers are sensitive to moisture. A study (Soroushian, Marikunte, and Won 1995) on cellulose FRC indicated that the performance of the cellulose fiber reinforced cement composites is altered in moist conditions (see Figure 1.5). It is pointed out that the wetting of the composite has significant effects on flexural strength, which reduces upon
wetting. Microstructural studies indicate that wetting leads to increased tendency toward fiber pullout rather than rupture of fibers at failure surfaces. This may illustrate why increased moisture condition tends to produce higher flexural toughness and lower flexural strengths in cellulose fiber reinforced cement composites as shown in Figure 1.6 and Figure 1.7 (Soroushian, Marikunte, and Won 1995). There is another interesting study (Kim et al. 1999) showing the sensitivity of the refined (150 CSF or Canadian Standard Freeness, which determines the rate at which water drains from a pad of pulp measured under standard test condition) and unrefined (700 CSF) kraft pulped Pinus radiata cellulose fibers to moisture (between dry and wet conditions) and aging (simulated with 30 carbonation cycles) as shown in Figure 1.7.

![Figure 1.5](image)

**Figure 1.5** Typical flexural load-deflection behavior of cellulose fiber reinforced cement composites in different moisture conditions (Soroushian, Marikunte, and Won 1995)
Figure 1.6  Interaction of fiber content and moisture condition on flexural performance of cellulose fiber reinforced cement composites: (a) flexural strength and (b) flexural toughness (Soroushian, Marikunte, and Won 1995)

(a) refined cellulose fibers  (b) unrefined cellulose fibers

Figure 1.7  Effects of moisture and aging on the flexural stress of (a) refined and (b) unrefined cellulose fibers (Kim et al. 1999)

Long-term performance of fibers is still questionable. An experimental study (Shah et al. 1988) was carried out to examine the regression of performance of glass fiber reinforced concrete (GFRC) on time scale in accelerated aging condition (fully submerged in Ca(OH)$_2$ saturated solution at temperature of 50ºC). GFRC composites fabricated either with
commonly used alkali-resistant glass fibers (AR-GFRC) or with E-glass fibers in combination with a polymer latex modified matrix (E-PGFRC) showed a reduction in flexural strength and toughness when exposed to the accelerated aging environment. The toughness reduction of AR-GFRC was far less than that of E-PGFRC as shown in Figure 1.8. However, the precise mechanism of the strength regression and embrittlement of GFRC is not clearly understood. It is believed that the Ca(OH)₂ plays an important role in reducing the bending and the tensile strength, and the chemical attack by OH⁻ ions is perhaps less important than the effect of lime crystal deposits on the surface of glass fiber strands.
(a) Alkaline resistant glass fiber reinforced composites (AR-GFRC)

(b) E-class glass fiber reinforced polymer-modified composites (E-PGFRC)

Figure 1.8  Results of toughness/cross-sectional area of (a) AR-GFRC and (b) E-PGFRC compositions 1 and 2 versus accelerated aging time at 50ºC (Shah et al. 1988)
1.4 Mechanism of Rebar Corrosion in Concrete

Prior to investigating an effect of fiber reinforcement on chloride induced corrosion of steel rebar, it is necessary to comprehend the mechanism of the steel corrosion in concrete. Early studies on this topic began some half of a century ago (Hausmann 1967; Boyd and Tripler 1968; Cornet, Ishikawa, and Bresler 1968). Since then, many more have explored rebar corrosion in various aspects from origin to prevention, diagnosis, and rehabilitation. An extensive review can be found in many publications (Neville 1995; Glass and Buenfeld 2000; Montemor, Simoes, and Ferreira 2003). Here, a brief synopsis is provided.

Corrosion of steel in concrete is an electrochemical process in which both chemical reactions and flow of electrical current are involved. It is simply comprised of four essential parts; anode, cathode, conductive medium, and electrolyte, which are shown in Figure 1.9 and described as follows.

1.4.1 Anode (a site having an anodic reaction)

This process is the oxidization of iron that liberates electrons in the steel rebar and forms iron ions,

\[ \text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \]  \hspace{1cm} (1.1)

The iron ion reacts with an alkaline solution in concrete pores and yields a ferrous hydroxide,
Chapter 1. Introduction

\[
\text{Fe}^{2+} + 2\text{OH}^- \rightarrow \text{Fe(OH)}_2. \quad (1.2)
\]

Subsequently, the ferrous hydroxide partly converts to a more stable ferric oxide,

\[
\text{Fe(OH)}_2 + \text{O}_2 \rightarrow \gamma\text{-FeOOH} + \text{H}_2\text{O}. \quad (1.3)
\]

In addition, a hydrolysis of corrosion products can produce acidity as

\[
\text{Fe}^{2+} + 2\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_2 + 2\text{H}^+. \quad (1.4)
\]

An area that this reaction occurs is called an anode (anodic or active site).

Figure 1.9  Corrosion processes on the surface of steel: (a) reactions at anodic and cathodic sites and electric current loop, (b) flow of electrical charge in the electric current loop during the corrosion process. (Bentur, Diamond, and Berke 1997)
1.4.2 **Cathode (a site having a cathodic reaction)**

It is the reduction of oxygen that consumes those electrons generated at the anode and produce alkalinity (when dissolved oxygen and water are present) as:

\[ O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \text{ and } O_2 + 4H^+ + 4e^- \rightarrow 2H_2O. \]  
(1.5)

There is another possible reaction (when pH is low) as follows.

\[ 2H^+ + 2e^- \rightarrow H_2. \]  
(1.6)

The area that this reaction takes place is called cathode (cathodic or passive site).

1.4.3 **Conductive medium (a path for electrons)**

Since those above two reactions simultaneously take place at two different sites, a conductive medium is necessary for electrons to move from an anodic to a cathodic region. It should be noted that a nominal electrical current flows in opposite direction to the movement of electrons as they carry negative charges.

1.4.4 **Electrolyte (a path for ions)**

In an electrical circuit, the charges between the active and the passive sites need to be balanced. To neutralize the charges, ions between the two areas attract each other to move in concrete pores and then to form a molecule. An ionic flow therefore depends on a transport
of the ions through pore solution in concrete around the rebar. The solution is considered as an electrolyte of the corrosion process.

All of the above four components must be present for the corrosion to occur. If one of them is removed, the whole corrosion process is ceased. In the case of reinforced concrete, a highly alkaline condition of concrete controls the anodic reaction at a steel rebar. As iron ions react with hydroxides, ferrous and ferric oxides are formed. These oxides provide stable impervious films on rebar surface and thereby inhibit further dissolution of iron ions. As a result, steel rebar in concrete has a very low rate of corrosion and is normally safe. But, if the level of alkalinity is low or chloride ions have arrived, those protective films will be dissolved and corrosion will become active.

The alkalinity may drop due to carbonation effects. When a concentration of hydroxide ions (OH\(^-\)) is too low (pH<\(~11\)), the oxide films are still formed but do not adhere to the steel surface and therefore are not protective. This condition commonly takes place over a large surface area of concrete and thereby affects an substantial length of steel rebar. A general corrosion is usually the consequence.

Concrete can also be contaminated with chlorides when exposed to seawater, deicing salts, or the inappropriate use of chlorides in the concrete mixture. Chloride diffuses through concrete to damage steel rebar. On steel surface, the protective films are a combination of ferric and ferrous oxides. Between these two oxides, the former is more resistant to chloride ions. The latter is more readily reacted with chloride ions and then turned to a soluble complex, which dissolves in the surrounding solution and thus does not provide protection. Corrosion then occurs on a particular spot where both ferrous oxides and high chloride
content are present. This process results in a pitting effect and is usually called chloride induced corrosion.

In this study, chloride was the only source employed to corrode a steel rebar. Concrete specimens were exposed to chlorides by being submerged in a sodium chloride solution. Chloride ingress originated at the concrete surface and then proceeded inside. A diffusion process principally governs the transport of chloride into concrete, which is driven by a concentration gradient and is characterized by a coefficient of chloride diffusion.

It is noted that an inclusion of fibers in concrete alters its microstructure and transport properties. In FRC, the diffusion properties of chlorides are expected to be altered. Since diffusion is a process that controls corrosion onset and can be affected by fiber reinforcement, the diffusion of chlorides in FRC is an important parameter that was experimentally investigated in the Chapter 3. In the subsequent section, a basic concept of diffusion is explained in greater detail.

### 1.5 Diffusion Process in a Cementitious Medium

In porous materials like concrete, permeability comes into a crucial consideration as it is relevant to durability problems. The permeability may in simplified terms be defined as a parameter to describe the ease with which an ion, molecule or fluid moves through the body of concrete. But, the actual processes involved in liquid and ion movement are different with flow under a pressure gradient or under a concentration gradient. Then, these two processes
Chapter 1. Introduction

should be differentiated as permeation (for liquid) and diffusion (for ions). However, it should be emphasized that the word “permeability” is frequently used to express the permeation.

Diffusion is denoted as a transport process when the flow of matter occurs under the influence of a concentration difference. The actual transport mechanism is by random molecular motions with diffusing molecules moving independently of one another. The migration of ions (e.g. chloride salts) corresponds to this class.

In concrete, ions (e.g. O₂, CO₂, Cl⁻ or SO₄²⁻) move through pores from the surface, where they are present in higher concentrations, to internal zones where their concentrations are lower. Gases diffuse much more rapidly through open pores than through water-saturated one (diffusion of gases in water is 4-5 orders of magnitude slower than in air). On the other hand, chloride and sulfate ions diffuse only when dissolved in pore water; the diffusion is more effective in fully saturated than in partially saturated pores.

1.5.1 Steady-state diffusion

Under conditions of steady-state (unidirectional and constant) mass transfer, Fick’s first law describes the phenomenon of diffusion (as shown in Figure 1.10):

\[ F = -D \frac{dC}{dx} \]  \hspace{1cm} (1.7)

where: \( F \) is the flux (kg/m²/s), \( C \) (kg/m³) is the concentration of the diffusing species present at distance \( x \) (m) from the surface. \( D \) is the diffusion coefficient, expressed in m²/s, which
depends on diffusing species, characteristics of concrete and environmental conditions (e.g. temperature). This coefficient can change as a function of position within the concrete and time, following variations in the pore structure (i.e. due to hydration of the cement paste), or of the external humidity (thus the degree of saturation of pores) or the temperature.

1.5.2 Non steady-state diffusion

As diffusion rarely reaches stationary conditions in concrete structures, the flux depends on time \( t \) and is governed by Fick’s second law (as shown in Figure 1.11):

\[
\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}
\]  

(1.8)

This equation is usually integrated under the simplified assumptions that the concentration of the diffusing ion measured on the surface of the concrete is constant in time and is equal to \( C_s \) (\( C = C_s \) for \( x = 0 \) and for any time \( t \)), that the coefficient of diffusion \( D \) does not vary in time, that the concrete is homogeneous, so that \( D \) does not vary through the thickness of the concrete, and that it does not initially contain any chloride (\( C = 0 \) for \( x > 0 \) and \( t = 0 \)). The solution thus is obtained:

\[
\frac{C(x,t)}{C_s} = 1 - \text{erf} \left( \frac{x}{2\sqrt{Dt}} \right)
\]  

(1.9)

where \( \text{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z \exp(-t^2)dt \) is the error function.
Figure 1.10  Fick’s first law of diffusion: the flux of chloride ions is proportional to the chloride concentration gradient normal to the section (Poulsen and Mejlbro 2006)

Figure 1.11  Fick’s second law of diffusion: the change in chloride ion content per unit time (on the t-axis) is equal to the change of flux per unit length (on the x-axis)

Results from both of them are just enough for an approximation purpose. They do not yield an exact result as they are limited due to the given assumptions in their models.
Another parameter that needs to be included in the diffusion process is the binding effect. Ions that diffuse into concrete can bind to a certain degree with components of the cement matrix, e.g. chlorides bind with aluminate phases or are adsorbed on C-S-H (in the case of chloride-induced corrosion) and carbon dioxide reacts with alkaline components, in particular Ca(OH)$_2$ (in the case of carbonation). The gradual consumption of these components modifies the conditions of diffusion, which can no longer simply be described by Fick’s second law and require a corrective term.

Very often only the total concentration of the diffusing ions is taken into consideration and the effects of chemical reactions in concrete are disregarded. Indeed, it is difficult to estimate the corrective term. In fact, the binding capacity of cement paste is a function of various parameters, such as the localized concentration differences of the various cement reaction products and differences in temperature. It will also depend on the chemical composition of the concrete (i.e. type of cement) and also on its variations (e.g. the binding capacity of chloride is considerably reduced in carbonated concrete). The binding of diffusing ions is important in experimentally determining the diffusion coefficient. In fact, as long as the binding capacity of the concrete has not been exhausted, the net flux of material will appear to be less, and the coefficient underestimated. Therefore, when a corrective term is not applied in evaluating the concentration of a diffusing compound, the diffusion coefficient derived in this way is an “apparent” one that is dependent on time. However, it has been shown that even in the presence of binding, chlorides move into concrete as if diffusion determines the penetration rate (i.e. the diffusion model tends to fit the observed penetration). As a first approach, therefore binding can be neglected in the calculation and the diffusion coefficient is termed apparent. As chloride penetration in
concrete structures is essentially a non steady-state process, tests should be carried out either under non steady-state conditions, or should take into account the effect of binding.

1.6 Cracks in Concrete Structures in Relation to Corrosion of Steel Rebar

Cracks commonly arise due to tensile stresses as concrete is generally poor in its tensile strength. Thus, cracks in concrete structures are not uncommon. They exist in various forms, locations and dimensions depending on several factors such as environmental changes, deficient skills in concrete practices, service and excessive loads, the attack of aggressive substances, etc. Whatever the cause be, cracks when apparent somewhat affect the durability of structures.

1.6.1 Cracks accelerated corrosion

One major durability problem is the corrosion of steel in concrete. In general, the reinforcing steel when embedded in high alkaline environment like concrete does not corrode. That is because a thin impervious oxide film is formed on the steel surface to inhibit the corrosion reaction. However this depassivating film is downgraded when two corrosive sources, namely carbon dioxide and chloride, diffuse from the surroundings through the concrete cover to the level of steel surface. When the amount of those substances reaches a critical
value, the film vanishes and the steel corrodes. The formation of corrosion is then due mainly to the rate of their diffusion.

In the past, it was strongly believed that cracks in concrete cover provide an easy bypass to the transport of carbon dioxide and chloride (as a level of ingress becomes deeper through the cracks), and would consequently pose more severe corrosion. This is likely the idea that has resulted in the control of the crack width in most design codes. For example, for the splash zone in marine environments, British Standards and the Federation of Prestressed Concrete define the allowable crack width as the concrete cover over the rebar multiplied by a constant 0.004 but not more than 0.3 mm (Bentur, Diamond, and Berke 1997) whereas the American Concrete Institute recommends a limit of it at 0.15 mm (ACI Committe 224 1994).

But, three decades ago, Beeby (1978b) questioned the validity of this belief as he reviewed and found that several experimental results did not agree very well with that suggestion. He argued that – the definition of permissible crack width as a function of environment and the design of members to ensure that these limits are not exceeded serve no useful function as a corrosion protection measure. He mentioned that studies cannot observe any significant influences of the crack width on the corrosion if the cracks formed are transverse. In addition, he suggested that the cracks parallel to steel bars in fact would have higher risk on corrosion (Beeby 1978a).

Even if some studies resulted in supporting his arguments (Wilkins and Stiliwell 1986), others indicated contradicted evidences (Lorentz and French 1995; Montes, Bremner, and Lister 2004). From a vast number of experiments, it can actually be concluded that there is
no precise correlation between the crack width (as long as they remain below 0.5 mm) and the risk of corrosion (Bertolini et al. 2004). However, in any case, cracks may reduce the corrosion initiation time in such a way that they provide a preferential path for the penetration of carbonation or chloride. Therefore, one can be confident that cracks will accelerate the initiation of corrosion.

An experiment with sectioned steel bars in intentionally cracked concrete beams (crack width of 0.1 to 0.5 mm) showed that the depassivation time decreases as the crack width increases (Schiessl and Raupach 1997). Yet, there is no relationship between crack width and corrosion rate (in term of mass loss of steel). Also, a crack width of 0.1 mm (with w/c ratio of 0.5 to 0.6 and a cover of 35 mm) showed no corrosion throughout the whole test period. However, the authors observed that the effect of cover depth was more significant.

Another experiment verified that the development of the corrosion of reinforcing steel bars is not remarkably influenced by the widths of cracks (for widths less than 0.5 mm) or by the existence of the crack itself (Francois and Arliguie 1998). Furthermore, the results also indicated that the load applied to a reinforced concrete beam rather plays an influential role in the diffusion of aggressive agents and thereby the corrosion of the reinforcement. A similar result was found in the testing of reinforced concrete beams under wetting and drying cycles with a single central crack (Mohammed et al. 2001). The crack widths influenced corrosion rates only at the very early stage of exposure. An evidence of crack healing in small cracks was also noted (Mohammed, Otsuki, and Hamada 2003).

The effect of crack frequency on corrosion was also investigated (Arya and Ofori-Darko 1996). In their study, the crack frequencies were controlled by varying the number of cracks
present on a concrete beam with an identical total width of 2.4 mm. After the two year testing, the test results indicated that the frequencies of cracks along with a critical crack width can exponentially increase the rate of corrosion.

Not only do cracks affect the initiation of corrosion but also the mechanism of corrosion. Schiessl and Raupach (Schiessl and Raupach 1997) assessed mechanisms of chloride-induced corrosion of steel in the cracked zone. They reported that the corrosion was dominated by macrocell current – after depassivation, the exposed steel at the cracks acted as an anode while the adjacent steels on both sides of the crack acted as a cathode. Thus, the quality and thickness of concrete covers in uncracked portions, which control the cathodic reaction, have more prominent effect than the anodic reaction of corroded steel at the crack location. However, they also concluded that, at initial period, the crack does affect the corrosion as observed from the measured current. This effect however declines as time progresses. After 2 years of testing, there was no systematic relationship between the crack width and corrosion. An investigation of corrosion current in reinforced concrete specimens containing gaps and voids found that microcell corrosion was formed at the steel surface at the location of the gaps and voids (Mohammed et al. 2002).

1.6.2 Corrosion induced cracks

Cracks can influence corrosion, and vice versa. Even in sound concrete, corrosion can occur but at a slow rate. Once the corrosion starts, its products, the so-called rust, are formed and accumulate on the corroding area. They tend to expand as they are lower in density than the parent steel. In addition, because they are confined with concrete cover, they bring about an
expansive stress to the surrounding concrete. In the concrete, if the principal tensile stress exceeds the ultimate tensile strength, cracks will take place. These cracks, when noticeable, frequently indicate a serious damage to reinforced concrete structures. Thus, most studies have been conducted mainly to determine the time of corrosion to develop the first crack.

To predict service life of the concrete structure, consideration of cracks caused by corrosion itself is very relevant. Several models have been proposed by researchers to determine the time of corrosion cracking. Liu and Weyers (1998) proposed a model based on a consideration of the critical amount of corrosion products – a quantity of rust needed to fill the interconnected void space around the reinforcing bar in addition to a quantity of rust required to generate sufficient tensile stresses to crack the cover concrete. Their model involved corrosion only caused by chloride penetration.

Based on the model mentioned above, Vu and co-workers (2005) developed a time-variant reliability based model to predict the time to excessive cracking for reinforced concrete structures. It can be used for the corrosion caused either by chloride or by carbonation by consideration of concrete quality and cover thickness. More importantly, the model includes the effect of time-variant corrosion rates and the effect of a high rate of loading associated with extrapolating accelerated corrosion test results to real situations.

The influence of external stresses on cracks induced by corrosion should not be overlooked. Under flexural loading, the expansive stresses from corrosion products plus the external tensile stresses can result in the appearance of early cracks on the tension surface of a concrete beam (El Maaddawy, Soudki, and Topper 2005). Conversely, in specimens with confinement, the compressive stresses can retard the crack formation. The influence of
cracks in a confined condition on the corrosion rate was experimentally conducted (Hearn and Aiello 1998). The experimental results verified that the confinement does retard the corrosion process except for the case of the poor quality concrete.

From the literatures reviewed above, cracks have most impact at an early stage of corrosion, especially at initiation of corrosion. But, at a later stage, there is no clear relationship between cracks and a growth of corrosion. Although cracks may not fully influence an entire corrosion process, they still should be limited particularly for concrete structures exposed to aggressive environments and generally from aesthetic considerations.

Since fibers are beneficial to crack reduction and cracks influence the time to corrosion initiation, fiber reinforcement in cracked concrete may delay corrosion onset of steel rebar. This advantage of fibers was verified in a corrosion test on reinforced concrete beams in the Chapter 4. The beams were subjected to flexural loads at about 25% and 50% of ultimate strength to create a single crack on the tension face. For a period of 56 weeks, the corrosion activity in each beam sample was monitored using the half-cell potential, the galvanic current, and the linear polarization resistance measurements. These are reviewed in the following section.
1.7 Electrochemical Techniques for Corrosion Monitoring

There are many methods of assessing and monitoring corrosion of steel in concrete. Most of them are based on electrochemical techniques and briefly described below.

1.7.1 Half-cell potential (ASTM C 876)

In a corrosion cell, a state of corrosion can be determined using the measurement of half-cell potential. In reinforced concrete structures, the potential of a steel rebar can be measured with respect to a reference electrode using a high impedance voltmeter. In the measurement, the rebar is connected to the positive terminal while the reference electrode is connected to the negative terminal of the voltmeter as shown in Figure 1.12. Because active corrosion has a higher rate of electrochemical reactions, areas of corroding rebar will yield a higher corrosion potential as shown in Figure 1.13. The potential reading will show a more negative value as the rebar is connected to the positive terminal. This measurement is the simplest corrosion monitoring technique and has been widely used in field practices. It is thoroughly detailed in a standard testing method, the ASTM C 876.
Following to the standard, a copper/copper sulfate electrode (CSE) is used as a reference electrode and corrosion states can be categorized into 3 ranges to define statistically a risk of corrosion. If a potential measured is lower (more negative) than –350 mV, there is a greater than 90% probability that steel corrosion is occurring. On the other hand, if a potential is greater (less negative) than –200 mV, there is a greater than 90% probability that no steel corrosion is taking place. Finally, if a potential is between –200 mV and –350 mV, the corrosion state is uncertain. This information is rather qualitative and normally used only for a preliminary inspection. If there is any indication of corrosion, additional tests are required.
Chapter 1. Introduction

1.7.2 Linear polarization resistance, (ASTM G 59 1997)

In this method, an excitation using an electrical current is applied to a steel reinforcement to vary half-cell potentials in a certain range around a corrosion potential ($E_{corr}$). This process is known as polarization. A device called a potentiostat is needed and the schematic of the test set-up is shown in Figure 1.14.

Figure 1.13 Electric field around a corrosion area

Figure 1.14 Schematic set-up for linear polarization measurements (Bentur, Diamond, and Berke 1997)
The corrosion potential is shifted from an equilibrium state to investigate the kinetic of corrosion. The potential change in an active corrosion requires less current than that in a passive corrosion. A rate of a variation of potentials ($\Delta E$ in mV) to a change of currents ($\Delta i$ in mA/m²) defines a polarization resistance ($R_P$ in $\Omega$-m²). Assuming the rate is linear in a vicinity of the corrosion potential, the resistance term is thus called a linear polarization resistance. It can be expressed as follows.

$$\frac{\Delta E}{\Delta i} = R_P$$  \hspace{1cm} (1.10)

Figure 1.15 demonstrates a typical relationship between the potential and current. A slope of the curve at a corrosion potential represents a polarization resistance. The resistance can be converted to a corrosion current ($I_{corr}$ in mA/m²) representing a corrosion rate by multiplying an inverse of the polarization resistance with a Stern-Geary constant ($B$ in mV) as

$$I_{corr} = \frac{B}{R_P}$$  \hspace{1cm} (1.11)

where $B = 26$ mV for an actively corroding steel and $B = 52$ mV for a passive steel.
1.7.3 Macrocell techniques (ASTM G 109 2007)

This method measures a current (called a macrocell current) of a corroding steel with respect to a given cathodic metal, which can be an inert metal or a sound steel bar in a safe environment. It is quite simple in practice. To evaluate the macrocell current ($I$ in mA), one can measure a potential ($V$ in mV) over a resistor with a known resistance ($R$ in $\Omega$) linking the measured anodic steel and the controlled cathodic metal as shown in Figure 1.16.

It indicates a corrosion of the whole anodic system in which many steel bars are connected. So it cannot measure the localized corrosion. Errors may arise when the cathodic metal assigned in the investigation turns into anodic and the concrete resistivity is too high.
Figure 1.16 Schematic description of a macrocell test (Bentur, Diamond, and Berke 1997)
1.8 References


Beeby, A.W., (1978b), "Cracking: What Are Crack Width Limits For?," *Concrete*, **12** (7), pp. 31-33.


Chapter 2

Cryoporometry Based Evidence of Pore Refinement in Cementitious Composites

2.1 Outline

Permeability plays an important role in governing the durability of concrete in deleterious environments. Previous permeability tests using water as the permeating medium have indicated that the addition of cellulose fiber is effective in reducing water permeability both in the presence and absence of stress and thereby making concrete more durable.

In this paper, further evidence was sought of pore-refinement in concrete reinforced with cellulose fiber using thermoporometry (TP) and mercury intrusion porosimetry (MIP) methods. Thermoporometry was carried out using a differential scanning calorimeter (DSC). Two volume fractions—0.1% and 0.3%—of a treated cellulose fiber were investigated. The results indicated a definite pore refinement due to cellulose fiber addition and a related improvement in durability.

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1 A version of this chapter has been published. Sappakittipakorn, M., Banthia, N., and Jiang, Z. (2010) Cryoporometry Based Evidence of Pore Refinement in Cementitious Composites. Indian Concrete Journal. 84:6:17-24.
2.2 Introduction

In porous cement-based materials like concrete, pore structures play a critical role not only in controlling the physical and mechanical properties but also in governing the long term durability (Aligizaki 2006). An understanding of the pore size distribution is therefore essential for evaluating the performance of such materials. In concrete, pore networks provide ingress and transport routes for deleterious chemicals, and truncating such networks through pore refinement and/or alteration is a recognized way of enhancing the durability. Ease with which chemicals can be transported within the body of concrete is often characterized by its permeability. Lower permeability concrete will be more durable.

Recent tests have demonstrated that the addition of fibers to concrete results in a reduction in the permeability of concrete to water (Banthia and Bhargava 2007). It therefore implies that addition of fibers refines/truncates the porosity in concrete and hinders the flow of fluids. Though criticized (Diamond 2000), mercury intrusion porosimetry (MIP) is often recognized as an effective technique for characterization of pore structure. Of late, some other techniques have been developed for the purpose. One such method is Thermoporometry that involves pore-size characterization using a calorimeter.

In Thermoporometry, any depression in the freezing point is assumed to be related to the interfacial curvature of the solid-liquid phases at transition in capillaries. The idea has been recognized and used for more than three decades to ascertain the pore structures of various mesoporous materials (Fagerlund 1973; Brun et al. 1977). It was verified experimentally with materials with a known pore size, e.g. silica gel and porous glass (Ishikiriyama et al.
advanced Differential Scanning Calorimeter (DSC), Thermoporometry becomes a simple
and effective technique.

The purpose of the study was to characterize the pore size distributions of fiber reinforced
cementitious composites reinforced with various volume fractions of a cellulose fiber using
Thermoporometry (TP) and compare the results to Mercury Intrusion Porosimetry (MIP).

2.3 Thermoporometry

Thermoporometry is a calorimetric method capable of characterizing pore structure from the
melting and freezing point depression ($\Delta T$ in $^\circ$K) of a liquid confined in porous materials,
due to the added contribution of surface curvature to the phase-transition free energy. At a
thermodynamic equilibrium, the freezing and melting points of the freezable pore water
deviate from those of bulk water based on the pore radius ($r_p$ in nm) as stated in semi-
empirical equations below:

$$r_p = -\frac{64.67}{\Delta T} + 0.57$$, for the freezing curve \hspace{1cm} (2.1a)

$$r_p = -\frac{32.33}{\Delta T} + 0.68$$, for the melting curve \hspace{1cm} (2.1b)

where the thickness of the non-freezable layer is 0.8 nm (Brun et al. 1977).

$$r_p = -\frac{56.36}{\Delta T} + 0.90 + \delta_f$$, for the freezing curve \hspace{1cm} (2.1c)
\[ r_p = -\frac{33.30}{\Delta T} + 0.32 + \delta_m, \] for the melting curve \hspace{1cm} (2.1d)

where \( \delta_f \) and \( \delta_m \) are thicknesses of non-freezable layers in freezing and melting phases, respectively, and \( 0.6 \text{ nm} < \delta_f < 2.8 \text{ nm} \) and \( 0.5 \text{ nm} < \delta_m < 2.2 \text{ nm} \) (Ishikiriyama, Todoki, and Motomusa 1995).

And,

\[ r_p = -\frac{38.558}{\Delta T - 0.1719} + \delta_f, \] for the freezing curve \hspace{1cm} (2.1e)

\[ r_p = -\frac{19.082}{\Delta T - 0.1207} + \delta_m, \] for the melting curve \hspace{1cm} (2.1f)

where \( \delta_f \) and \( \delta_m \) are 0.04 nm and 1.12 nm, respectively (Landry 2005).

These equations were derived from Gibb’s phase rule considering only liquid and solid phases of a pure substance coexistent in a cylindrical pore system. In the case of ice propagating from a larger pore to a smaller pore in a porous material, Defay (Defay, Prigogine, and Bellemans 1966) described the influence of pore radii on freezing points as follows.

\[ \ln\left(\frac{T}{T_o}\right) = -\frac{2\nu_l\gamma_{sl}}{\Delta h_f r_{sl}} \hspace{1cm} \text{where} \hspace{1cm} \ln\left(\frac{T}{T_o}\right) = \ln\left(\frac{T_o + \Delta T}{T_o}\right) \approx \frac{\Delta T}{T_o} \] \hspace{1cm} (2.2a)

where \( T \) is temperature, \( T_o \) is the triple point of bulk water, \( \nu_l \) is molar volume, \( \gamma_{sl} \) is surface tension, \( \Delta h_f \) is molar heat of fusion and \( r_{sl} \) is radius of curvature.

Employing the approximated term of logarithm, it thus yields
Equation (2.2b) provides a relationship between the freezing or melting point depression and the pore radii.

By using water as a probe liquid in calorimetric experiments in a variety of well-defined porous materials, the Equation (2.2b) was experimentally calibrated by different researchers and Equations (2.1a) – (2.1f) were formulated. For comparison, they are plotted together in Figure 2.1. The formulae found by Ishikiriyama et al. (1996) conform well to those found by Brun et al. (1977). But, the recent findings of results of Landry (2005) show discrepancy to earlier results. Landry claimed that the differences are a consequence of a wider range of pore sizes involved in his experiment, and further supported his Thermoporometry findings by direct comparison with results from Mercury Intrusion Porosimetry. In any case, the semi-empirical results are fairly consistent except in the cases of very small changes (depression) in the freezing or melting points.

Given a calorimetric thermogram, the Thermoporometry begins with a rescaling of the temperature depression on the abscissa to pore radii according to the Equation (2.1). The thermogram further links pore radii with heat flow rate, which can then be used to calculate the amount of freezable pore water in a particular pore size by means of the enthalpy of fusion.
Figure 2.1  Correlation between freezing and melting point depression of water as a function of pore radii

Assuming that the pore water has similar enthalpy of fusion, expressed as $\Delta H_f(T)$, to bulk water as a function of temperature $T$ (Ishikiriyama, Todoki, and Motomusa 1995),

$$
\Delta H_f(T) = 334.1 + 2.119 \ (T - T_o) - 0.00783 \ (T - T_o)^2
$$

where enthalpy has units of J/g and the temperature is measured in °K.

The mass of the freezable pore water, expressed as $m_{fp}(T)$, is therefore directly proportional to the resulting heat $Q(T)$ measured by the calorimeter,

$$
m_{fp}(T) = \frac{Q(T)}{\Delta H_f(T)}
$$
A calorimeter generally measures the rate of heat flow (J/s). By multiplying the heat flow rate with the scan rate, one can obtain the change of heat as a function of temperature. For a finite change of temperatures, $\Delta T$, the mass of pore water under phase transition is given by:

$$m_{fp}(T) = \left( \frac{dQ}{dt} \frac{dt}{dT} \right) \frac{\Delta T}{\Delta H_f(T)}$$ (2.5)

Let’s consider the density of water by taking the temperature effect into account; the freezable pore water occupies the volume,

$$V_{fp}(T) = \left( \frac{1}{\rho_{fp}(T)} \right) \left( \frac{dQ}{dt} \frac{dt}{dT} \right) \frac{\Delta T}{\Delta H_f(T)}$$ (2.6)

If the exothermic energy is used, $\rho_{fp}(T)$ is the density of supercooled water (Hare and Sorensen 1986; Ishikiriyama, Todoki, and Motomusa 1995),

$$\rho_{water}(T) = -7.1114 + 8.82 \times 10^{-2} T - 3.1959 \times 10^{-4} T^2 + 3.8649 \times 10^{-7} T^3$$ (2.7a)

If the endothermic energy is considered, $\rho_{fp}(T)$ is the density of ice (Fukusako 1990; Ishikiriyama, Todoki, and Motomusa 1995),

$$\rho_{ice}(T) = 0.917(1.032 - 1.17 \times 10^{-4} T)$$ (2.7b)

By differentiating the volume in Equation (2.6) with respect to pore radius and then normalizing it with the mass of dried porous materials, $m_d$, the distribution of pore size is given by:
Chapter 2. Cryoporometry Based Evidence of Pore Refinement in Cementitious Composites

\[
\frac{dV_{fp}}{dr_p} = \left( \frac{dQ}{dt} \frac{dT}{dt} \right) \frac{1}{m_d \Delta H_f(T) \rho_{fp}(T)}
\]  

(2.8)

2.4 Mercury Intrusion Porosimetry

To measure the pore volume of a porous material, one simple way is to find the volume of a given substance required to fill up the pores. The substance commonly used is mercury as it is a non-wetting liquid and stable over a wide temperature range (from 234.32°K to 629.88°K). Pores, however, are rather so small that the mercury cannot access them at ambient pressure. Applying pressure is therefore necessary.

Assuming that pores are formed as a bunch of parallel, non-interconnected cylinders with various dimensions, the applied pressure \( P \) is correlated to the pore radius \( r_p \) by the Washburn equation as follows;

\[
P = \frac{2\gamma \cos\theta}{r_p}
\]

(2.9)

where \( \gamma \) is the air-mercury surface tension (485 N/mm) and \( \theta \) is the contact angle of mercury on a hardened cement paste (130°).

In a test, small pieces of samples are put in a dilatometer, which is a calibrated capillary tube always filled up with mercury. An intrusion process begins as the pressure applied into the dilatometer increases. With an increase in the pressure, smaller and smaller pores are filled up while more mercury is added to the system. The weight increment due to the additional
mercury corresponding to the applied pressure is recorded and related to the pore size
distribution as per Equation (2.9).

2.5 Experimental Protocol

Cement paste specimens with mix proportions given in Table 2.1 were cast in 50 mm \( \times \) 100 mm cylindrical molds. Normal Portland cement (CSA Type 10 equivalent to ASTM Type GP), and potable tap water were used. The fiber used was a virgin, fully purified plantation softwood fiber. These fibers, with an average length of approximately 2.3 mm and diameter of 10 µm, were collated in the form of a chip and surface treated to enhance their alkali tolerance and bond with concrete (Figure 2.2). The fiber had a specific gravity of 1.1, a tensile strength of 750 MPa, and an elastic modulus of 8.3 GPa (as reported by Buckeye Technologies Inc.). It was added to the cement paste at 0.1% and 0.3% by volume fraction.

<table>
<thead>
<tr>
<th>Table 2.1 Mixture proportions</th>
<th>Water/Cement</th>
<th>Cellulose Fibers (% by volume fraction)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixture Type</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 Plain Cement Paste (PC)</td>
<td>0.55</td>
<td>-</td>
</tr>
<tr>
<td>2 0.1% Cellulose Fiber</td>
<td></td>
<td>0.1</td>
</tr>
<tr>
<td>3 0.3% Cellulose Fiber</td>
<td></td>
<td>0.3</td>
</tr>
</tbody>
</table>
Figure 2.2  Cellulose fiber investigated. The 2.3 mm long fibers are collated in the form of a chip for improved fiber dispersion during mixing.

After curing in a saturated calcium hydroxide solution for 28 days, each sample was cut at the middle into a 4-mm thick disc. By using a milling machine with a diamond coated coring bit, several small cylinders (about 4-mm diameter) were cored from the center of the discs. Three of them were randomly chosen for the thermal analysis in the DSC while the others were used for pore size measurements using an MIP apparatus.

For Thermoporometry, a model Q1000 Differential Scanning Calorimeter by TA Instrument Inc was used. The DSC was calibrated using Indium at a similar range and rate as the specimens to be tested. In a vacuum desiccator, the samples were vacuum saturated (being dried for 1 hour and then saturated with water for 5 hours). Each of them was then weighed in a saturated surface dry condition and encapsulated in a sealable aluminum pan as shown in Figure 2.3. In general, when a porous sample is tested in TP it is immersed in water to create liquid/solid interfaces in the test sample. During the cooling process, the surrounding bulk water crystallizes at first and can be identified at a phase transition in a thermogram. The nucleation of ice thus begins in the surrounding bulk water and then propagates to water confined in pore network. While the surrounding bulk water solidifies, pore water is still in a state of supercooling but can now be frozen with further cooling. The delay of ice formation
in pore structures is due to a capillary action, which creates a surface tension at the solid/liquid transition zone. The energy required to overcome the surface tension is manifested in the form of a depression in the freezing temperature. Strictly speaking, a sequential thermal cyclic (cooling then heating to bulk melting point) is initially required to eliminate the nucleation energy and the second freezing curve then represents a valid thermal energy for crystal growth in pore networks. Unfortunately, in the case of cementitious materials, a temperature cycling can potentially damage the pore network (Banthia, Pigeon, and Lachance 1989). In this study, out of necessity, therefore, thermal cycling was not carried out and the first freezing curve itself was introduced and analyzed. The specimen was cooled from 5°C to -40°C and then heated from -40°C to 5°C at the rate of 0.31°C/min to prevent temperature and time delay in a DSC instrument. The corresponding heat flow rates were recorded and analyzed. At the end of the test, the sealed aluminum pans were opened; the samples were removed and dried in an oven at 105°C for 12 h to determine the weight of dry samples. Freezing and melting temperature data were converted to the pore size distributions based on the analysis presented above (Ishikiriyama and Todoki 1995; Ishikiriyama, Todoki, and Motomusa 1995).

![Figure 2.3](image)

**Figure 2.3** A cored specimen (*left*) with a sealable aluminium pan (*middle*) and a lid (*right*)
For the MIP test, after the curing period, the samples were dried for 1 hour and then vacuum saturated with ethanol for 23 hours in a vacuum desiccator. Next, they were oven dried at 65 °C for 5 hours. Finally, they were sealed in a plastic bag until tested. The test was performed in the Micromeritics 9320 PoreSizer with a maximum intrusion pressure at 207 MPa. The contact angle was 130 degree. The mercury surface tension was 485 dyne/cm and its density was taken as 13.5335 g/ml. Masses of samples were about 0.5 g.

2.6 Results and Discussion

2.6.1 Thermoporometry with differential scanning calorimeter

The result of the heat flow rates measured in a DSC is shown in Figure 2.4. On the cooling stage, the first exothermic peak took place far below the triple point of bulk water. It was between -12 to -14 °C, which is a few degrees below that reported by others (Stockhausen et al. 1979; Banthia, Pigeon, and Lachance 1989). In our tests, the samples were fully saturated so the phase transition of capillary water is mainly associated with the exothermic upsurge. Thus, in reference to Equation (2.2b), the small pore radius of capillaries dropped the freezing point as stated above. The second exothermic peak occurred at around -25 °C associated with freezable pore water in yet smaller pores. This was, however, relatively insignificant.
At the same scanning rate, the heat flow in the melting process was also recorded. Similar to the others (Ishikiriyama et al. 1996; Iza et al. 2000; Landry 2005; Yamamoto et al. 2005), a hysteresis in the thermal energy was observed. The endothermic energy in heating curves continuously increased from a temperature of about -10 °C and peaked at approximately the triple point of the bulk water. It was quite different from a usual thermogram in which there exists a certain degree of melting point depression. Results of these tests are given in Table 2.2.

In the DSC tests, since the samples were tested in a saturated surface dry condition, water (or pore water) is the probe liquid. During the thermal scan, the water underwent a phase transition (solidified or liquefied) resulting in an increment in the thermal energy involved. When a greater amount of the water undergoes a phase-change, clearly a greater amount of energy is required. In addition, the energy gradient varies with the degree of confinement following the effect of surface tension on surface free energy.

Figure 2.4  Thermograms for multiple specimens: a) plain cement paste; b) 0.1% FRC paste; and c) 0.3% FRC paste (Each specimen has 3 replicates)
Table 2.2 Average of the heat flow rates and corresponding temperatures

<table>
<thead>
<tr>
<th>Mix#</th>
<th>Type</th>
<th>Average of Peak Heat Flow Rate [Mean ±SD] (mW)</th>
<th>Average of Temperature at Peak Energy [Mean ±SD] (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Freezing Phase</td>
<td>Melting Phase</td>
</tr>
<tr>
<td>1</td>
<td>Plain Cement Paste</td>
<td>-7.2 ±3.7</td>
<td>+2.2 ±0.3</td>
</tr>
<tr>
<td>2</td>
<td>0.1% Cellulose Fiber</td>
<td>-6.8 ±2.0</td>
<td>+2.6 ±0.4</td>
</tr>
<tr>
<td>3</td>
<td>0.3% Cellulose Fiber</td>
<td>-8.1 ±3.6</td>
<td>+2.5 ±0.8</td>
</tr>
</tbody>
</table>

Employing Equation (2.1), the heat flow rate from the DSC results was correlated with the radii of confining pores. In accordance with the heat of fusion, the heat flow was related to the volume of water under phase transition. Since the pores were fully saturated, the volume of water is equivalent to that of pores. Hence, the pore volume calculated from heat flow rates can be simply plotted with the pore radii. The plot provides the pore size distribution.

The pore size distribution is plotted in Figure 2.5. Thermoporometry tests indicate that all samples have a critical pore radius (the mean size of pore entryways that allow maximum percolation throughout the pore system (Aligizaki 2006)) in the range of 5-6 nm, and it can be noted that the pore volume in this range is increased in proportion to the amount of fibers added. It is well known that pores in this size do not allow permeation and hence do no influence the water permeability (Nokken and Hooton 2008).
2.6.2 Ice formation

Based on the past research (Banthia, Pigeon, and Lachance 1989), the calorimetric results can be used to determine the ice formation in cement paste. In the calorimetry, the changes of thermal energy depend on the specific heat of the object in the system, which in this case is a combination of cement paste and the pore water. As the paste is relatively inert to freezing, the phase transition of the water alone governs such a change.

Considering the first freezing point in the calorimetric results, the exothermic energy dropped sharply and then gradually flattened indicating a phase transition. The area under the curve in the thermogram measures how much pore water has transformed to ice. As depicted in Figure 2.6, it was divided into 2 parts – A and B – representing the heat involved in the phase transitioning of pore water and that involved in simply cooling of the sample,
respectively. The mean and standard derivation values for these areas are also shown in Figure 2.6.

Regardless of fiber presence or volume, Figure 2.6 indicates that all samples released the same amount of energy during transition. To find the amount of frozen water, the latent heat was taken into account—the latent heat of water increases as the supercooling occurs. Since the data in Table 2.2 implies that the freezing points dropped when fibers were introduced, and given that identical energy was released in all samples, it can be deduced that there is less ice formation in cement pastes that have fibers in them.

Figure 2.6 Exothermic energy in samples
2.6.3 **Mercury intrusion porosimetry**

The pore volumes of the samples tested in the MIP experiment are plotted with respect to pore radii in Figure 2.7 (the solid lines with respect to the right ordinate). The results from the Thermoporometry are reproduced for comparison. Furthermore, the porosity of all mixes was calculated and is reported in Table 2.3.

The MIP experiment indicates that the critical pore sizes exist in the range of 60-80 nm and the smallest pore radius is about 10 nm. Notice that there is a decrease in the MIP porosity with an increase in the fiber content. When juxtaposed with the Thermoporometry data which indicated an increase in the porosity in the 5-6 nm range due to fiber reinforcement, it appears that fibers transform some of the porosity in the higher pore sizes into porosity at smaller pore sizes. This pore refinement is very beneficial in enhancing durability.

![Pore sizes distributions in plain and fiber reinforced cement pastes based on thermoporometry and mercury intrusion porosimetry](image)

**Figure 2.7** The pore sizes distributions in plain and fiber reinforced cement pastes based on thermoporometry and mercury intrusion porosimetry
While the exact reasons for the noted pore-refinement due to fiber reinforcement are not entirely clear, it is possible that cellulose fibers, being hydrophilic, hold some excess water during mixing and this water is then available for later hydration. This internal curing is likely the most probable reason behind the noted pore refinement.

<table>
<thead>
<tr>
<th>Table 2.3 Porosity from MIP tests</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixture</td>
</tr>
<tr>
<td>Plain Cement Paste</td>
</tr>
<tr>
<td>0.1% Cellulose FRC Paste</td>
</tr>
<tr>
<td>0.3% Cellulose FRC Paste</td>
</tr>
</tbody>
</table>

In a study by Banthia and Bhargava (2007), fibers have been proven to reduce the water permeability in concrete as indicated by the permeability ratio between FRC and plain concrete. The permeability ratios reported in that study are plotted in correlation with the porosity values obtained in this study in Figure 2.8. It is clear that the addition of fibers even at a low amount will reduce the water permeability in concrete and the porosity in cement paste. Even a small decrease in porosity appears to result in a significant reduction in the permeability. That indicates that the internal curing by fibers is likely more active in interfacial zones that are known to be highly porous.
Figure 2.8  Relationship between porosity and permeability ratio of FRC, noting that permeability data from the study by Banthia and Bhargava (2007)

2.7  Conclusions

The influence of the cellulose fibers on the pore structure of cement pastes was investigated by using Thermoporometry (TP) and Mercury Intrusion Porosimetry (MIP) methods. Two fiber volume fractions of 0.1% and 0.3% were investigated. The results indicate that there is an improvement in the pore structure due to cellulose fiber addition in the form of pore refinement and reduced porosity. These observations correspond well with the previously noted reduction in permeability due to fiber addition.
2.8 Acknowledgements

Continued financial support of the Natural Sciences and Engineering Research Council of Canada (NSERC) is gratefully acknowledged.

2.9 Notation

\[ \Delta T \] : melting and freezing point depression  
\[ r_p \] : effective pore radius  
\[ \delta_f \] : thickness of non-freezable layers in the freezing process  
\[ \delta_m \] : thickness of non-freezable layers in the melting process  
\[ T \] : temperature  
\[ T_o \] : the triple point of bulk water  
\[ v_l \] : molar volume  
\[ \gamma_{sl} \] : surface tension  
\[ \Delta h_f \] : molar heat of fusion  
\[ r_{sl} \] : radius of curvature  
\[ \Delta H_f (T) \] : enthalpy of fusion  
\[ m_{fp}(T) \] : mass of the freezable pore water  
\[ Q(T) \] : heat resulted from a calorimeter  
\[ dQ/dt \] : heat flow rates from a calorimeter  
\[ dt / dT \] : scanning rate in a calorimeter  
\[ V_{fp}(T) \] : the volume of freezable pore water,  
\[ \rho_{fp}(T) \] : the density of supercooled water or ice  
\[ m_d \] : the mass of dried porous materials,
\[ \frac{dV_{fp}}{dr_p} \]: the distribution of pore size

\( P \): the applied pressure

\( \gamma \): the air-mercury surface tension

\( \theta \): the contact angle of mercury on a hardened cement paste
2.10 References


Chapter 3

Corrosion of Rebar and Role of Fiber Reinforced Concrete, Part 1: Chloride Transport

3.1 Outline

Recent studies have shown that fiber reinforcement of concrete reduces its permeability to water and enhance its service life. In this two part paper, further evidence was sought of the ability of fiber reinforcement to enhance the durability of traditionally reinforced concrete structures. Two fiber types, cellulose and polypropylene, at 0.1% and 0.3% volume fraction, were examined.

In this Part 1 of the paper, diffusion of chloride in concrete was investigated using the bulk diffusion test as well as a silver nitrate spray test. A rapid chloride permeability test was also performed. The results clearly show that while the presence of fibers increased the coefficient of chloride diffusion based on total chlorides, there was a decrease in the coefficient related to free chlorides. Fibers therefore appear to bind the chlorides and inhibit their transport.

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In Part 2 of this paper, results from corrosion tests will be presented where electrochemical corrosion readings will be taken in an aggressive environment in the presence and absence of fiber reinforcement.

### 3.2 Introduction

A functionally adequate and safe infrastructure is vitally important to any country’s socio-economic progress. Unfortunately, severe corrosion of steel in reinforced concrete elements, missed maintenance, changes in the code provisions, increases in design loads, and last but not least, lack of durable repair and strengthening technologies, have created an infrastructure crisis of unprecedented proportions. Not surprisingly, nearly a third of all current construction activity in developed countries is geared towards repair and strengthening of our infrastructure.

Chlorides, a trigger of rebar corrosion, are transported through pore networks in concrete by several processes including permeation, convection, migration, and particularly diffusion (Poulsen and Mejlbro 2006). In reinforced concrete structures exposed to a chloride-rich environment, chlorides accumulate on the surface of steel reinforcement, and once a threshold concentration of chlorides is attained, passivity of steel breaks down and corrosion initiates. Prevention of corrosion of steel in concrete in most construction practices relies on specifying an extra cover thickness and concrete with low permeability and diffusion such that the time required for chloride ions to reach the reinforcing steel is extended. Since chloride ions diffuse only through water in capillaries, chloride diffusion is principally
dependent on water permeability. Lately, the addition of fiber has been proven to decrease water permeability in concrete (Bhargava and Banthia 2008). By slowing down the rate of chloride diffusion, the inclusion of fiber in concrete could be a feasible solution to prolonging the life of our concrete structures. This is particularly relevant in the context of repair materials which are always the first line of defense against a chloride attack.

Corrosion of steel fibers themselves in concrete is sometimes expressed as a concern. Investigations of the corrosion of fibers in steel fiber reinforced concrete (SFRC) were first carried out some three decades ago (Hannant and Edgington 1975; Morse and Williamson 1977; Schupack 1985), and it was generally reported that when the SFRC was exposed to a corrosive environment, only the steel fibers on the surface were prone to corrosion (Mangat and Gurusamy 1988). While a loss in the mechanical properties such as flexural strength and toughness were reported (Kosa and Naaman 1990), an improvement in the chloride resistivity of cracked concrete has been apparent (Mangat and Gurusamy 1987). In uncracked concrete, however, steel fiber are known to unfavorably affect electrical migration of chlorides as in a rapid chloride permeability test (El-Dieb 2009).

More recently, polypropylene (PP) FRC has been identified as a possible way of mitigating corrosion of steel fiber in concrete (Kosa, Naaman, and Hansen 1991). Additional studies using an electrical migration technique on polypropylene FRC have produced mixed results. The effect of polypropylene fiber was seen as insignificant when a low-voltage power supply (5 V) was used (Al-Tayyib and Al-Zahrani 1990) but a decrease in the resistivity was noted at higher voltages (Toutanji, Mcneil, and Bayasi 1998; Zhang and Li 2006). Under load, however, polypropylene FRC resisted chloride penetration well (Antoni, Horiguchi, and Saeki 2005); similar to the situation with steel FRC. A delay of corrosion cracking and
an improvement in the post-crack bond strength of rebar have also been reported as the benefits of using polypropylene fiber (Haddad and Ashteyate 2001).

Since the past chloride resistivity tests on FRC have been limited to electrical migration only, experiments to determine how chloride ions diffuse more naturally in polypropylene FRC were conducted in this study. At the outset, a bulk diffusion test as per ASTM C 1556 (2004) was conducted to expose the test specimens to chlorides. A silver nitrate spray test was then conducted to reveal how far the chlorides had penetrated in the samples. The chloride profile, which is the concentration of chloride penetrating along the depth, was then analyzed and coefficients of chloride diffusion were evaluated using Fick’s second law. Finally, for comparison and completeness purposes, Rapid Chloride-Ion Permeability Tests (RCPT) as per ASTM C 1202 (1997) were performed to assess chloride migration in FRC under a controlled electrical potential. These results collectively provided information on the overall ability of fibers in concrete to resist chloride ingress. An excellent summary of available methods for measuring the chloride penetration resistance of concrete are given by Stanish, Hooton and Thomas (Stanish, Hooton, and Thomas 1997).

### 3.3 Research Significance

Chloride induced corrosion of reinforcing steel in concrete remains the most serious durability concern of our time. Need exists therefore to curb transport mechanisms that allow an ingress of chlorides in concrete and promote corrosion. Earlier studies have shown that fiber reinforcement of concrete reduces its permeability to water both with and without
an applied stress. However, if fiber reinforcement also reduces diffusion of chlorides and mitigates corrosion of reinforcing steel is not known. Such evidence was sought in this two part paper. In the first part, transport mechanisms were studied using the bulk diffusion tests and rapid chloride-ion permeability tests. In the second part, electrochemical corrosion data from reinforced concrete elements will be presented.

### Experimental Procedures

#### Materials and specimens

Concrete with mixture proportions given in Table 3.1 was used throughout. Normal Portland cement (CSA Type 10, equivalent to ASTM Type GP), saturated surface dry river sand, gravel with a maximum size of 12.5 mm (0.5 in.) and potable tap water were used. The mixes developed an average 28-day compressive strength of 46 MPa. Two types of non-metallic fibers were introduced into the concrete at 0.1% and 0.3% volume fractions (Figure 3.1). One was a virgin, fully purified softwood cellulose fiber with an average length of about 2.3 mm collated in the form of a chip and carrying a surface treatment employed to enhance their alkali tolerance and bond with concrete (Figure 3.1a). The other was an alkali-resistant polypropylene multifilament fiber (Figure 3.1b). Physical properties of the fibers are given in Table 3.2. A total of five mixes—four fiber reinforced mixes and one control with no fiber—were investigated.
Table 3.1  Concrete mixture proportions

<table>
<thead>
<tr>
<th></th>
<th>Cement kg/m³ (lb/yd³)</th>
<th>Water kg/m³ (lb/yd³)</th>
<th>Sand kg/m³ (lb/yd³)</th>
<th>Gravel kg/m³ (lb/yd³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>335 (565)</td>
<td>184 (310)</td>
<td>860 (1450)</td>
<td>950 (1601)</td>
</tr>
</tbody>
</table>

For each of the mixes, three 75 mm Φ × 150 mm cylinders were cast for bulk diffusion tests and three 100 mm Φ × 200 mm cylinders were cast for the Rapid Chloride-Ion Permeability Test. Specimens were de-molded 24 h after casting and stored in lime-saturated water until an age of 28 days at which time further specimen preparation and testing began.

Table 3.2  Properties of fibers investigated

<table>
<thead>
<tr>
<th>Property</th>
<th>Cellulose fiber</th>
<th>Polypropylene fiber</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity</td>
<td>1.10</td>
<td>0.91</td>
</tr>
<tr>
<td>Tensile strength, N/mm² (ksi)</td>
<td>600–900 (87–131)</td>
<td>200–500 (29–73)</td>
</tr>
<tr>
<td>Average length, mm (in.)</td>
<td>2.1 (0.08)</td>
<td>16 (0.63)</td>
</tr>
<tr>
<td>Denier, g/9000 m (lb/9842 yd)</td>
<td>2.5 (5.5 × 10⁻³)</td>
<td>6 (13.2 × 10⁻³)</td>
</tr>
<tr>
<td>Diameter, µm (in.)</td>
<td>18 (0.71 × 10⁻³)</td>
<td>30 (1.18 × 10⁻³)</td>
</tr>
<tr>
<td>Surface area, cm²/g (ft²/lb)</td>
<td>25 000 (12 206)</td>
<td>1500 (732)</td>
</tr>
</tbody>
</table>

Figure 3.1  Photographs of fibers investigated (a) cellulose fiber and (b) polypropylene fiber
3.4.2 **Bulk diffusion test**

Bulk diffusion tests were carried out on 75 mm $\Phi \times 150$ mm specimens as per ASTM C 1556 (Figure 3.2). Specimens were kept in an air-dried condition for 28 days after which they were sliced in the middle into two pieces (Figure 3.2a). Thus, for each of the five mixes, six half-cut cylinders of 75 mm $\Phi \times 75$ mm were obtained. Three of them were used for the silver nitrate spray test and the other three for the chloride profile test. Except for the cut-opened face, the outer surfaces of cylinders were coated with an epoxy and cured as per epoxy manufacturer’s recommendation. After coating the specimens with epoxy, the specimens were stored in lime saturated solution for 1 week after which they were submerged in the 3.5% sodium chloride (NaCl) solution for an additional 90 days (Figure 3.2b).
Figure 3.2  Bulk diffusion test as per ASTM C 1556 ; (a) specimen with epoxy coating and cut in the middle, (b) submersion in NaCl solution, and (c) determination of chloride profile

3.4.3  Silver nitrate spray test

Based on a chemical colorimetric method, the silver nitrate (AgNO₃) spray technique is often applied as a field test for a quick and simple assessment of chloride penetration in
concrete. Reactions of chemicals applied on concrete samples result in different colors in uncontaminated and chloride-contaminated zones. The line dividing these two areas indicates where the chloride advancement front is. Fundamental concepts and procedures have been reviewed thoroughly in the literature (Otsuki, Nagataki, and Nakashita 1992; Meck and Sirivivatnanon 2003; Baroghel-Bouny et al. 2007a, 2007b).

In this study, silver nitrate (AgNO₃) was used in conjunction with potassium dichromate (K₂Cr₂O₇). The test procedure was as follows. The 0.1 N AgNO₃ solution was sprayed on the freshly split surface of the concrete cylinders from the bulk diffusion test. The silver ions from the solution reacted with chlorides present on the concrete surface to form a white precipitate. They also reacted with hydroxyl-ions present in concrete to form a light brownish precipitate. Typically, there is no clear borderline between these two precipitates. To distinguish further, a potassium dichromate solution was sprayed in order to increase the contrast of the resulting colors. Potassium dichromate reacts with the excess AgNO₃, creating a reddish-brown precipitate, but does not react with AgCl, thus leaving the contaminated surface a light yellow color. The line between two differently colored areas clearly indicates the chloride penetration front (Figure 3.3).

![Figure 3.3](image)

**Figure 3.3** The color changes on a concrete sample tested with silver nitrate spray
3.4.4 Chloride profiles and chloride diffusion coefficients

After the 90-day exposure to chlorides, the chloride profile was determined on the test samples at varying depths from the exposed surface (Figure 3.2c). A portable grinding machine (a part of the PROOVE’it system produced by Germann Instruments, Inc.) was used to pulverize the samples layer-by-layer at an incremental depth of 2.5 mm for four layers and then 5 mm for another three layers. Powdered samples collected after passing the pulverized material through an 850 μm (No. 20) sieve were stored in sealed plastic bags for quantitative chloride determination.

The chlorides in concrete may be divided into two groups: free chlorides and bound chlorides. While diffusing in concrete, the free chlorides move without restraint toward a location where the chloride concentration is lower. The bound chlorides, on the other hand, are chemically bound to cement hydration products and are not free to move. To measure the contents of free and total (free plus bound) chlorides, the water-soluble chloride test as per ASTM C 1218 (1999) and the acid-soluble chloride test as per ASTM C 1152 (2004), respectively, were carried out.

A plot of the chloride content measured at various layers with respect to the mid-layer depths gave profiles of chloride penetrating into concrete samples. Through the use of least squares nonlinear regression, the profiles measured were fitted to the solution of Fick’s second law of diffusion. Two coefficients, the apparent diffusion coefficients and the effective chloride diffusion coefficients, were determined from the acid-soluble and water-soluble chloride profiles, respectively.


3.4.5 Rapid chloride permeability test

![Figure 3.4 Rapid chloride permeability test as per ASTM C 1202](image)

As indicated previously, for the Rapid Chloride Permeability Test (RCPT), three 100 mm $\Phi \times 200$ mm concrete cylinders were cast for each of the five mixes. After air-drying them in the laboratory for 28 days, epoxy was applied on all surfaces. These were then sawn to produce two 50 mm thick discs from the middle of the samples. This gave a total of six replicates for each of the mixes.

Prior to the test, the disc specimens were pre-conditioned as per ASTM C 1202. They were first vacuum-dried in a desiccator for 3 hours and then vacuum saturated with degassed water for 21 hours. Immediately after removal from the desiccator, they were wiped of excess water and then put in the RCPT test cells (Figure 3.4). Each of the cells contains a sliced concrete sample placed between two reservoirs of 3.0% NaCl and 0.3 N NaOH.
solutions. The RCPT apparatus is configured to supply 60 V for 6 hours. During the 6 hours, the corresponding currents were recorded and converted to determine the amount of charge (presumably Cl\(^-\) ion) that passed through each of the samples. The amount of charge passed is an indication of the chloride permeability of the tested concrete.

3.4.6 Chloride binding

Five different cement paste samples having the same w/c ratio of 0.55 were prepared. One was plain cement paste and the others were reinforced with the cellulose and polypropylene fibers at 0.1% and 0.3% volume fractions. The samples were cured in saturated calcium hydroxide solution for 28 days before crushed to small pieces. Using an automated sieve machine, the crushed samples having the particle sizes ranging from 0.25 mm to 2.00 mm were collected. Each 5 g of the sieved samples was stored in a 50-ml test tube for the chloride binding test. The test began with the filling of the test tubes with NaCl solutions at three different chloride concentrations of 0.1, 0.3, and 0.6 Molar. At each chloride concentration, three replicates of the powdered samples were tested. Due to the chloride binding effect, the samples will bind the chlorides in the solutions. The decrease of the chloride concentration of the solutions then indicates the binding effect. In the present experiment, the chloride concentration in each of the test tubes was measured at various times of 7, 14, and 21 days.

The measurement of chloride concentration was carried out using the Accumet® Chloride Combination Ion Selective Electrodes. The electrode was calibrated with chloride standard solutions at the beginning of the measurement in each day. Prior to each measurement, the
solution was prepared as follows. First, 1 ml of the solution from each test tube was taken out using an Automatic Micro Pipette and poured into a 50 ml graduated cylinder. It was then diluted to 10 ml with distilled water using an automatic water dispenser. Using a graduated pipette, 0.3 ml of Ionic Strength Adjuster (ISA) which is 5 Molar solution of NaNO₃, was added to the same graduated cylinder. The electrode was then put into the graduated cylinder for one minute before the reading was taken.

3.5 Results and Discussions

3.5.1 Chloride penetration front

The chloride penetration front as detected by the silver nitrate spray test for the five mixes is shown in Figure 3.5. The middle one-third of the sample’s width was considered for determination of the penetration front. The specimens clearly illustrated two different zones in color, the top portion in light grey and yellow and the bottom in reddish-brown; these color differences are due to the chloride exposure on the top surface of the test samples. The line at the color change boundary indicated the front of chloride penetration.
Because of the tortuous lines and the unevenly spreading colors in the transition zone, the process of identifying the exact depth of chloride penetration is at best a subjective process. However, excluding the region of coarse aggregates and measuring the lowest depth of perceived chloride front, plain concrete (Mix #1) yielded a depth of chloride penetration at approximately 24 mm (0.95 in.). The same for cellulose FRC (Mixes #2 and #3) and polypropylene FRC (Mixes #4 and #5) were, respectively, 25, 26, 30, and 32 mm (0.98, 1.02, 1.18, and 1.26 in.). These depths are denoted as $d_f$ in the following discussion.

Since the significance of the test is to quickly determine how chlorides advance in concrete, it is generally of interest to report the penetration depth with the corresponding chloride content. The depths of chloride penetration from the chloride ponding test are compiled in Table 3.3 along with the total and free chloride contents at the last measured layer (at depths between 20 and 25 mm and reported as measured $\text{Cl}^-$ at 22.5 mm). The chloride diffusion coefficients resulting from the chloride profile test were used to calculate the total chloride...
and the free chloride contents at the penetration depths, \( d_f \); and are also given in Table 3.3. Notice that the measured depth of penetration from the colorimetric test correlates well with the calculated total chloride contents at that depth from the ponding test. The averaged total and free chlorides are 0.06\% and 0.04\% by weight of concrete with a standard deviation of 0.01\%. These results and the diffusion coefficient are further discussed in the next section.

### Table 3.3 The chloride contents, the depth of chloride front (\( d_f \)) and the diffusion coefficients

<table>
<thead>
<tr>
<th>Mix#</th>
<th>Mix Description</th>
<th>Chloride Penetration Depth ( d_f ) (mm)</th>
<th>Measured [Cl(^{-})] at 22.5 mm (% w/w of concrete)</th>
<th>Calculated [Cl(^{-})] at the Depth ( d_f ) (% w/w of concrete)</th>
<th>( D_{\text{apparent}} ) ((×10^{-7} \text{ cm}^2/\text{s}))</th>
<th>( D_{\text{effective}} ) ((×10^{-7} \text{ cm}^2/\text{s}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Total Chloride</td>
<td>Free Chloride</td>
<td>Total Chloride</td>
<td>Free Chloride</td>
<td>Total Chloride</td>
</tr>
<tr>
<td>1</td>
<td>Plain Concrete</td>
<td>24</td>
<td>0.07</td>
<td>0.06</td>
<td>0.07</td>
<td>0.06</td>
</tr>
<tr>
<td>2</td>
<td>0.1% Cellulose FRC</td>
<td>25</td>
<td>0.09</td>
<td>0.06</td>
<td>0.07</td>
<td>0.05</td>
</tr>
<tr>
<td>3</td>
<td>0.3% Cellulose FRC</td>
<td>26</td>
<td>0.09</td>
<td>0.05</td>
<td>0.07</td>
<td>0.03</td>
</tr>
<tr>
<td>4</td>
<td>0.1% PP FRC</td>
<td>30</td>
<td>0.11</td>
<td>0.06</td>
<td>0.06</td>
<td>0.03</td>
</tr>
<tr>
<td>5</td>
<td>0.3% PP FRC</td>
<td>32</td>
<td>0.10</td>
<td>0.06</td>
<td>0.04</td>
<td>0.03</td>
</tr>
</tbody>
</table>

#### 3.5.2 Chloride diffusion coefficients

The results of free and total chlorides, as determined from the chloride profile tests and the coefficients of chloride diffusion are further discussed in this section (Table 3.3).
average chloride profiles of all mixes were plotted with the noted spread as shown in Figure 3.6. As expected, the concentration of the chlorides is the highest at the topmost layer and declined exponentially with depth. The average water-soluble and acid-soluble chloride concentrations for all mixes are presented with a solid line, whereas the upper and lower bounds are presented with the two dashed lines.

By fitting the solution of Fick’s second law to the results of the chloride profiles, the apparent and effective chloride diffusion coefficients were determined corresponding to the total and free chloride profiles, respectively. Among the mixes investigated, notice that the chloride concentrations vary in a narrow range. At 22.5 mm depth, the free chlorides are the same for all mixes. But, given that the surface chloride concentrations in the case of FRCs are higher, the Fick’s second law predicted a lower coefficient of effective diffusion (Figure 3.7a). When the total chlorides are considered, although surface chloride concentrations in the case of FRCs at the surface is higher, at the depth of 22.5 mm, Fick’s second law still predicted a higher coefficient of apparent diffusion for FRCs (Figure 3.7b). The plots in Figure 3.8 show the effect of the fiber reinforcement.

The apparent diffusion coefficients are higher in the FRC samples possibly because of an increase of the volume of interfacial porosity at fiber-matrix interfaces that provided easier paths for chloride to transport. In the case of cellulose fibers, the hydrophobic nature of the fiber and the internal moisture entrapment most likely caused the upsurge. However, the effective diffusion coefficients are lower in the FRC as a consequence of the chloride binding effect. This binding may be a result of the sizing and chemical treatments applied to the fiber surfaces for enhanced chemical resistance and bond.
Figure 3.6  Chloride profiles of the average water-soluble (free) and acid-soluble (total) chlorides

Figure 3.7  Influence of surface chloride concentration on coefficient of diffusion (a) free chlorides with effective coefficient and (b) total chlorides with apparent coefficient
3.5.3 Rapid chloride permeability test

The total charge passed through the test samples and their corresponding chloride ion penetrability are given in Figure 3.9. The charge passed shows how well the concrete samples can resist the migration of chloride ions — a lower number means a higher resistivity. With reference to ASTM C 1202, the chloride ion penetrability is “high” if the charge passed is greater than 4000 C, “moderate” if it is between 2000 and 4000 C, “low” if it is between 1000 and 2000 C, “very low” if it is between 200 and 1000 C, and “negligible” if it is less than 200 C.

As seen in Figure 3.9, the level of charge passed through the various samples can be categorized from moderate to high. There are, however, slightly more chloride ions migrating through the FRC samples, especially the cellulose FRC. This is, once again, likely due to the increased interfacial porosity at fiber-matrix interfacial zones in FRC and the

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**Figure 3.8** Apparent and effective coefficients of chloride diffusion for various volume fractions of fibers

(a) Apparent coefficient of chloride diffusion

(b) Effective coefficient of chloride diffusion

<table>
<thead>
<tr>
<th>Volume Fraction of Fiber (%)</th>
<th>Cellulose Fiber</th>
<th>Polypropylene Fiber</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.00E-07</td>
<td>1.20E-07</td>
</tr>
<tr>
<td>0.1</td>
<td>1.20E-07</td>
<td>1.40E-07</td>
</tr>
<tr>
<td>0.2</td>
<td>1.40E-07</td>
<td>1.60E-07</td>
</tr>
<tr>
<td>0.3</td>
<td>1.60E-07</td>
<td>1.80E-07</td>
</tr>
</tbody>
</table>
existence of a well connected network. In addition, the results in the FRC are more scattered, as indicated in the standard deviation values, which also points to the random nature of fiber and interface distribution.

The RCPT results are sensitive to the water-to-cement (w/c) ratio as reported by Whiting (Whiting 1981). The chloride permeability of a 0.4 to 0.6 w/c ratio concrete could fall into the medium level, corresponding to the passed charge range from 2000 to 4000 C. In this study, the control mix, which is the ordinary concrete with w/c of 0.55, yielded a total charge passed of about 3600 C, showing a good agreement between this result and Whiting’s work. As regards the volume fraction of the FRC, the charge passed shown in Figure 3.10 has a similar trend to that of the result of the apparent chloride diffusion coefficients.

![Figure 3.9](image_url)  
**Figure 3.9** Charge passed in rapid chloride ion permeability test (RCPT). The results are listed in the format: average ± standard deviation (coefficient of variation).
3.5.4 Chloride binding effect

The decrease of the chloride concentration of the NaCl solutions due to the chloride binding effect in the cement pastes with and without the presence of the cellulose and polypropylene fibers was reported here as shown in Figure 3.11. All of the samples showed a similar trend. The binding effect was increased with time and more chlorides were bound in the solution having higher initial chloride concentration. The influence of the fibers on the chloride binding effect was noticed in the 0.6 M solution.
Figure 3.11  The changes of the chloride concentration as a function of time due to the chloride binding effect of the cement pastes (5 g) with and without the presence of the cellulose and polypropylene fibers (0.1% and 0.3% volume fractions)

The bound chlorides of the cement paste samples after submerged in the NaCl solutions for 21 days were calculated and plotted in Figure 3.12. The bound chlorides were increased with the initial chloride concentration. The difference of the bound chlorides among the test samples was insignificant when the solution has low initial chloride concentrations. When the initial chloride concentration is 0.6 M, there was more bound chloride in FRC pastes. Also, the increase of the bound chloride was higher in the cellulose FRC than in the polypropylene FRC paste samples and appeared to increase with increasing fiber content.
3.6 Conclusions

The influence of cellulose and polypropylene fiber on chloride diffusion in concrete was investigated. The silver nitrate spray test, chloride profile test and the rapid chloride-ion permeability tests were performed. The following conclusions were drawn:

- The silver nitrate spray test results indicate that the chloride penetration front in the case of the fiber reinforced concrete samples is more advanced than in plain concrete. The penetration depth in the silver nitrate spray test correlates well with the total chloride content, calculated for this depth using the diffusion coefficient, determined from the chloride profile test. At the depth of the chloride penetration...
The mean concentrations of calculated total and free chlorides of all mixes are approximately 0.06% and 0.04% by weight of concrete.

- Even though all mixes have very similar chloride profiles, their chloride diffusion coefficients, according to the solution of Fick’s second law, are different. The coefficient of apparent chloride diffusion increases with an increase in the amount of fiber added, but the coefficient of effective chloride diffusion decreases. In addition, the effect of the cellulose fiber is greater than that of the polypropylene fiber.

- The rapid chloride-ion permeability tests showed good agreement with the apparent chloride diffusion coefficients. Compared with the plain concrete, the fiber reinforced concrete samples showed higher chloride permeability than the plain concrete. The results also showed higher deviation, probably due to the random nature of the fiber distribution.

- The results of the chloride binding test indicated that the chloride binding capacity of the fibers became prominent in the NaCl solution of 0.6 M initial chloride concentration and was increased with the fiber dosages. It was implied that the binding capacity of the fibers is depended on the chloride concentrations and the fiber dosages. It was also found that the cellulose fibers have a higher binding capacity than the polypropylene fibers. Hence, such chloride binding effect of the fibers would cause the differences of the chloride diffusion coefficients between the plain concrete and the FRC samples.

- The fibers clearly have a major effect on chloride diffusion in concrete. They provide more interconnected paths for chloride transport through the additional
interfacial transition zones created due to fibers. Thus, chlorides ingress into the fiber reinforced concrete is greater than into the plain concrete. However, the chloride binding effect in fiber reinforced concrete results in a reduced amount of chlorides to be available for steel corrosion as it is normally assumed that it is the free chloride that is available for steel corrosion.
3.7 References


Hannant, D.J. and Edgington, J., (1975), "Durability of Steel Fibre Concrete," *SAE Preprints*, pp. 159-169.


Chapter 4

Corrosion of Rebar and Role of Fiber Reinforced Concrete, Part 2: Electrochemical Measurements\(^3\)

4.1 Outline

Crack bridging characteristics of fibers in concrete and an improved internal microstructure are both expected to enhance the long term durability of fiber reinforced concrete (FRC) over its plain counterpart. Indeed, recent water permeability tests in unstressed and stressed conditions support this hypothesis. In this two part paper, further evidence was sought of the ability of fiber reinforcement to control corrosion of reinforcing steel in concrete structures. In Part 1, transport of chlorides was investigated using the bulk diffusion test and the rapid chloride-ion permeability test. Results clearly showed that while the presence of fibers increased the coefficient of chloride diffusion based on total chlorides, there was a decrease in the coefficient related to free chlorides. Fibers thus appeared to bind the chlorides and inhibit their transport.

Here, in Part 2 of the paper, results from corrosion tests are presented. Corrosion activity in reinforcing steels was monitored in stressed beam specimens both in the presence and

\(^3\) A version of this chapter has been submitted for publication. Sappakittipakorn, M. and Banthia, N. (2010) Corrosion of Rebar and Role of Fiber Reinforced Concrete, Part 2: Electrochemical Measurements.
absence of fiber reinforcement. A simulated tidal zone marine environment was chosen. Corrosion measurements were made for a period of 56 weeks using three electrochemical methods: half-cell potential, galvanic current and linear polarization resistance. As in Part 1, two fibers — cellulose and polypropylene — at 0.1% and 0.3% by volume fraction were investigated. Results supported the findings of Part 1 of the paper and indicated that the fibers were effective in delaying the onset of steel corrosion.

4.2 Introduction

Corrosion of steel in concrete remains a major durability concern of our time. Chloride contamination of concrete is to blame and the mechanisms by which chloride-ions promote rebar corrosion in concrete have been well understood (Neville 1995; Glass and Buenfeld 2000). Briefly, in healthy concrete, a highly alkaline pore solution produces an impermeable and protective layer of ferrous and ferric oxides on the surface of embedded steel which prevents the incoming water and oxygen from reacting with steel. This process is called ‘passivation’. Chlorides enter the body of concrete through various transport mechanisms including diffusion, migration, adsorption, and permeation, and weaken the passive film on the surface of steel. It is believed that the chlorides react with the ferrous oxides, most likely at its thinnest layer, and form a soluble compound which then dissolves in the surrounding solution and reverses passivation. The area first affected is usually an area with higher residual stresses or elevated cementite content where local pitting corrosion takes place. The amount of chlorides needed to break the passive film (so-called chloride threshold) thus
depends on the availability of the hydroxides to react with the additional oxidation products
to re-strengthen the film against the chlorides. Alonso et al. (Alonso et al. 2000) provide an
extensive review of chloride thresholds that cause corrosion of steel in concrete.

Unfortunately, cracks in concrete allow an easy ingress of chlorides and other deleterious
c hemicals and further promote corrosion (Bentur, Diamond, and Berke 1997). The
influence of cracks has been the subject of extensive investigation and review (Schiessl and
Raupach 1997; Francois and Arliguie 1998; Mohammed et al. 2001; Granju and Balouch
2005; Sahmaran 2007; Jaffer and Hansson 2009). Most studies have employed reinforced
concrete beams loaded under 3- or 4-point bending to generate cracks. In the context of the
influence of cracking on corrosion, two parameters are often of interest: first the
onset/initiation of corrosion, and second, the rate of corrosion once initiation has occurred.
Enormous amount of data suggests that regardless of their size, cracks accelerate the onset
of corrosion (Schiessl and Raupach 1997) and the characteristics of the cementitious matrix
and load intensity are both important with respect to when corrosion begins (Francois and
Arliguie 1998; Mohammed et al. 2001). Surprisingly, results also indicate that after its onset,
there is no clear correlation between surface crack widths and the rate of corrosion (Beeby
1978).

It can be hypothesized from the above that if the cracking in concrete can be controlled, the
initiation of corrosion in reinforcing steel can be delayed and the service life of concrete
structures can be extended. It is well known that the addition of fiber to concrete can
substantially reduce cracking and hence fiber reinforced concrete (FRC) can be expected to
provide a superior resistance to steel corrosion than its plain counterparts. Indeed, many
studies indicate this benefit of fiber reinforcement. In addition to acting as crack arresters,
both surface-modified steel fibers such as galvanized steel fibers (Keyvani Someh and Saeki 1997) and zinc coated steel fibers (Keyvani and Saeki 2001) are shown to act as sacrificial anodes and provide cathodic protection for reinforcing steel. Effectiveness of polypropylene fibers in enhancing the corrosion resistance of rebar has also been reported (Al-Tayyib and Al-Zahrani 1990; Sanjuan, Andrade, and Bentur 1997; Haddad and Ashteyate 2001).

When the corrosion of fibers themselves is considered, there is no doubt that steel fibers will suffer from corrosion at least on the surface and especially in highly corrosive environments (Hannant and Edgington 1975; Morse and Williamson 1977; Schupack 1985; Mangat and Gurusamy 1987; Banthia, Pigeon, and Krishnadev 1988; Mangat and Gurusamy 1988; Kosa and Naaman 1990; Kosa, Naaman, and Hansen 1991; Janotka et al. 1992; Min, Ditao, and Xiong 2009; Balouch, Forth, and Granju 2010). On the positive side, corrosion products formed on lightly corroded steel fibers may in fact improve the interfacial bond and result in higher flexural toughness (Mangat and Gurusamy 1988; Granju and Balouch 2005), but such gains are not dependable.

Banthia and Bhargava (Banthia and Bhargava 2007) recently showed that cellulose fiber reduced the water permeability of concrete both in the presence and absence of stress, thus postulating that cellulose fiber may inhibit the ingress of corrosive chemicals and delay the onset of rebar corrosion. In Part 1 of this paper, some data on chloride transport in concrete with cellulose and polypropylene fiber was presented and it was shown that fibers inhibit the transport of free chlorides. In this Part 2 of the paper, ability of the fibers to delay corrosion of reinforcing steel is investigated by performing electrochemical measurements.
### 4.3 Research Significance

Severe corrosion of steel in concrete structures has created an infrastructure crisis of unprecedented proportions. In some extreme instances, even the safety of the users may be compromised. Of the many factors that control corrosion, severity of exposure, existence of cracks, intensity of loading and the transport properties of concrete, are among the most critical. Fiber reinforcement of concrete is known to reduce both environmentally-initiated and load-induced cracks and alter the transport properties, but a direct evidence of fibers mitigating rebar corrosion is lacking. This two-part study was prompted by a desire to fill this gap.

### 4.4 Experimental Program

#### 4.4.1 Materials

As in Part 1 of the paper, the mixture proportions of the concrete matrix investigated are given in Table 4.1. Normal Portland cement (CSA Type 10/ASTM Type GP), river sand, crushed stone, and tap water were used. This matrix was reinforced with two types of fibers—cellulose and polypropylene—at volume fractions of 0.1% and 0.3%. This yielded five overall mixes, one control and four with two volume fractions of the each of the two fibers. Fiber properties are given in Table 4.2 and they are pictorially shown in Figure 4.1.
Notice that one fiber is a virgin cellulose (CL) fiber treated with an alkali-resistant coating and packed in the form of small chips. The other is a multifilament, alkali proof polypropylene (PP) fiber. The average compressive strength of the mix (ASTM C39) was 46 MPa (6.67 ksi) with a standard deviation of 2 MPa (0.29 ksi).

**Table 4.1  Mixture proportions**

<table>
<thead>
<tr>
<th></th>
<th>Cement, kg (lb)</th>
<th>Water, kg (lb)</th>
<th>Sand, kg (lb)</th>
<th>Gravel, kg (lb)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>335 (739)</td>
<td>184 (406)</td>
<td>860 (1896)</td>
<td>950 (2094)</td>
</tr>
</tbody>
</table>

**Table 4.2  Properties of fibers investigated**

<table>
<thead>
<tr>
<th>Property</th>
<th>Cellulose fiber</th>
<th>Polypropylene fiber</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity</td>
<td>1.10</td>
<td>0.91</td>
</tr>
<tr>
<td>Tensile strength, N/mm² (ksi)</td>
<td>600–900 (87–131)</td>
<td>200–500 (29–73)</td>
</tr>
<tr>
<td>Average length, mm (in.)</td>
<td>2.1 (0.08)</td>
<td>16 (0.63)</td>
</tr>
<tr>
<td>Denier, g/9000 m (lb/9842 yd)</td>
<td>2.5 (5.5 × 10⁻³)</td>
<td>6 (13.2 × 10⁻³)</td>
</tr>
<tr>
<td>Diameter, µm (in.)</td>
<td>18 (0.71 × 10⁻³)</td>
<td>30 (1.18 × 10⁻³)</td>
</tr>
<tr>
<td>Surface area, cm²/g (ft²/lb)</td>
<td>25 000 (12 206)</td>
<td>1500 (732)</td>
</tr>
</tbody>
</table>
4.4.2 Specimens

The specimens were designed to study the effect of fibers on the initiation of corrosion of reinforcing steel in concrete beams. Beams, 100 mm × 100 mm × 350 mm, were reinforced with three 10 mm carbon steel rebars (AISI 1018 Steel) similar to the specimen in ASTM G 109. One of the bars (working electrode) was put in a tension zone and was corrosion monitored during the experiment. The other two were in a compression zone and were used as auxiliary electrodes. All of the bars were covered with rubber paint at a distance of 140 mm from both ends so that the corrosion could take place only within the middle 70 mm of the bars. The concrete cover was uniform at 25 mm. The bars were electrically connected to wires for corrosion measurements. Each beam was coated with epoxy on all sides except for the side at the bottom, which was stressed in tension and exposed to chloride solution. A schematic of the beam specimens is shown in Figure 4.2.
Two sets of beams were investigated: one with load and the other without. The test program is given in Figure 4.3. Across the middle of the tension surface, all the beams were pre-notched by the insertion of a thin steel sheet (0.2-mm thick and 5-mm deep) prior to concrete casting. In addition, in order to evaluate the flexural capacity of the specimens, three additional beams were cast for each of the five mixes (calibration set). All specimens were moist cured in saturated calcium hydroxide solution for 28 days. After that, the specimens from the calibration set were tested to failure in a displacement-controlled testing machine in four-point bending. The resulting load–displacement curves were plotted as shown in Figure 4.4. Their ultimate flexural strengths varied between 60 and 66 kN at a mean value of approximately 63 kN and a standard deviation of 2.5 kN.

**Figure 4.2  Schematic of a test specimen**
Chapter 4. Corrosion of Rebar and Role of Fiber Reinforced Concrete, Part 2: Electrochemical Measurements

Figure 4.3  Corrosion test program

Figure 4.4  Load–displacement curves for beam specimens in 4-point bending

Figure 4.5  Steel frame used for applying a steady flexural load on the specimen
After a moist curing of 28 days, specimens designed for corrosion measurements were continuously loaded to two applied load levels of 15 and 30 kN; these are approximately 25% and 50% of the ultimate capacity of the beams (Figure 4.4). A steel frame was employed to maintain the loads on the beams, as shown in Figure 4.5. A torque was applied at the nuts on the threaded rods at both sides of the beam to control the flexural load. The torque associated with the bending was computed from the calibration chart correlating the torque and the bending load as shown in Figure 4.6. After the beams were loaded and secured in the frame, the torque was regularly maintained for 4 weeks to counteract the effect of creep and relaxation. In the last 2 weeks, the beams were stored in the saturated calcium hydroxide solution.

As mentioned before, across the middle of the tension surface, all the beams were pre-notched by the insertion of a thin steel sheet (0.2-mm thick and 5-mm deep) prior to

---

**Figure 4.6** Relationship between the applied torques and the corresponding bending load for the specimen shown in Figure 4.5
concrete casting. When loaded, the beams were thus cracked at the notch. To ensure the formation of ‘first’ crack, the beams were loaded until the sudden drop of the applied load was noticed. Then the loading was continued to the assigned value of either 15 kN or 30 kN. The widths of the transverse cracks were measured by using an optical microscope at five equally spaced points within a width of 40 mm at the center of the beam. The crack widths among the mixes were slightly different. The mean values were 0.25–0.30 mm and 0.6–0.8 mm, respectively, for loads of 15 and 30 kN.

Fifty-six day old specimens (28 days of moist curing followed by 28 days of load application) were then exposed to chlorides in a salt water tank (Figure 4.7) with the loading frame in-place. To accelerate the corrosion, a condition simulating a tidal zone marine environment was applied by using wet/dry cycles in 3.5% sodium chloride solution (4 days in dry and 3 days in wet conditions). In the wet cycle, the salt water in which the beams were submerged was circulated and controlled at 20–25°C. To begin the dry cycle, the tank was drained with the salt water transferred to another tank. The dry tank with the specimens sitting inside was covered. Relative humidity and temperature were controlled at 50–60% and 20–25°C, respectively, by using the salt water sprayer and hot air blower. The process began with the wet cycle, and all corrosion measurements were performed just before the next wet cycle. To monitor the corrosion process, a potentiostat (Reference 600 from Gamry Instruments) was utilized to perform three electrochemical measurements, i.e., half-cell potential, galvanic current, and linear polarization resistance.
4.5 Electrochemical Measurements and Results

4.5.1 Half-cell potential

In the half-cell potential measurement, a copper/copper sulfate electrode (CSE) was used as a reference as per ASTM standard C 876 (American Society of Testing and Materials 1998), see Figure 4.8. As per the standard, there is a greater than 90% probability that steel corrosion is occurring in an area at the time of measurement if the potentials over that area are lower (more negative) than –350 mV. On the other hand, if potentials are greater (less negative) than –200 mV, there is a greater than 90% probability that no steel corrosion is taking place. Finally, if the potentials are between –200 mV and –350 mV, the corrosion activity is uncertain.
Figure 4.8  **Schematic of half-cell potential measurement**

The half-cell potentials of all samples monitored for 56 weeks are shown in Figure 4.9, Figure 4.10, and Figure 4.11, corresponding to continuous flexural loads of 0, 15, and 30 kN, respectively. Their potentials reveal the progression of corrosion on steel reinforcement during the time of exposure. Before the samples were placed in the chloride solution, the potential results were much greater (less negative) than –200 mV. Soon after the samples were exposed to a simulated marine environment, the potential values showed a substantial drop.

Once the potential is lower (more negative) than –350 mV, presumably the steel rebar is actively corroding. The potential data shown in Figure 4.9 and Figure 4.10 indicated that the onset of the active corrosion among the five mixes was delayed as a consequence of the fiber addition for a 0 kN and a 15kN load application. However, for a 30 kN load application (Figure 4.11), there appears to be an active corrosion in the first week of the exposure itself,
regardless of fiber presence or type, presumably due to the creation of a large crack due to the heavy load.

Figure 4.9  Half-cell potentials (with respect to copper/copper sulfate electrode) measured in samples without load

Figure 4.10  Half-cell potentials (with respect to copper/copper sulfate electrode) measured in samples with 15 kN flexural load
4.5.2 **Galvanic current**

In a galvanic cell (Figure 4.12), a galvanic current flows between two dissimilar metals from anode to cathode. The rate of the current is proportional to the dissimilarity of their standard potentials. This concept was applied successfully to develop a galvanic sensor (using steel coupled with copper) for corrosion detection (Park et al. 2005).

In this study, an identical steel rebar (auxiliary electrode) was chosen to pair with the reinforcing steel (working electrode) and was placed in the compression zone of the beams. The outer surfaces of the concrete adjacent the auxiliary electrode were painted with epoxy to maintain a passive condition of the auxiliary rebar. The potentiostat was switched into a zero resistance ammeter (ZRA) mode to measure galvanic current between these two rebars after the half-cell potential measurement. Ideally, when both rebars are in the same corrosion
state, the galvanic current is infinitesimal. The current will increase only if the inspected rebar is corroding. The change in the galvanic current can then indicate the time of corrosion initiation.

Since the galvanic current results may vary with the size of the rebar, they were normalized with the effective surface area of steel that resulted in the galvanic current density (in $\mu$A/cm$^2$). The working electrode was a rebar 10 mm with an effective length of 7 cm so that the effective area was approximately 22 cm$^2$. The results of the galvanic current density were plotted as a function of time, as shown in Figure 4.13, Figure 4.14, and Figure 4.15, corresponding to the samples subject to 0, 15, and 30 kN loading, respectively.

![Diagram of galvanic current measurement](image-url)

Figure 4.12  Schematic of galvanic current measurement
Figure 4.13  Galvanic current densities measured in specimens without load

Figure 4.14  Galvanic current densities measured in specimens with a 15 kN flexural load
In Figure 4.13, the curves initially were close to zero, indicating no corrosion in the samples. They later showed a sharp rise, and then they dropped to a very low current. The time at which the galvanic current peaks conformed to the time of the active corrosion in the half-cell potential result (Figure 4.9). For the 15 kN loaded samples, the peaks in Figure 4.14 appeared at earlier times, markedly consistent with the half-cell potential in Figure 4.10.

When large cracks were involved as in the specimens carrying the 30 kN load, the peaks in the current density appeared within the first 2 weeks and then stayed at a high value afterwards, as shown in Figure 4.15. After 12 weeks, the current density fluctuated considerably and sometimes even became negative, probably because the auxiliary rebar was depassivated. Therefore, in such circumstances, the galvanic current data needs careful scrutiny.

**Figure 4.15**  Galvanic current densities measured in specimens with a 30 kN flexural load
4.5.3 Linear polarization resistance

At a steady state of corrosion, the ratio of an applied small potential ($\Delta E$) to the resulting current ($\Delta I$) signifies a linear polarization resistance ($R_p$).

$$R_p = \frac{\Delta E}{\Delta I}$$  \hspace{1cm} (4.1)

Employing the Stern-Geary Constant (B) allows conversion of the linear polarization resistance to a corrosion current density ($i_{corr}$) corresponding to the area of polarized steel ($A_s$) (Andrade and Alonso 2004).

$$i_{corr} = \frac{B}{R_p \times A_s}$$  \hspace{1cm} (2)

The potentiostatic measurement of the voltage–current curve in the immediate vicinity of the corrosion potential was performed with the Gamry potentiostat featuring an automatic compensation of the ohmic drop effect. Three electrodes were connected to the apparatus. A CSE electrode connected to the reference electrode terminal was used for controlling the applied potential. A stainless steel ring ($\varnothing_{outer} = 64$ mm and $\varnothing_{inner} = 35$ mm) connected to the counter electrode terminal was used to sense the resulting current. The reinforcing steel connected to the working electrode terminal was then inspected (see Figure 4.16). The area of polarized steel was 22 cm$^2$ (7 cm long rebar #10), which was the surface of the exposed steel. The potential was scanned in the range of $\pm20$ mV of the corrosion potential (with respect to CSE) at the rate of 0.5 mV/s. The B constant of 26 mV was used as a mean value to calculate the corrosion current density of all samples. The plots of the current density...
results versus time are shown in Figure 4.17, Figure 4.18, and Figure 4.19, corresponding to the samples subject to the flexural loading of 0, 15, and 30 kN, respectively.

![Figure 4.16 Schematic of the linear polarization resistance measurement](image)

![Figure 4.17 Corrosion current densities measured in a linear polarization test in specimens without load](image)
Figure 4.18  Corrosion current densities measured in a linear polarization test in specimens with a 15 kN load

Figure 4.19  Corrosion current densities measured in a linear polarization test in specimens with a 30 kN load

As shown in Table 4.3, the corrosion current density defines the severity of corrosion. All samples showed low level of corrosion at the beginning. Shortly after they were exposed to chloride, their corrosion worsened. The non-loaded and the 15 kN loaded samples in Figure
4.17 and Figure 4.18 showed a low-moderate and a moderate level of corrosion, respectively. During the period of chloride exposure, the corrosion rate increased sharply from time to time, indicating more corrosion activity. The increase started in the 15 kN loading samples before the non-loaded samples, in the plain concrete before the FRC, in the polypropylene FRC before the cellulose FRC, and in the low fiber dosage before the high fiber dosage. It is noted that the variation of the corrosion level was consistent with that of the half-cell potential.

<table>
<thead>
<tr>
<th>Corrosion current density ($i_{\text{corr}}$, μA/cm²)</th>
<th>Corrosion level</th>
</tr>
</thead>
<tbody>
<tr>
<td>≤ 0.1</td>
<td>Negligible</td>
</tr>
<tr>
<td>0.1 – 0.5</td>
<td>Low</td>
</tr>
<tr>
<td>0.5 – 1</td>
<td>Moderate</td>
</tr>
<tr>
<td>&gt; 1</td>
<td>High</td>
</tr>
</tbody>
</table>

In the case of the 30 kN loaded samples, their corrosion was elevated to a high level rapidly (within 6 weeks), and the fiber influence on the corrosion faded away. Those were the consequences of the large crack induced by the heavy flexural load. The crack exposed the reinforcing steel directly to chloride, resulting in pitting corrosion. During the 16th and 28th weeks, the corrosion current fluctuated between high and low, while the corrosion potential was very high at all times. At this point, the corrosion dropped, probably because the corrosion products accumulated at the steel under the crack tip blocked the access of corrosive agents and the pitting corrosion at the middle became uniform corrosion on the entire surface of rebar. After 28 weeks, the corrosion current was fairly uniform; it then steadily increased.
4.5.4 *Time to onset of corrosion in reinforcing steel*

The electrochemical responses described above varied with time, type and volume fraction of fiber reinforcement and the applied load level, and depicted the activity of corrosion in the reinforcement. The initiation of corrosion was assumed when the electrical potential dropped below –350 mV (versus CSE). It follows the recommendation of ASTM C 876 stating that an active corrosion is likely to occur in this circumstance. Based on this criterion, the times to onset of corrosion recorded with different monitoring methods were fairly consistent and are given in Table 4.4. It is noted that, at the time corresponding to that potential threshold, the galvanic current density was increased considerably and the corrosion current density was elevated to moderate-high level.

<table>
<thead>
<tr>
<th>Concrete samples</th>
<th>Time to corrosion onset (weeks)</th>
<th>No loading</th>
<th>15 kN loading</th>
<th>30 kN loading</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plain concrete</td>
<td></td>
<td>27</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>0.1% cellulose FRC</td>
<td></td>
<td>56</td>
<td>38</td>
<td>1</td>
</tr>
<tr>
<td>0.3% cellulose FRC</td>
<td></td>
<td>&gt;56</td>
<td>51</td>
<td>1</td>
</tr>
<tr>
<td>0.1% polypropylene FRC</td>
<td></td>
<td>41</td>
<td>8</td>
<td>1</td>
</tr>
<tr>
<td>0.3% polypropylene FRC</td>
<td></td>
<td>47</td>
<td>13</td>
<td>1</td>
</tr>
</tbody>
</table>

As seen in Table 4.4, clearly, cracking induced in the concrete cover by loading accelerated the corrosion substantially. In the case of non-loaded specimens, there were no cracks involved, so that the corrosion developed very slowly. It was found that the 15 kN loaded samples responded in a manner similar to the non-loaded samples but the corrosion initiated sooner as a result of the crack. Because of the large crack in all samples subject to the 30 kN
loading, the corrosion began sometime within the first week itself. The influence of the fiber was found in all samples if no extensive crack existed. The corrosion initiation was delayed at a rate proportion to the fiber dosage.

4.6 Conclusions

During the 56 weeks of corrosion testing, the results from three electrochemical measurements of reinforced concrete beams subject to loading and exposed to corrosive atmosphere indicated that fiber reinforcement delays the onset of corrosion. However, when the reinforcement was directly exposed to chloride because of extensive cracking of the concrete cover, the fibers were ineffective. Other details of the fiber performance are summarized below:

- The active state of corrosion began in the FRC more slowly than in plain concrete. A comparison of the performance of the two fibers tested in the study reveals that the cellulose fiber provided a better result in slowing down the corrosion than the polypropylene fiber. In addition, the greater the fiber volume fraction, the later the corrosion began.

- With respect to the rate of corrosion, the presence of cracks affected not only the corrosion onset but also the severity of corrosion that followed. When the corrosion was active, the corrosion current density generally jumped to moderate or high levels and then varied differently, depending on the crack. After the onset of corrosion, the rate in the severely cracked samples (30 kN loaded samples) quickly
reached a high corrosion level and then steadily increased with time. In comparison, the corrosion level was only moderate in the moderately cracked samples (15 kN samples), and it was low to moderate in the non-cracked samples.

- The measurement of half-cell potential was quite simple. It was reliable if the result was much more negative than the threshold (−350 mV with respect to the CSE). In the galvanic current measurement, the passivity of the auxiliary steel must be ensured. The change of its corrosion state considerably alters the result. Once the auxiliary steel is corroded, the result must be discarded or interpreted carefully. The linear polarization resistance measured the kinetic of corrosion. While assuming that the corrosion was uniform and the Stern-Geary Constant was 26 mV/decade, the measured polarization resistances were converted to a corrosion current density. It was thus an estimate. Nonetheless, all of the three electrochemical corrosion measurements provided a fairly consistent evidence of the corrosion initiation.
4.7 References


Hannant, D.J. and Edgington, J., (1975), "Durability of Steel Fibre Concrete," *SAE Preprints*, pp. 159-169.


Chapter 5
Role of Fiber Reinforcement on Service Life of Concrete Structures in Marine Environments\(^4\)

5.1 Outline

Corrosion of steel reinforcement is a major source of concern for deteriorating concrete structures in severe environments. Maintenances are needed from time to time to extend the service life of structures. An optimal maintenance regime requires a proper service life model consisting of corrosion initiation and corrosion propagation periods. In the present work, the period of corrosion initiation was studied by using a model called LIGHTCON (Poulsen and Mejlbro 2006). It is modified to take the effects of fiber reinforcement and load intensity into consideration. The modification is carried out empirically based on the test results obtained from studies carried out here. The modified model is then verified with two case studies. The first example is the case of concrete beams exposed to accelerated corrosion in a chamber as described in Chapter 4. The predicted time to corrosion initiation matched well with the experimental results. In the second case, a concrete girder in a marine splash zone made of cellulose FRC and silica fume concrete was investigated. Predicted

\(^4\) A version of this chapter will be submitted for publication. Sappakittipakorn, M. and Banthia, N. (2010) Role of Fiber Reinforcement on Service Life of Concrete Structures in Marine Environments.
result of the model indicated a superior performance of the cellulose FRC and the silica fume concrete in comparison to their plain concrete counterparts.

5.2 Introduction

An exposure to chloride-rich environment shortens the service life of reinforced concrete structures due to the chloride induced corrosion of reinforcing steel (Bentur, Diamond, and Berke 1997; Bertolini et al. 2004). Since concrete cover protects steel, chlorides must first penetrate concrete and steel corrosion will take place only when a critical amount of chlorides reach the steel. From this point onwards, the degradation of a structure is initiated and accumulated. During an active corrosion period, not only does the rusting of the steel reduce the load carrying capacity of the contaminated structure, but an expansion of corrosion products also occurs and creates internal pressure sufficient to damage concrete cover. Once the damage exceeds a given permissible level, an end to the serviceability of the structures is said to have occurred. A service life model assists in making a decision on repair and rehabilitation, which is essential in order to extend the life of the structure with a minimum life cycle cost.

In our experimental studies, fiber reinforcement showed a promise in terms of delaying corrosion initiation of reinforcing steel in concrete. It also lowered the diffusion coefficient of free chlorides. As these findings emanated from conditions limited to the laboratory, it is important to extend these fiber influences to actual marine environments. For this purpose, the LIGHTCON model was selected and modified. The model solely considers the initiation
period of corrosion. The modified model is first verified with earlier experimental results of concrete beams exposed to accelerated corrosion. Next, the model is extended to the case of a reinforced concrete girder in a marine splash zone. A comparative study was conducted to estimate to what extent fiber and silica fume can prolong the service life of such a girder.

5.3 Service Life Models

A basic bi-linear model by Tuutti (Tuutti 1980) is well known for predicting the service life of structures during chloride-induced corrosion of steel reinforcement. It comprises of two parts, i.e. corrosion initiation period (dormant or diffusion period) and corrosion propagation period (active period), see Figure 5.1. Assuming that concrete is sound during the initiation phase; reinforcing steel will not corrode until a threshold chloride is reached at the steel surface. The level of chloride threshold needed for corrosion is still in dispute as large variation has been reported in this value (Alonso et al. 2000; Angst et al. 2009). The rate of chloride penetration is dependent on the diffusion coefficient and the surrounding conditions such as chloride concentration at concrete surface, humidity and temperature. The higher the threshold value and the lower the diffusion rate, the longer the initiation time will be. In the initiation period represented with the horizontal line in Figure 5.1, there is no corrosion damage. Afterwards the period of corrosion propagation (see a slanted line in Figure 5.1) takes place in relation to the corrosion rate, which can be estimated from a corrosion current density (Andrade, Alonso, and Gonzalez 1990). The corrosion damage is then escalating toward the permissible level which signals the end of the service life.
Corresponding to complex corrosion processes and its consequences, an intensity of deterioration is characterized into several stages by using more sophisticated models (Weyers 1998; Melchers and Li 2006; Bertolini 2008; Suwito and Xi 2008). Concrete cracking either induced by loads or due to the expansion of corrosion products has become a crucial factor to speed up the deterioration process. Its influence has also been included in aforementioned service life models. The stress-induced cracks shorten the initiation time of active corrosion in proportion to how severe cracks are. Once corrosion begins, the corrosion products expand creating internal stresses. When the stresses exceed the ultimate tensile strength of concrete, the so-called corrosion-induced cracks appear thus greatly influencing the corrosion rate in the propagation stage. Many researches attempted to mathematically express such cracking phenomena in reinforced concrete structures (Molina, Alonso, and Andrade 1993; Alonso et al. 1998; Liu and Weyers 1998; El Maaddawy and Soudki 2007; Oh, Kim, and Jang 2009).
In the present work, the focus was entirely on the corrosion initiation period. Due to restrictions on the use of chlorides in new construction, most chlorides intrude concrete from external sources. The chloride ingress takes place through several processes, i.e. diffusion by concentration gradients, permeation under hydraulic pressure (including the related “capillary adsorption”), migration by electrical driving field, and convection by moisture variation (Poulsen and Mejlbro 2006). Among those processes, diffusion is generally the most prevalent mechanism of chloride transport in concrete. The well-known research work by Collepardi et al. (1972) is among the first to explore the chloride diffusion in concrete. The Fick’s law of diffusion was employed in their work to quantify the chloride diffusivity of concrete. Further work on applying the diffusion theory to corrosion of steel in concrete has been extensively reviewed elsewhere (Nilsson 2009).

The ingress of chloride in concrete structures is commonly modelled with the Fick’s second law of diffusion as it follows the non-steady state of diffusion. In case of a unidirectional transport, the progress of chloride can be expressed as follows.

\[ \frac{\partial c}{\partial t} - D \frac{\partial^2 c}{\partial x^2} = 0 \]  

(5.1)

It characterizes the relationship among the chloride concentration \((C)\), time \((t)\), and location \((x)\) with a diffusion coefficient \((D)\). A time-dependent chloride diffusion coefficient is considered here and is predicted by means of the LIGHTCON model described in the following section. Considering the time to corrosion initiation, the diffusion coefficient is influential as much as the chloride threshold level, the chloride concentration at the concrete surface, the thickness of concrete cover, and the conditions of exposure. Later, in the proposed model, the influence of fiber reinforcement and service loads on steel corrosion in
concrete structures is also introduced as they also have a remarkable influence on the initiation of corrosion (Sanjuan, Andrade, and Bentur 1997; Yoon et al. 2000; Sahmaran 2007).

5.4 The LIGHTCON Model

To represent the effect of fiber on service life of concrete structures, the LIGHTCON Model (Poulsen and Mejlbø 2006) is employed. The model assumes a constant chloride content at the surface (constant boundary condition) but varies the coefficient of chloride diffusion with time. The other general assumptions of the model are as follows;

- Chloride concentration $C$ in concrete is defined as the ‘total, acid soluble chlorides’.
- Transport of chloride in concrete takes place only by diffusion.
- The flow of chloride is proportional to the gradient of chloride concentration. The factor of proportionality is the achieved chloride diffusion coefficient $D_a$.
- The achieved chloride diffusion coefficient $D_a$ depends on time, the composition of the concrete and the environment.
- The boundary condition $C_s$ is constant, i.e. independent of time, but it depends on the composition of the concrete and the environment. This assumption results in an exaggerated ingress of chlorides as it has been shown that chloride concentration at the surface exhibits a gradual accumulation with time (Ann, Ahn, and Ryou 2009),
The initial chloride content of concrete $C_i$ is uniformly distributed at the time of the first chloride exposure.

The model uses determinative parameters with respect to the environment, the time and the composition of the concrete as those occurring at the Träslövsläge Marine Exposure Station on the West Coast of Sweden (Poulsen and Mejlbø 2006).

In the LIGHTCON model, the relationship between the chloride diffusion coefficient, concrete composition, and the environment is formulated from the experimental results after 1 year of exposure at the Träslövsläge Marine Exposure Station. It expresses the chloride diffusion coefficient after 1 year of exposure as a function of the composition of cementing materials and the environments as follows.

\[
F_1 = 25000k_D \times \exp \left( - \sqrt{10 \times \frac{PC+FA+7SF}{W}} \right) \text{mm}^2/\text{year} \quad (5.2)
\]

where

\[
D_1 = \text{coefficient of chloride diffusion after 1 year of exposure}
\]

\[
W = \text{content of water in the concrete}
\]

\[
PC = \text{content of cement in the concrete}
\]

\[
FA = \text{content of fly ash in the concrete}
\]

\[
SF = \text{content of silica fume in the concrete}
\]

\[
k_D = \begin{cases} 
0.4 & \text{for concrete exposed to marine atmosphere (ATM)} \\
0.6 & \text{for concrete exposed to marine splash zone (SPL)} \\
1.0 & \text{for concrete submerged in seawater (SUB)} 
\end{cases}
\]

The chloride diffusion coefficient is time-dependent and is expressed mathematically by a power function as follows.

\[
D_a(t) = D_1 \times \left( \frac{t}{t_1} \right)^{-\alpha} = D_1 \times t^{-\alpha} \text{mm}^2/\text{year} \quad (5.3)
\]
where
\[ t_1 = 1 \text{ year and } t = \text{time of exposure} \]

\[ \alpha = k_\alpha \times \left( 1 - 1.5 \times \left( \frac{w}{PC+FA+7\times SF} \right) \right) \quad (5.4) \]

\[ k_\alpha = \begin{cases} 
1.0 & \text{for concrete exposed to marine atmosphere (ATM)} \\
0.1 & \text{for concrete exposed to marine splash zone (SPL)} \\
0.6 & \text{for concrete submerged in seawater (SUB)} 
\end{cases} \]

In addition, the LIGHTCON model provides an empirical function in Eq. (5.5) to estimate the chloride threshold level (as a percentage by weight of binders) of concrete exposed to marine environments.

\[ C_{cr} = k_{cr} \times \exp \left( -1.5 \times \frac{w}{PC-1.4\times FA-4.7\times SF} \right) \quad (5.5) \]

where
\[ C_{cr} = \text{chloride threshold level} \]

\[ k_{cr} = \begin{cases} 
1.25 & \text{for concrete exposed to marine atmosphere (ATM)} \\
1.25 & \text{for concrete exposed to marine splash zone (SPL)} \\
3.35 & \text{for concrete submerged in seawater (SUB)} 
\end{cases} \]

5.4.1 Modification of the LIGHTCON model for the accelerated corrosion environment

In our study, reinforced concrete beams made of plain concrete and four different FRCs were exposed to a weekly, cyclic wet and dry condition in a saline atmosphere to accelerate the onset of rebar corrosion. They simultaneously maintained third point bending loads of 0, 15, and 30 kN by using a loading jig. Reinforcing steel bars in the beams were electrochemically monitored by means of half-cell potential, galvanic current, and linear
polarization resistance for 56 weeks. According to results of those measurements, a time at which corrosion of the steel started was identified and is given in Table 5.1.

Table 5.1  Time to corrosion onset in plain concrete and FRCs

<table>
<thead>
<tr>
<th>Mix#</th>
<th>Mix Description</th>
<th>Time to Corrosion Onset (week)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>No Loading</td>
</tr>
<tr>
<td>1</td>
<td>Plain Concrete</td>
<td>27</td>
</tr>
<tr>
<td>2</td>
<td>0.1% CL FRC</td>
<td>56</td>
</tr>
<tr>
<td>3</td>
<td>0.3% CL FRC</td>
<td>&gt; 56</td>
</tr>
<tr>
<td>4</td>
<td>0.1% PP FRC</td>
<td>41</td>
</tr>
<tr>
<td>5</td>
<td>0.3% PP FRC</td>
<td>47</td>
</tr>
</tbody>
</table>

After the exposure of 56 weeks, a profile of total and free chloride concentrations was measured and then apparent and effective coefficients of chloride diffusion were calculated, respectively. Plain concrete was also investigated and compared to the four fiber reinforced concretes. The chloride contents on the surfaces were estimated using curve fitting. The diffusion coefficients were found to decrease as the fiber content was increased. The results of the diffusion coefficient of five mixes are given in Table 5.2.

None of the exposures in the LIGHTCON model was applicable to the test conditions used in this study as the tests were conducted in an accelerated corrosion atmosphere. Hence, before the model could be implemented, some modifications were necessary. Firstly, it was assumed that Eq. (5.5) with the factor $k_{cr}$ of 1.25 is valid to determine the chloride threshold level of plain concrete. For this particular case, the chloride threshold level was increased by 25% because the tested rebar was initially sandblasted to remove any mill scale (Mohammed and Hamada 2006). Once a chloride threshold was set, new factors, i.e. $k_D$ in the Eq. (5.2)
and $k_\alpha$ in the Eq. (5.4), were sought out to match the model predictions to the test results (i.e. the apparent coefficient of chloride diffusion and the time to corrosion onset) of the plain concrete in the corrosion chamber. It was found that the factor $k_D$ is 1.03 and the factor $k_\alpha$ is 0.07.

**Table 5.2**  Chloride diffusion of specimens subjected to wet-dry cyclic exposure in a saline environment

<table>
<thead>
<tr>
<th>Mix#</th>
<th>Mix Description</th>
<th>$C_0$, Total Chloride (% w/w of concrete)</th>
<th>$D_{\text{apparent}}$, ($\times 10^{-7}$ cm$^2$/s)</th>
<th>$C_0$, Free Chloride (% w/w of concrete)</th>
<th>$D_{\text{effective}}$, ($\times 10^{-7}$ cm$^2$/s)</th>
<th>$C_{cr}^*$ (% w/w of concrete)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Plain Concrete</td>
<td>0.48</td>
<td>1.15</td>
<td>0.38</td>
<td>1.56</td>
<td>0.072†</td>
</tr>
<tr>
<td>2</td>
<td>0.1% CL FRC</td>
<td>0.48</td>
<td>0.97</td>
<td>0.39</td>
<td>1.27</td>
<td>0.119‡</td>
</tr>
<tr>
<td>3</td>
<td>0.3% CL FRC</td>
<td>0.48</td>
<td>0.79</td>
<td>0.38</td>
<td>1.07</td>
<td>&gt; 0.101‡</td>
</tr>
<tr>
<td>4</td>
<td>0.1% PP FRC</td>
<td>0.48</td>
<td>1.11</td>
<td>0.39</td>
<td>1.39</td>
<td>0.104‡</td>
</tr>
<tr>
<td>5</td>
<td>0.3% PP FRC</td>
<td>0.48</td>
<td>0.88</td>
<td>0.39</td>
<td>1.20</td>
<td>0.095‡</td>
</tr>
</tbody>
</table>

* Predicted chloride threshold in terms of acid-soluble chlorides for regular carbon steel rebar (excluding the effect of surface treatments)

† Chloride threshold of plain concrete predicted from the LIGHTCON model by using Eq. (5.5) with $k_{cr} = 1.25$

‡ Chloride threshold of fiber reinforced concrete predicted from the Fick’s diffusion law using the LIGHTCON model [Eq. (5.3), (5.6), and (5.7)] and the test results in Table 5.1
In the previous section, the LIGHTCON model was modified by assigning new values to the factors, $k_D$ and $k_\alpha$, to account for the test conditions of accelerating corrosion. Next, the influence of fibers on the corrosion initiation was expressed in terms of fiber type and fiber dosages. Since these terms are material related, a modification was made to the material parameters such as was done in the original model with respect to the ratio of water to cementitious materials. An empirical term, consisting of one fiber dosage and two fiber-dependent constants, was proposed to be added to Equations (5.2) and (5.4) to match the model to the test results of the apparent chloride diffusion coefficients in FRCs given in Table 5.2. A modified LIGHTCON model incorporating the factors of the accelerating corrosion test and the fiber effect was expressed as follows.

\[
D_1 = 25000k_D \times \exp \left( -\sqrt{10 \times \left( \frac{PC+FA+7\times SF}{W} \right) \times \left( 1 + a \times (V_f)^b \right)} \right) \text{mm}^2/\text{year} \tag{5.6}
\]

\[
D_a(t) = D_1 \times \left( \frac{t}{t_1} \right)^{-\alpha} = D_1 \times t^{-\alpha} \text{ mm}^2/\text{year} \tag{5.3}
\]

where

\[ W, PC, FA, SF = \text{content of water, cement, fly ash, and silica fume in the concrete by mass} \]

\[ k_D = \begin{cases} 
0.40 & \text{for concrete exposed to marine atmosphere (ATM)} \\
0.60 & \text{for concrete exposed to marine splash zone (SPL)} \\
1.00 & \text{for concrete submerged in seawater (SUB)} \\
1.03 & \text{for concrete in corrosion chamber} 
\end{cases} \]

\[ t_1 = 1 \text{ year and } t = \text{time of exposure (in year)} \]

\[ \alpha = k_\alpha \times \left( 1 - 1.5 \times \left( \frac{W}{PC+FA+7\times SF} \right) \times \left( 1 + a \times (V_f)^b \right)^{-1} \right) \tag{5.7} \]
where

\[ k_\alpha = \begin{cases} 
1.00 & \text{for concrete exposed to marine atmosphere (ATM)} \\
0.10 & \text{for concrete exposed to marine splash zone (SPL)} \\
0.60 & \text{for concrete submerged in seawater (SUB)} \\
0.07 & \text{for concrete in corrosion chamber}
\end{cases} \]

\( V_f \) = fiber volume fraction

\( a = 0.45 \) for cellulose fiber and 1.23 for polypropylene fiber

\( b = 0.74 \) for cellulose fiber and 1.89 for polypropylene fiber

The two constants represented as \( a \) and \( b \) in Eqs. (5.6) and (5.7) represent the influence of fiber type on the chloride diffusion coefficient while the fiber volume fraction amplifies the outcome. In the present study, the constants are validated to the maximum fiber dosage of 0.3%. Figure 5.2 shows a good fit between the chloride diffusion coefficients predicted from the modified model and those obtained from the experiment.

**Figure 5.2** The apparent chloride diffusion coefficients as a function of the fiber volume fraction (lines represent the predicted values and markers represent the experimental results)
By applying the modified Equations into the Fick’s second law of diffusion, a chloride content in FRC at a given time and location is found. It yields the chloride threshold at the location of a rebar which would then determine the time of its corrosion onset. Providing in the present study that a clear concrete cover of rebar is 25 mm and the corrosion initiation results are given in Table 5.1, the chloride threshold values of FRCs was thus achieved and listed in Table 5.2.

5.4.3 Influence of applied flexural loadings

Reinforced concrete beams in bending typically contain cracks when the flexural load exceeds the cracking moment. Load induced cracks in concrete structures have a serious impact on corrosion of reinforcing steel in both initiation and propagation periods. The time to corrosion onset results in Table 5.1 is a clear evidence. Practically speaking a cracked concrete beam has a reduced cover depth depending on the load intensity. In a loaded concrete beam, corrosion will occur sooner. Also, tensile stresses at a crack tip may generate micro-cracks that will also increase chloride diffusion. It is however assumed that chloride diffusion coefficients and the chloride threshold values are load-independent. Load, if create cracking, thus only reduce the cover.

To take the influence of loading into consideration, a depth \( x \) in the Fick’s diffusion law is substituted with an effective depth \( x^* \) as a function of applied load and ultimate load with a power factor \( \lambda \). Furthermore, a fiber effect expressed in terms of the fiber volume fraction is also included. The effective depth function could thus be expressed as follows:
Chapter 5. Role of Fiber Reinforcement on Service Life of Concrete Structures in Marine Environments

\[ x^* = x \times \exp \left( -63 \times \exp \left( -V_f \right) \times \left( \frac{P}{P_u} \right)^\lambda \right) \]  \hspace{1cm} (5.8)

where
\[ x = \text{concrete cover (mm)} \]
\[ P = \text{applying load (kN)} \]
\[ P_u = \text{ultimate strength (kN)} \]
\[ V_f = \text{fiber volume fraction (%)} \]
\[ \lambda = \text{power factor} \begin{cases} 2.8 & \text{for plain concrete} \\ 4.0 & \text{for cellulose FRC} \\ 3.0 & \text{for polypropylene FRC} \end{cases} \]

5.5 Case Studies

Based on the LIGHTCON model and the Fick’s diffusion law, the modified model to predict the corrosion initiation of reinforced concrete beams was developed. It incorporated the influence of an accelerated corrosion environment, fiber reinforcement and flexural loading. In this section, the model was compared with the test results of the experimental study. After that, it was implemented in a comparative study of a bridge deck made of different concrete mixes exposed to a marine environment.

5.5.1 Beam specimens of the laboratory corrosion test with a corrosion accelerated environment

The time to corrosion onset of rebar in plain concrete and FRCs predicted from the modified model was compared with that obtained from the experimental results as shown in Figure
5.3. In the model, the concrete cover of 25 mm, a w/c ratio of 0.55, and the surface chloride contents given in Table 5.2 were employed. For plain concrete, a chloride threshold was calculated from the Eq. (5.5) in the LIGHTCON model. But, for the FRCs, it was from the test data.

Since functions in the modified model are empirical, the predicted results fit well to the experimental results. In non-loaded beam specimens, the corrosion onset of steel takes place slower when fibers are introduced. That is mainly because of the development of lower chloride diffusion coefficients in FRCs. The study strongly indicated that a chloride binding effect occurs in FRCs and contributes to restricting chloride diffusion (Martin-Perez et al. 2000).

At a small applied load, the model expects only a small change in the initiation time. When the load reaches the cracking moment, the initiation time rapidly drops as a consequence of the cracks. The specimens loaded to about 25% of the ultimate strength contain a critical crack so that a corresponding time to corrosion decreases significantly. In the cellulose FRCs, the time reduction is noticeably less which is probably due to the self healing effect. When the applied load approaches 50% of the load capacity, reinforcing steel corrosion is expected in all beam specimens regardless of fiber presence.
5.5.2 Reinforced concrete bridge girders incorporating silica fume and fibers located in a splash zone of marine environment

An example of a reinforced concrete girder in a splash zone of marine environment is considered here. It is generally known that its service life is shortened drastically due to reinforcing steel corrosion. By using the modified model, a variation in time to corrosion is demonstrated in accordance with parameters such as concrete compositions, cover thickness, and stress intensity. In this example, several concrete mixes, i.e. plain concrete, cellulose
FRC at three fiber dosages (0.1% 0.2%, and 0.3%), and silica fume concrete at four cement replacement amounts (2%, 4%, 6%, and 8%) are employed. It is assumed that the w/c ratio of concrete mixes is 0.4 and the surface chloride content is 0.3% w/w of concrete.

For the present demonstration, two case scenarios are considered. One is a non-loaded girder with a variation of concrete cover thickness from 25 mm to 50 mm. The other one is a girder having a cover thickness of 50 mm and being subject to an applied load from 0% to 80% of the ultimate capacity. According to those two scenarios, a predicted time to corrosion onset is illustrated as a function of cover thickness and load intensity as shown in Figures 5.4 and 5.5, respectively.

Figure 5.4 clearly indicates a significant benefit of the concrete cover on the time to corrosion initiation. Increasing of cover thickness enlarges the thickness of barrier between reinforcing steels and chloride laden atmospheres so that chlorides take more time to reach the steel and delay corrosion initiation. Incorporating silica fume and cellulose fiber in concrete is another alternative to achieving a similar positive outcome. The addition of either silica fume or cellulose fiber to plain concrete not only reduces the rate of chloride ingress but also alters the chloride threshold. Due to the micro-filler effect, silica fume creates a denser cementitious matrix that results in a further decrease in water permeability and chloride diffusion. In a similar manner but to a lesser extent, cellulose fibers improve those parameters by providing internal curing. The reduction of a chloride diffusion coefficient in the silica fume concrete is thus superior to that in the cellulose FRC.
Figure 5.4  Predicted time to corrosion onset of reinforcing steel in a concrete bridge girder in a marine splash zone varied with thickness of concrete cover in non-loaded condition

In terms of the chloride threshold, silica fume yields an adverse result. Due to its pozzolanic property, silica fume converts calcium hydroxides to calcium silicate hydrates so that the level of alkalinity in the pore network is lessened. Accordingly, the passive oxide film protecting the steel from corrosion is weakened and the chloride threshold is lowered. Contrary to silica fume, cellulose fiber develops a higher threshold in FRC as a consequence of its chloride binding capacity and an improved interfacial transition zone between cementitious matrix and the reinforcing steel (Ann and Song 2007). Hence the cellulose FRC is more efficient than the silica fume mixed concrete in delaying the initiation of corrosion as shown in Figure 5.4. In any case, both cellulose FRC and silica fume concrete outperform their plain concrete counterparts.

In the second case scenario, an influence of applying loads on the time to corrosion initiation is examined by using the modified model. Since the model assumes a single crack at the mid
span of the girder, an increase in the load widens the crack and thereby lessens an effectiveness of the cover concrete. Regardless of the mix composition, an increase of load intensity applied to the girder shortens the time to corrosion onset as shown in Figure 5.5.

The predicted time starts differently for different concrete mixes depending on their performance in non-loaded condition discussed above. With regard to an increase in the load intensity, the initiation time decreases exponentially. It is to be noted that a power factor of plain concrete is assumed for silica fume concrete. As a result, the plain concrete and the silica fume concrete have the similar falling trend and become ineffectual at the same load intensity of 30%. In addition, the predicted time of silica fume concrete is likely overestimated. The cellulose FRC yields a slower decline and is effective until the load intensity approaches 45%. This result is principally due to the crack bridging and self healing effects of cellulose fibers. Therefore, from a corrosion resisting materials point of view, silica fume concrete is superior to plain concrete but not to cellulose FRC when loads are present.
Figure 5.5 Predicted time to corrosion onset of reinforcing steel in a concrete bridge girder in a marine splash zone varied with applied loads (concrete cover = 50 mm)

5.6 Conclusions

The effect of fiber reinforcement and load-induced cracks on the time to corrosion initiation is predicted using a modified LIGHTCON model. The modifications are achieved empirically using the experimental results obtained in this thesis. Firstly, some new factors corresponding to an accelerated corrosion in the laboratory are developed to adjust the diffusion coefficient in the model. Next, an expression identifying the effect of fiber reinforcement is proposed into a mix composition part of the model. In the Fick’s diffusion,
a cover depth is also replaced with an effective cover depth to represent an influence of applied loads. A prediction of the modified model yields results that are in good agreement with the experiments.

Further, the model is applied to the case of a reinforced concrete girder to illustrate the performance of cellulose fiber and silica fume. A condition of a marine splash zone is assumed. The model points out that a prolonged service life of the girder is achieved in both cases. The cellulose FRC is superior to the silica fume concrete, especially when cracks are involved. Last, but not least, the model also shows that the load intensity has a critical impact on the service life of concrete structures.
5.7 References


Chapter 6

Conclusions and Recommendations

6.1 Concluding Remarks

6.1.1 Pore refinement

The effect of cellulose fibers on a pore structure of cement pastes was investigated using Thermoporometry (TP) and Mercury Intrusion Porosimetry (MIP) methods. Two fiber dosages of 0.1% and 0.3% volume fractions were tested. The results indicate that there is an improvement in the pore structure due to the addition of cellulose fiber in the form of pore refinement (see Figure 6.1) and reduced porosity (see Figure 6.2). These observations correspond well with the previously noted reduction in water permeability due to fiber addition.
Figure 6.1  The pore sizes distributions in plain and fiber reinforced cement pastes based on thermoporometry and mercury intrusion porosimetry

Figure 6.2  Relationship between porosity and permeability ratio of FRC, with permeability data from the study by Banthia and Bhargava (2007)
6.1.2 Transport properties

The influences of the cellulose and polypropylene fiber on chloride diffusion in concrete were investigated in several experiments. First, the rapid chloride permeability test (RCPT) was performed. Then, test specimens after being exposed to the chloride bulk diffusion test (the submersion in salt solution for 90 days) were examined for chloride penetration using the silver nitrate spray test and the chloride profile test. The test results were reported in the Chapter 3. The beam specimens exposed to the accelerated corrosion (wet-dry cycles in salt solution in the Chapter 4) were also examined in the chloride profile test and the results were reported in the Chapter 5. According to the results of those experiments, the following conclusions were drawn.

6.1.2.1 Rapid chloride permeability test (RCPT)

Using the RCPT, the chloride permeability of concrete samples can be quickly evaluated. The RCPT results were represented with the total amount of charge passing the test specimens as shown in Figure 6.3. According to the classification of the ASTM C 1202, the chloride permeability is moderate in the plain concrete samples and is increased to moderate-to-high in the FRC samples. In addition, the chloride permeability is higher in the cellulose FRC than the polypropylene FRC, and is increased with the fiber dosages as shown in Figure 6.4. The interfacial zones between fibers and cement paste probably provide the additional connected routes for chloride transport in concrete. The variation of the results in the FRC samples is also greater than in the plain concrete probably because of the random nature of the fiber distribution.
Figure 6.3 Charge passed in rapid chloride ion permeability test (RCPT). The results are listed in the format: average ± standard deviation (coefficient of variation).

Figure 6.4 Influence of fiber volume fraction on the charge passed in rapid chloride ion permeability test (RCPT)
6.1.2.2 **Silver nitrate spray test**

The silver nitrate spray test results as shown in Figure 6.5 revealed the chloride penetration fronts at which the color was changed from light yellow to reddish brown in the concrete specimens. The depths from the exposed surfaces to the penetration fronts were measured and plotted in Figure 6.6, which indicated that the chloride penetration front in the FRC samples (varied from 25 to 32 mm) is deeper than in plain concrete (24 mm). At the depth of the chloride penetration front, the mean concentrations of calculated total and free chlorides of all mixes are approximately 0.06% and 0.04% by weight of concrete. Hence, the silver nitrate spray test can be used as a preliminary inspection to approximate the depth where a significant content of penetrating chlorides is present in concrete.

![Figure 6.5](image)

**Figure 6.5** Chloride penetration fronts as detected by the silver nitrate spray for various mixtures (from left to right, mix #1: plain concrete, mix #2: 0.1% cellulose FRC, mix #3: 0.3% cellulose FRC, mix #4: 0.1% polypropylene FRC, and mix #5: 0.3% polypropylene FRC).
Penetration depth of chloride in FRC from the silver nitrate spray test

6.1.2.3 Chloride profile test (under the exposure of chloride bulk diffusion)

The chloride profile test results showed the distributions of the total and free chloride concentrations along the penetrating depths in concrete specimens, which was subsequently converted to the diffusion coefficients using the Fick’s law of diffusion. Based on the exposure of chloride bulk diffusion, the coefficient of total chloride diffusion is increased with an increase of fiber dosages while the coefficient of free chloride diffusion is decreased as shown in Figure 6.7. It is noted that the effect of the cellulose fiber is greater than that of the polypropylene fiber and the result of total chloride diffusion coefficient has a similar trend to the charge passed in the RCPT results as shown in Figure 6.4. Also, the diffusion coefficients and the surface chloride contents were tabulated in Table 6.1.
Chapter 6. Conclusions and Recommendations

(a) Coefficients of Total Chloride Diffusion

(b) Coefficients of Free Chloride Diffusion

Figure 6.7 Coefficients of total and free chloride diffusion of FRC
Table 6.1  Coefficients of chloride diffusion of specimens subjected to chloride bulk diffusion exposure

<table>
<thead>
<tr>
<th>Mix#</th>
<th>Plain Concrete</th>
<th>0.1% CL FRC</th>
<th>0.3% CL FRC</th>
<th>0.1% PP FRC</th>
<th>0.3% PP FRC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coefficient of Total Chloride Diffusion, $D_{apparent}$, ($x10^{-7}$ cm²/s)</td>
<td>1.34</td>
<td>1.53</td>
<td>1.59</td>
<td>1.37</td>
<td>1.41</td>
</tr>
<tr>
<td>Total Chloride at Concrete Surface, $C_0$, Total Chloride (% w/w of concrete)</td>
<td>0.46</td>
<td>0.48</td>
<td>0.44</td>
<td>0.5</td>
<td>0.48</td>
</tr>
<tr>
<td>Coefficient of Free Chloride Diffusion, $D_{apparent}$, ($x10^{-7}$ cm²/s)</td>
<td>1.58</td>
<td>1.49</td>
<td>1.10</td>
<td>1.52</td>
<td>1.35</td>
</tr>
<tr>
<td>Free Chloride at Concrete Surface, $C_0$, Free Chloride (% w/w of concrete)</td>
<td>0.26</td>
<td>0.27</td>
<td>0.27</td>
<td>0.26</td>
<td>0.26</td>
</tr>
</tbody>
</table>

6.1.2.4  Chloride profile test (under the exposure of wet-dry cyclic condition in saline environment)

The chloride profiles of the beam specimens exposed to the accelerated corrosion condition for 56 weeks were also investigated. The results of the diffusion coefficients and surface chloride contents of FRC and plain concrete exposed to the wet-dry cyclic condition in saline environment were listed in Table 6.2. The chloride diffusion coefficients found in the specimens in such case are different from those found in the case of the bulk diffusion.

From the results, it is noted that fibers become very effective in the wet and dry cyclic condition to reduce the diffusion of both total and free chlorides in the FRC samples. The reduction of chloride diffusion is directly proportional to the fiber dosages. Clearly, the exposure condition altered the coefficients of diffusion since it changed the moisture distribution in concrete and thereby the process of chloride transport. During wetting and drying periods, chlorides do not move merely by diffusion but adsorption as well. It was noticed that, in drying periods, surfaces of FRC specimens were more moist compared to
plain concrete. When a wetting process is repeated, plain concrete would then adsorb sodium chloride solutions more quickly and would allow a faster penetration of chlorides than FRC. It is plausible that the adsorption somewhat affects the diffusion coefficients of total chlorides measured in the corrosion test.

Another possible reason of why the diffusion coefficients of total chlorides in plain concrete are greater than FRC is the presence of shrinkage cracks in plain concrete. Fibers can efficiently minimize shrinkage cracks in concrete and the cracks thus affect the penetration of chloride particularly in plain concrete more than in FRC (Table 6.2). The large beam specimens and the wetting and drying environment created more severe shrinkage crack potential in the wet dry specimens compared to ponded specimens.

### Table 6.2  Coefficients of chloride diffusion of specimens subjected to the wet-dry cyclic exposure in saline environment

<table>
<thead>
<tr>
<th>Mix#</th>
<th>Plain Concrete</th>
<th>0.1% CL FRC</th>
<th>0.3% CL FRC</th>
<th>0.1% PP FRC</th>
<th>0.3% PP FRC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coefficient of Total Chloride Diffusion, $D_{apparent}$, ($x10^{-7}$ cm$^2$/s)</td>
<td>1.15</td>
<td>0.97</td>
<td>0.79</td>
<td>1.11</td>
<td>0.88</td>
</tr>
<tr>
<td>Total Chloride at Concrete Surface, $C_0$, Total Chloride (% w/w of concrete)</td>
<td>0.48</td>
<td>0.48</td>
<td>0.48</td>
<td>0.48</td>
<td>0.48</td>
</tr>
<tr>
<td>Coefficient of Free Chloride Diffusion, $D_{apparent}$, ($x10^{-7}$ cm$^2$/s)</td>
<td>1.56</td>
<td>1.27</td>
<td>1.07</td>
<td>1.39</td>
<td>1.20</td>
</tr>
<tr>
<td>Free Chloride at Concrete Surface, $C_0$, Free Chloride (% w/w of concrete)</td>
<td>0.38</td>
<td>0.39</td>
<td>0.38</td>
<td>0.39</td>
<td>0.39</td>
</tr>
</tbody>
</table>

6.1.2.5   Chloride binding

The results of the chloride binding test indicated that the chloride binding capacity of the fibers became prominent in the NaCl solution of 0.6 M initial chloride concentration and
was increased with the fiber dosages (see Figure 6.8). It was further implied that the binding capacity of the fibers is dependent on chloride concentration and fiber dosage. Cellulose fibers have a greater binding capacity than the polypropylene fibers. Such chloride binding effect of the fibers would cause the differences of the chloride diffusion coefficients between the plain concrete and the FRC samples.

Fibers clearly have an effect on chloride diffusion in concrete. It is postulated that fibers cause more interfacial transition zones, which become additional interconnected paths for the chloride transport. Thus, the chlorides ingress in the FRC happens more quickly than in the plain concrete. However, the chloride binding effect in FRC allows for only limited amounts of chlorides to be available for rebar corrosion.

![Figure 6.8](image.png)  
**Figure 6.8**  The bound chloride of the PC and FRC pastes in the NaCl solution at various initial chloride concentrations (0.1, 0.3, and 0.6 molar) after the test duration of 21 days
6.1.3 Electrochemical measurements

The corrosion of the test beams exposed to the accelerated corrosion was monitored for 56 weeks using three electrochemical measurements: the half-cell potential, the galvanic current, and the linear polarization resistance. An initiation of corrosion was assumed either when a half-cell potential was below –350 mV (versus CSE) or when a galvanic current density and a corrosion current density were increased rapidly. Based on such assumption, the times of corrosion initiation of the test beams were determined. They are plotted in Figure 6.9 and tabulated in Table 6.3.

![Figure 6.9](image)

**Figure 6.9** Time to corrosion onset in FRC beams subjected to flexural loads (noting that a time to corrosion in 0.3% CL FRC beam in a case of no loading was assumed to represent its superior performance as at the end of the test corrosion was not yet active)
Table 6.3  Time to corrosion onset in FRC (weeks)

<table>
<thead>
<tr>
<th>Mix#</th>
<th>Plain Concrete</th>
<th>0.1% CL FRC</th>
<th>0.3% CL FRC</th>
<th>0.1% PP FRC</th>
<th>0.3% PP FRC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-Stressed Beams</td>
<td>27</td>
<td>56</td>
<td>&gt;56</td>
<td>41</td>
<td>47</td>
</tr>
<tr>
<td>Stressed Beams with a Flexural Load at 25% of Ultimate Strength</td>
<td>3 38</td>
<td>51</td>
<td>8</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>Stressed Beams with a Flexural Load at 50% of Ultimate Strength</td>
<td>1 1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

6.1.3.1  Time to corrosion initiation of the non-loaded beam specimens

The results of the non-loaded beams indicated that the corrosion became active in the FRC much slower than in plain concrete. Fibers thus delay the initiation of steel rebar corrosion proportionally to their dosage. Between the two fibers, the cellulose fiber is seen as more effective than polypropylene fiber. The times to corrosion onset of the test beams are in a good agreement with the chloride diffusion coefficient measured in these beams (see Table 6.2). It is noted that the corrosion in the 0.1% cellulose FRC samples had just started at the end of the test (56 weeks) while the corrosion in the 0.3% cellulose FRC samples was still passive.

6.1.3.2  Time to corrosion initiation of the loaded beam specimens

The influence of the flexural loadings on the corrosion initiation in the beams specimens was also investigated. The beams were loaded in flexure at approximately 25% and 50% of ultimate capacity in an accelerated corrosion chamber.

In the case of the 25% flexural loading, the cracks that occurred in the beam specimens were in the range of 0.25 - 0.30 mm. The corrosion onset in these beams started earlier than the
non-loaded beams and showed that the stress-induced cracks have a significant effect on the corrosion. Similar to the results of the non-loaded beams, the results indicated that fiber reinforcement impedes the onset of steel corrosion, especially the cellulose fibers. The bridging fibers at the crack tips probably created the self healing effect and resulted in the delay of the corrosion onset.

When the applied flexural load was 50%, the cracks were very wide varying between 0.60 and 0.80 mm. Once the beams were exposed to the chamber, chlorides instantaneously attacked steel reinforcement through such large cracks. The results indicated that, either in both plain concrete and FRC, corrosion initiated within the first week of the test. Fibers are therefore ineffective if cracks are excessively large.

### 6.1.4 Predicting the FRC performance using the modified LIGHTCON model

Based on the accelerated corrosion test, one could see a remarkable performance of the fiber reinforcement as well as the adverse effect of the applied loads on the onset of steel corrosion. In the present study, a service life model called LIGHTCON model was modified to take these two factors into account.

The modifications were achieved empirically based on the experimental results of the corrosion test. Firstly, some new factors corresponding to the acceleration of corrosion in laboratory were developed to adjust the diffusion coefficient in the model. Next, the expression identifying the effect of fibers was proposed into the mix composition part of the model. After that, to represent the influence of the applied loads, the effective cover depth
was proposed to replace the cover depth in the solution of Fick’s law of diffusion. Using the modified model, the prediction of the time to corrosion onset was seen to be in good agreement with the experimental results as shown in Figure 6.10.

Further, the model was applied to the case of a reinforced concrete girder to illustrate the performance of cellulose fiber and silica fume in a marine splash zone. The model points out that a prolonged service life of the girder is achieved in both cases as shown in Figure 6.11. However, when the load-induced cracks are involved, cellulose fibers are superior to silica fume. Last, but not least, the model also shows that the load intensity has a critical impact on the service life of concrete structures as shown in Figure 6.12.

![Figure 6.10](image)

**Figure 6.10** Time to corrosion initiation of steel in plain concrete and FRC beams subject to flexural loads from the modified model compared to the experimental results
Figure 6.11  Predicted time to corrosion onset of reinforcing steel in a concrete bridge girder in a marine splash zone varied with thickness of concrete cover in non-loaded condition

Figure 6.12  Predicted time to corrosion onset of reinforcing steel in a concrete bridge girder in a marine splash zone varied with applying loads (concrete cover = 50 mm)
6.2 Recommendation for Future Works

6.2.1 Influence of fibers on chloride binding should be investigated further.

An effective chloride binding can significantly hinder the diffusion of chlorides in concrete. In the process of binding, some of the total chlorides (the so-called bound chlorides) transporting through the media are arrested and only the remainder of the total chlorides (i.e. free chloride) can diffuse through the pore solution. Chlorides can be bound both chemically and physically within the microstructure of concrete. Therefore, chloride diffusion can be decreased if the chloride binding is encouraged. Chloride binding however may be reversed in some cases such as during carbonation, in which case there will be more free chlorides to increase the chances of steel corrosion. This will have a clear influence on the service life of concrete structures.

There are many factors that affect chloride binding. Not only does a C₃A content appear to be a decisive factor but Cl⁻, OH⁻, and SO₄²⁻ contents also have significant effects. Further, the binding capacity is increased when the tricalcium aluminate content is increased, the total chloride content is increased, the hydroxide content is increased, and the sulfate content is decreased. Many other studies on chloride binding also investigated the influence of cement types and hydroxide ions. Recently, an overview of chloride binding has been extensively reviewed by Yuan et al. (2009).

From the results described in Chapter 3, fibers showed a remarkable capability of chloride binding. But, the exact mechanisms by which fibers bind chlorides are not understood.
There are a couple possible mechanisms. First, as the fibers are treated to be alkali resistant, special chemicals are applied on its surface that may chemically bind with chlorides. Secondly, the small size and high specific surface area of fibers create a vast amount of interfacial transition zones that could also cause a physical binding.

In addition, water-soluble chlorides as measured in this study do not truly represent the free chloride. A pore press method seems to be more suitable for measuring free chlorides. In an experimental study, a comparison between the pore press method and an extraction method (used for determining water-soluble chlorides) showed no simple relationship between their results (Haque and Kayyali 1995). Unfortunately, it is not easy to conduct the pore press method. An alternative testing method for determining free chlorides was proposed by Luping and Nilsson (1993). It measures free chlorides in a control solution with known chloride concentration when mixed with a pulverized concrete sample.

Since chloride binding always affects chloride diffusion and fibers have some binding ability, it is necessary to clarify the role of fibers on the binding mechanism. Once the actual behavior of fibers is known, it is possible to formulate a mechanistic model of chloride diffusion in FRC, which can predict the service life of concrete structures more precisely. Understanding these mechanisms may also help us develop fibers with improved performance. Therefore, it is suggested to investigate fibers in more details relevant to chloride binding.
6.2.2 *Investigating the role of fibers in controlling corrosion induced cracking*

Cracks can influence corrosion, and vice versa. Even in sound concrete, corrosion can occur but at a slower rate. Once corrosion starts corrosion products (rust) accumulate on the corroding steel and exert expansive stresses on the surrounding concrete causing cracking. These cracks can exacerbate corrosion and a significant number of studies regarding corrosion-induced cracking in concrete were conducted. An extensive review of both experiment and modeling on corrosion-induced cracking can be found elsewhere (Aligizaki 2006; Chernin, Val, and Volokh 2010).

There are many factors affecting corrosion-induced cracking. First is the porosity of an area around a corroded rebar. In this area, corrosion products expand and diffuse through concrete pores. If concrete is very dense, the expansion and diffusion will be confined and thereby a radial pressure will be quickly built up at the steel/concrete interface. Stiffness of concrete is another important factor. The pressure accumulated is space dependent – the pressure is increased when the space is limited. A low stiffness concrete that yields higher strain would be able to carry the pressure for a longer time. Once an elastic strain reaches a threshold level, cracks will be formed in the inner concrete around the rebar. The cracks then propagate toward outer concrete. In this state, the propagation is controlled mainly by the thickness and the strength of cover concrete.

In a numerical study (Ahmed, Maalej, and Mihashi 2007), a simulation of corrosion-induced cracking in ordinary concrete and fiber reinforced concrete was demonstrated. It was found that the fiber reinforced concrete exhibited a better performance due to its higher tensile
strain capacity. It is likely that, in practice, an addition of fibers in concrete will substantially enhance the concrete durability. Further studies to investigate the role of fibers on corrosion propagation will be of most interest.

6.2.3 Field studies on the influence of fibers on corrosion in actual structures

As the present study was carried out only under laboratory conditions, it is of interest to conduct field studies on the influence of fibers on corrosion in actual structures. Field conditions typically comprise of many variables such as the type and content of deleterious substances, temperature, relative humidity, construction practices, applied loading, structural design, etc. Concrete that is subjected to the carbonation effect, sulphate attack and alkali-silica reaction can prematurely lose its protection to the corrosion of steel rebar. High temperature and moderate humidity can accelerate the rate of chloride diffusion as well as the rate of corrosion. Poor quality control and inadequate design of concrete construction can also cause a severe corrosion in concrete structures. In addition, concrete cracks tend to intensify the damage of steel corrosion. The variation of those variables can result in different corrosion outcomes. Consequences of such variation on fiber performances are still unknown. Therefore, corrosion assessments on FRC structures exposed to various corrosive environments should be considered in field studies.
6.2.4 Studies on other fibers and hybridization of fibers in the role of corrosion inhibitors

The fibers investigated in the present study were limited to two fiber types: cellulose and polypropylene. Their shapes and physical properties were unique to their producers. While they both performed well, it is of interest to investigate other types of fibers. A number of various fibers varying in geometrical configurations and physical properties are available in markets today that may yield superior performances on the delay of corrosion onset than the two fibers tested here.

To bridge large cracks induced by extensive loadings, macro fibers having greater cross sectional areas and lengths are more effective. At a certain fiber dosage, the increase of fiber size will reduce the number of fibers in concrete. Since the chloride binding ability depends on the amount of fibers, large fibers will have reduced chloride binding ability. Hence, the change of fiber size will affect the fiber performance. The optimization of fiber dimensions is thus necessary and should be studied. Furthermore, to achieve most benefit of fibers on both crack bridging and chloride binding, the concept of fiber hybridization should be considered. A combination of different fibers such as a large fiber (macro-fiber) and a small fiber (micro-fiber) can boost the fiber performance on inhibiting the initiation of rebar corrosion.
6.2.5  Use of chloride binding fibers in repair materials

Chloride induced corrosion of steel rebar is a serious problem affecting concrete structures. The symptoms of deterioration appear in many forms depending on the severity of corrosion and may range from mere reddish brown strains on concrete surfaces to cracks, delamination, and spalling. When these occur, a repair work must be considered.

It is highly feasible to use fiber reinforced cementitious composites in repair applications. It is generally known that an elastic compatibility between the repair material and the substrate materials is essential. The addition of the cellulose and polypropylene fibers does not alter the elastic modulus so that these FRC materials are highly compatible elastically with old concrete. Also, they have less shrinkage, and low water permeability, which are both very useful characteristics for repair materials. In the present study, it was found that additionally fibers have chloride binding ability. This advantageous feature could add an extra value to FRC materials when used as repair materials. Further studies on the use of the FRC as a repair material having chloride-binding fibers should therefore be conducted.
6.3 References


Appendix A

Results of the Thermal Scan on Cellulose Fiber Reinforced Concrete Using Differential Scanning Calorimeter

Figure A.1  Heat flow of plain concrete samples during the freezing stage in the differential scanning calorimeter
Appendix A. Results of the Thermal Scan on Cellulose Fiber Reinforced Concrete Using Differential Scanning Calorimeter

Figure A.2  Heat flow of 0.1% cellulose FRC samples during the freezing stage in the differential scanning calorimeter

Figure A.3  Heat flow of 0.3% cellulose FRC samples during the freezing stage in the differential scanning calorimeter
Appendix B

Profiles of Acid-Soluble and Water-Soluble Chlorides after Bulk Diffusion Test

Figure B.1  Chloride profiles of plain concrete exposed to the bulk diffusion for 90 days
Figure B.2  Chloride profiles of 0.1% cellulose FRC exposed to the bulk diffusion for 90 days
Figure B.3 Chloride profiles of 0.3% cellulose FRC exposed to the bulk diffusion for 90 days
Figure B.4  Chloride profiles of 0.1% polypropylene FRC exposed to the bulk diffusion for 90 days
Figure B.5  Chloride profiles of 0.3% polypropylene FRC exposed to the bulk diffusion for 90 days
Appendix C

Profiles of Acid-Soluble and Water-Soluble Chlorides after Accelerating Corrosion Test

Figure C.1  Profile of acid-soluble chlorides in plain concrete exposed to the accelerating corrosion chamber for 56 weeks
Appendix C. Profiles of Acid-Soluble and Water-Soluble Chlorides after Accelerating Corrosion Test

Figure C.2  Profile of acid-soluble chlorides in 0.1% cellulose FRC exposed to the accelerating corrosion chamber for 56 weeks

Figure C.3  Profile of acid-soluble chlorides in 0.3% cellulose FRC exposed to the accelerating corrosion chamber for 56 weeks
Appendix C. Profiles of Acid-Soluble and Water-Soluble Chlorides after Accelerating Corrosion Test

Figure C.4  Profile of acid-soluble chlorides in 0.1% polypropylene FRC exposed to the accelerating corrosion chamber for 56 weeks

Figure C.5  Profile of acid-soluble chlorides in 0.3% polypropylene FRC exposed to the accelerating corrosion chamber for 56 weeks
Figure C.6  Profile of water-soluble chlorides in plain concrete exposed to the accelerating corrosion chamber for 56 weeks

Figure C.7  Profile of water-soluble chlorides in 0.1% cellulose FRC exposed to the accelerating corrosion chamber for 56 weeks
Figure C.8  Profile of water-soluble chlorides in 0.3% cellulose FRC exposed to the accelerating corrosion chamber for 56 weeks

Figure C.9  Profile of water-soluble chlorides in 0.1% polypropylene FRC exposed to the accelerating corrosion chamber for 56 weeks
Figure C.10  Profile of water-soluble chlorides in 0.3% polypropylene FRC exposed to the accelerating corrosion chamber for 56 weeks.
Appendix D

Details of the Modification of the LIGHTCON Model

In this section, the LIGHTCON model and the modification of the model to include the effect of fiber reinforcement and applying loads was explained more in details. It is an extension of the chapter 5 so many tables and figures in the chapter 5 were referred here.

D.1 The LIGHTCON Model

The LIGHTCON model is a service life model regarding an initiation of steel corrosion based on time-dependent chloride diffusivity. Originally it was proposed by Maage et al. (1995) and its details of formulation was then published publicly one year later (Maage et al. 1996). The model was formulated on a basis of the following findings;

- Chloride diffusion coefficient achieved is decreasing with time.
- Chloride content of the near-to-surface layer of the exposed concrete surface is increasing with time. For two specific conditions of splash zone and submersion in seawater, it can be considered a constant after approximately 2-5 years of exposure.
Both of the parameters above are depending on the composition of concrete and their environments.

A test for determining a coefficient of chloride diffusion was required as an input in the original model. Since then more experimental results of chloride diffusion were reported. Based on test data of “one-year diffusion coefficient” (Sandberg 1995), the model was thus revised with an addition of an empirical function to predict a one-year chloride diffusion coefficient. It was well described in a book written by Poulsen and Mejlbro (2006). The revised model requires the following input parameters and assumptions.

**D.1.1 Input parameters**

- The age of a concrete structure at the time of inspection
- The age of a concrete structure at the time of first exposure to chloride
- The composition of concrete
- The exposure conditions, i.e. marine atmosphere (ATM), marine splash (SPL), and submerging in seawater (SUB)
- The chloride profile of concrete at an inspection time

**D.1.2 Assumptions**

- Chloride $C$ in concrete is here defined as a total, acid soluble chloride.
- Transport of chloride in concrete takes place by diffusion.
- The chloride flux $F$ is proportional to the gradient of chloride. The factor of proportionality is an achieved chloride diffusion coefficient $D$. 
• An achieved chloride diffusion coefficient $D$ depends on time, a composition of concrete, and an environment.

• A chloride concentration at the surface of concrete (as a boundary condition) $C_s$ is constant, i.e. independent of time, but it depends on a composition of concrete and an environment.

• An initial chloride content of concrete $C_i$ is uniformly distributed at time of the first chloride exposure.

• The relations used for the determinative parameters with respect to the environment, the time, and the composition of the concrete are documented at the Träslövsläge Marine Exposure Station on the west coast of Sweden (south of Gothenburg).

\[D.1.3\] \textbf{Mass balance of chloride in concrete}

The equation of mass balance (equilibrium) for chloride in concrete is expressed by Fick’s general law of diffusion,

\[ \frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial C}{\partial x} \right) \]  

(D.1)

where $C$ is the chloride content at the locality $x$ at time $t$ and $D$ is the chloride diffusion coefficient which may depend on the time $t$, the locality $x$, the chloride content $C$, and the composition and environment of the concrete. It is, however, an assumption of the LIGHTCON model that the chloride diffusion coefficient $D$ is independent of the locality $x$ and the chloride content, though it may depend on time.
The solution of the Fick’s law of diffusion is simplified by Crank (1975) as follows.

\[ C(x,t) = C_i + (C_s - C_i) \text{erfc} \left( \frac{x}{2\sqrt{Dt}} \right) \]  

(D.2)

where \( \text{erfc}(u) \) is a complementary of the error function,

\[ \text{erf}(u) = \frac{2}{\sqrt{\pi}} \int_{-\infty}^{u} e^{-t^2} dt \]

### D.1.4 Predicting of chloride diffusion coefficients

In this model, the relationship among a chloride diffusion coefficient, a concrete composition, and an environment is formulated from the experimental results after 1 year of exposure at the Träslövsläge Marine Exposure Station. It expresses the chloride diffusion coefficient after 1 year of exposure \( D_1 \) as a function of the composition of cementing materials and the environments as follows.

\[ D_1 = 25000k_D \times \exp \left( -\sqrt{10 \times \frac{PC+FA+7 \times SF}{W}} \right) \text{mm}^2/\text{year} \]  

(D.3)

where

- \( W = \) content of water in the concrete
- \( PC = \) content of cement in the concrete
- \( FA = \) content of fly ash in the concrete
- \( SF = \) content of silica fume in the concrete

- \( k_D = \begin{cases} 0.4 & \text{for concrete exposed to marine atmosphere (ATM)} \\ 0.6 & \text{for concrete exposed to marine splash zone (SPL)} \\ 1.0 & \text{for concrete submerged in seawater (SUB)} \end{cases} \)

The chloride diffusion coefficient is time-dependent and is expressed mathematically by a power function as follows.
\[ D_{a}(t) = D_1 \times \left( \frac{t}{t_1} \right)^{-\alpha} = D_1 \times t^{-\alpha} \text{ mm}^2/\text{year} \] (D.4)

where
\[ t_1 = 1 \text{ year and } t = \text{time of exposure} \]

\[ \alpha = k_\alpha \times \left( 1 - 1.5 \times \left( \frac{W}{PC+FA+7\times SF} \right) \right) \] (D.5)

\[ k_\alpha = \begin{cases} 1.0 \text{ for concrete exposed to marine atmosphere (ATM)} \\ 0.1 \text{ for concrete exposed to marine splash zone (SPL)} \\ 0.6 \text{ for concrete submerged in seawater (SUB)} \end{cases} \]

In addition, the LIGHTCON model provides an empirical function in Eq. (D.6) to estimate a chloride threshold level (in a unit of percentage by weight of binders) of concrete exposed to marine environments.

\[ C_{cr} = k_{cr} \times \exp \left( -1.5 \times \frac{W}{PC-1.4\times FA-4.7\times SF} \right) \] (D.6)

where
\[ k_{cr} = \begin{cases} 1.25 \text{ for concrete exposed to marine atmosphere (ATM)} \\ 1.25 \text{ for concrete exposed to marine splash zone (SPL)} \\ 3.35 \text{ for concrete submerged in seawater (SUB)} \end{cases} \]

**D.2 Modification of the LIGHTCON Model for the Accelerating Corrosion Environment**

In a previous study of corrosion test (Chapter 4), reinforced concrete beams made of plain concrete and four different FRCs were exposed to a weekly cyclic wet and dry condition in a saline atmosphere to accelerate an outset of rebar corrosion. They simultaneously
maintained in third point bending loads of 0, 15, and 30 kN by using a loading jig. Reinforcing steels in the beams were electrochemically monitored by means of half-cell potential, galvanic current, and linear polarization resistance for 56 weeks. According to results of those measurements, a time at which corrosion of the steel started was identified and given in 0.

After the exposure of 56 weeks, a profile of total and free chloride concentrations was measured and then apparent and effective coefficients of chloride diffusion were calculated, respectively. A plain concrete mix was investigated in comparison to the four fiber reinforced concretes. The chloride contents on surfaces of the five mixes were also estimated during a curve fitting. The diffusion coefficients were decreased as the fiber was increased. The results of the diffusion coefficient of five mixes were given in Table 5.2.

None of exposures in the LIGHTCON model was applicable to the testing condition used in this corrosion test since it was conducted in an accelerating corrosion atmosphere. Hence, before the model could be implemented to predict a variation of the experimental results, a modification was necessary.

Considering the plain concrete beam, the basic input parameters were as follows.

\[ \frac{w}{pc} = 0.55 \]

\[ x = 25 \text{ mm} \]

\[ D_a = 1.15 \times 10^{-7} \text{ cm}^2/\text{s} \]

\[ t = 56 \text{ weeks (or 1.074 year)} \]
$t_{cr} = 27$ weeks (or 0.5178 year)

$C_0 = 0.48 \% \text{ w/w concrete}$

It was assumed that the constant $k_{cr}$ of the ATM condition ($k_{cr} = 1.25$) is applicable to the laboratory accelerating corrosion condition. Using the Eq. (D.6), the chloride threshold of the plain concrete beam was then estimated as 0.0765\% w/w concrete.

In this particular case, the chloride threshold level was increased by 25\% because the tested rebar was initially sandblasted to remove mill scale (Mohammed and Hamada 2006).

$C_{cr}$ of plain concrete = 0.0956 \% w/w concrete

Once a chloride threshold was set, new factors, i.e. $k_D$ in the Eq. (D.3) and $k_\alpha$ in the Eq. (D.5), were sought out to match the model to the test results (i.e. the apparent coefficient of chloride diffusion and the time to corrosion onset) of the plain concrete in the corrosion accelerating chamber.

Using the Eq. (D.2), a coefficient of chloride diffusion at the time of corrosion initiation in plain concrete (at 27 weeks) was reckoned, i.e. $D_a$ of plain concrete = 1.1607e-7 cm$^2$/s.

By substituting $D_a(t = 27\text{ weeks})$ and $D(t = 56 \text{ weeks})$ in the Eq. (D.4), the factor $\alpha = 0.0127$ was found. According to that factor, the Eq. (D.5) yielded the parameter $k_\alpha = 0.07$ for the accelerating corrosion condition.

Then, using the Eq. (D.4) could determine the $D_1$ of the plain concrete in the accelerating corrosion condition, which was equal to 1.1510e-7 cm$^2$/s.
From the Eq. (D.3), it was then found that the parameter $k_D$ is equal to 1.03.

### D.3 Influence of Fiber Reinforcement

In previous section, the LIGHTCON model was adapted by assigning a new value of the factors, $k_D$ and $k_\alpha$, to suit the test condition of accelerating corrosion. Next, the influence of fibers on the corrosion initiation was expressed in terms of fiber types and fiber dosages. Since these terms are material related, a modification was made to a material parameter such as a ratio of water to cementitious materials. An empirical term consisting of one fiber dosage and two fiber-dependent constants was proposed into the Equations (D.3) and (D.5) to match the model to the test results of the apparent chloride diffusion coefficients in FRCs given in Table 5.2. A modified LIGHTCON model incorporating the factors of the accelerating corrosion test and the fiber effect was expressed as follows.

$$
D_1 = 25000k_D \times \exp \left( - \sqrt{10 \times \left( \frac{PC + FA + 7 \times SF}{W} \right) \times \left( 1 + a \times (V_f)^b \right)} \right) \text{mm}^2/\text{year} \tag{D.7}
$$

$$
D_\alpha(t) = D_1 \times \left( \frac{t}{t_1} \right)^{-\alpha} = D_1 \times t^{-\alpha} \text{mm}^2/\text{year} \tag{D.4}
$$

where

$W, PC, FA, SF =$ content of water, cement, fly ash, and silica fume in the concrete by mass

$$
k_D = \begin{cases} 
0.40 & \text{for concrete exposed to marine atmosphere (ATM)} \\
0.60 & \text{for concrete exposed to marine splash zone (SPL)} \\
1.00 & \text{for concrete submerged in seawater (SUB)} \\
1.03 & \text{for concrete in corrosion accelerating corrosion}
\end{cases}
$$

$t_1 = 1$ year and $t =$ time of exposure
\[
\alpha = k_\alpha \times \left(1 - 1.5 \times \left(\frac{W}{P_C + F_A + 7 \times S_F}\right) \times \left(1 + a \times (V_f)^b\right)^{-1}\right)
\]  

(D.8)

\[k_\alpha = \begin{cases} 
1.00 & \text{for concrete exposed to marine atmosphere (ATM)} \\
0.10 & \text{for concrete exposed to marine splash zone (SPL)} \\
0.60 & \text{for concrete submerged in seawater (SUB)} \\
0.07 & \text{for concrete in corrosion accelerating chamber} 
\end{cases} \]

\[V_f = \text{fiber volume fraction}\]

\[a = 0.45 \text{ for cellulose fiber and 1.23 for polypropylene fiber}\]

\[b = 0.74 \text{ for cellulose fiber and 1.89 for polypropylene fiber}\]

The two constants represented as \(a\) and \(b\) in Eq. (D.7) and (D.8) cope with an influence of fiber types on a chloride diffusion coefficient while the fiber volume fraction amplifies an outcome. In present study, the constants are validated to the maximum fiber dosage of 0.3%.

Figure 5.2 shows a good fit between the chloride diffusion coefficients predicted from the modified model and those received from the experiment.

By applying the modified equations above into the Fick’s second law of diffusion, a chloride content in FRC at a given time and location can be figured out. If a location of a rebar and a time of its corrosion onset are given, a chloride threshold is then yielded. Providing in the present study that a clear concrete cover of rebar is 25 mm and the corrosion initiation results are given in 0, the chloride threshold of FRCs was thus achieved and listed in Table 5.2.
D.4 Influence of Applied Flexural Loadings

Reinforced concrete beams in bending contain cracks typically when flexural loadings exceed a cracking moment. Load induced cracks in concrete structures have a serious impact on corrosion of reinforcing steel in both initiation and propagation period. The time to corrosion onset results in 0 is a clear evidence. Practically a cracked concrete has less cover depth at some extent depending on load intensity. In the loaded concrete beams, corrosion then takes place sooner because chlorides attack rebar more rapidly through cracks. Also, tensile stresses at a crack tip may generate micro-cracks and then increase chloride diffusion. It is however assumed that chloride diffusion coefficients and chloride threshold are load-independent.

To take the influence of loading into consideration, a depth ($x$) in the Fick’s diffusion law is substituted with an effective depth ($x^*$) proposed in a function of applying load and ultimate load with a power factor $\lambda$ of 2.8. Furthermore, a fiber effect expressed in term of a fiber volume fraction and the power factor is next included. The effective depths converted from the test results and proposed here were plotted in Figure D.1. It is noted that the model is quite conservative when a load intensity approaches 50%. Its function could be expressed as follows.

$$x^* = x \times \exp \left( -63 \times \exp \left( -V_f \right) \times \left( \frac{P}{P_{tu}} \right)^\lambda \right)$$  \hspace{1cm} (D.9)

where

$x$ = concrete cover (mm)

$P$ = applying load (kN)
Appendix D. Details of the Modification of the LIGHTCON Model

$P_u = \text{ultimate strength (kN)}$
$V_f = \text{fiber volume fraction (%)}$
$\lambda = \text{power factor}$
\[
\lambda = \begin{cases} 
2.8 \text{ for plain concrete} \\
4.0 \text{ for cellulose FRC} \\
3.0 \text{ for polypropylene FRC}
\end{cases}
\]

Figure D.1  Relationship of load intensity and effective depth of the tested beams
D.5 References


Appendix E

Limits of Chloride Content in Concrete

Ingredients in concrete may contain some chlorides from its original source or manufacturing processes. Therefore, allowable chloride ion limits in concrete must be specified and have been established in three ACI technical committees, i.e. ACI 201 Durability of Concrete, ACI 222 Corrosion of Metals in Concrete and ACI 318 Structural Concrete Build Code. They are summarized in the Table E.1 below.

<table>
<thead>
<tr>
<th>Category</th>
<th>ACI 201 and ACI 222</th>
<th>ACI 318</th>
<th>Water-soluble ASTM C 1218 or Soxhlet*</th>
<th>Type of Member</th>
<th>Water-soluble ASTM C 1218</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prestressed concrete</td>
<td>0.08</td>
<td>0.06</td>
<td>Prestressed concrete</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>Reinforced concrete in wet conditions</td>
<td>0.10</td>
<td>0.08</td>
<td>Reinforced concrete exposed to chloride in service</td>
<td>0.15</td>
<td></td>
</tr>
<tr>
<td>Reinforced concrete in dry condition</td>
<td>0.20</td>
<td>0.15</td>
<td>Reinforced concrete that will be dry or protected from moisture in service</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td>Other reinforced concrete construction</td>
<td></td>
<td></td>
<td>Other reinforced concrete construction</td>
<td>0.30</td>
<td></td>
</tr>
</tbody>
</table>

* The soxhlet test method is described in ACI 222.1.