

DIFFUSIVITY AND RESISTANCE TO DETERIORATION FROM FREEZING AND  
THAWING OF BINARY AND TERNARY CONCRETE MIXTURE BLENDS

by

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## **Abstract**

Corrosion of reinforcing steel is one of the most common and serious causes of reinforced concrete deterioration. While corrosion is normally inhibited by a passive layer that develops around the reinforcing steel due to the high pH environment of the surrounding concrete, chlorides will break down this protective layer, leading to reinforcement corrosion. Decreasing the diffusivity of the concrete would slow the ingress of chlorides into concrete, and is one of the most economical ways to increase the concrete service life.

Optimized concrete mixtures blending portland cement and supplementary cementing materials (SCMs) have become popular throughout the construction industry as a method of improving both fresh and long-term concrete properties such as workability, strength and porosity. It has been shown that use of Class F fly ash, silica fume and ground granulated blast furnace slag (GGBFS) in binary concrete mixture blends can result in a significant reduction in concrete diffusivity. This study investigates the ability of Class C fly ash and ternary concrete mixture blends to also aid in diffusivity reduction. In order to study the effect of incorporation of SCMs into concrete, mixtures containing Class C and Class F fly ash, silica fume and GGBFS were tested following the ASTM C 1556 procedures to measure the concrete's apparent chloride diffusivity. Structure life cycles were modeled using the measured apparent chloride diffusivities with two finite-difference based life-cycle analysis software packages. To determine whether a correlation between diffusivity and deterioration due to freezing and thawing exists, samples were also tested for their ability to resist deterioration from freezing and thawing cycles using a modified ASTM C 666 Procedure B test.

Results show that the use of Class C fly ash yields some service life improvements as compared to the portland cement control mixtures, while ternary mixture blends performed significantly better than the control mixture and equal to or better than the binary SCM mixtures tested. Freeze-thaw tests showed all mixtures to be equally resistant to deterioration due to freezing and thawing.

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## **Dedication**

I would like to dedicate this work to my mother, Judith Beck, who has always pushed and inspired me to be my best.

# Chapter 1 - Introduction

## Theoretical Background and Short Literature Review

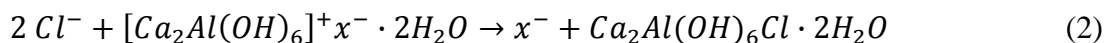
Corrosion of reinforcing steel is one of the most serious causes of reinforced concrete deterioration. Once corrosion begins in the reinforcement, expansion from the corrosion product formation can lead to cracking, spalling and significant section loss. While corrosion is normally inhibited by a passive layer that develops around the reinforcing steel due to the high pH environment of the concrete, chlorides will break down this protective layer, leading to reinforcement corrosion. Decreasing the diffusivity of the concrete would slow the ingress of chlorides into concrete, and is one of the most economical ways to prevent or delay concrete deterioration due to reinforcement corrosion.<sup>1</sup>

Chlorides enter concrete through absorption, electromigration, diffusion, thermal migration and hydrostatic pressure.<sup>2</sup> Adsorption, which draws moisture into smaller pore spaces through capillary suction, can also play a significant role in concrete chloride ingress. The mechanism of diffusion is a function of the concrete porosity, pore size distribution, continuity of pore structure, and temperature. The concrete pore characteristics are determined by the concrete's hydration through water-cementitious material ratio (w/cm), use of supplementary cementing material, curing, and the amount of concrete consolidation.<sup>3-5</sup>

Diffusion of concrete is often modeled using Fick's 2<sup>nd</sup> Law of Diffusion as shown in Equation 1:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left( D_c \frac{\partial C}{\partial x} \right) \quad (1)$$

where C represents chloride concentration, t is time, x is the depth from the concrete surface, and  $D_c$  is the apparent diffusion coefficient.<sup>6</sup> Additionally, the chloride ingress rate is affected by a chemical reaction that occurs between chloride ions and the concrete's aluminum hydrates, forming Freidel's salt as shown in Equation 2,



where  $x^-$  is an anion, usually  $OH^-$ ,  $SO_4^{2-}$  or  $CO_3^{2-}$ .<sup>7</sup> The formation of Freidel's salt binds a portion of the chloride ions entering the concrete and reduces the chloride ingress rate from that

predicted by diffusion alone. To model the chloride ingress in saturated concrete, one must either explicitly model the diffusion and chloride binding as separate processes, or model the chloride diffusion and chloride binding using an apparent diffusion coefficient in Fick's 2<sup>nd</sup> Law of Diffusion. The apparent diffusion coefficient is calculated from chloride ponding tests, where a concrete sample is immersed in a salt solution for a known period of time, after which layers of the specimen are ground and the chloride concentration of the concrete powder is measured at the different depths. As this chloride profile is a result of both the diffusion process and chloride binding, this diffusion coefficient represents the effects of both processes. Although the chloride binding process technically violates the assumption made by Fick's second law of pure diffusion mass transport, indirect inclusion of the binding process with the diffusion of ions from chloride profile tests will result in an effective reduction in the diffusion coefficient that models both effects. For concrete, this indirect reduction will yield results close to what would be expected if the diffusion alone were to be modeled, allowing Fick's second law to be used to accurately describe the processes occurring in the concrete.<sup>8</sup> The diffusion coefficient, strictly speaking, was originally formulated to model only the pore solution chloride concentration, so the term is renamed to be the apparent diffusion coefficient to include both the diffusion and chloride binding processes.

Fick's second law of diffusion can be solved using the error function by assuming a constant diffusion coefficient with time, as shown in Equation 3:

$$C(x, t) = C_s \operatorname{erf} \left( \frac{x}{\sqrt{4Dt}} \right) \quad (3)$$

where  $C_s$  is the surface chloride concentration. However, using a constant diffusion coefficient does not accurately represent concrete diffusivity over time as long-term hydration of the concrete will result in a continuous decrease in porosity and a reduction in the concrete's chloride diffusion coefficient. This effect has been noted by several researchers and is particularly evident in concrete mixtures containing pozzolans.<sup>9, 10</sup> Use of the error function solution, which assumes a constant diffusion coefficient, will result in a greater concrete diffusivity over the life of the structure and an underestimated service life. The reduction in the concrete apparent diffusion coefficient with time can be modeled using an exponential decay, as shown in Equations 4 and 5, and can be numerically approximated using finite difference or finite element methods:

$$D_{ult} = D_{28} \left( \frac{28}{36500} \right)^m \quad (4)$$

$$D_t = D_{28} \left( \frac{t_{28}}{t_d} \right)^m + D_{ult} \left( 1 - \left( \frac{t_{28}}{t_d} \right)^m \right) \quad (5)$$

where  $D_{28}$  is the diffusion coefficient after 28 days of curing,  $D_{ult}$  is diffusion coefficient after 100 years, which has been assumed by other studies to be the lower bound value the diffusion coefficient will reach with time,  $D_t$  is the instantaneous diffusion coefficient at a time  $t$ , and  $m$  is a decay coefficient describing the rate of change in diffusivity over time due to hydration.

Studies have determined the decay coefficient to be a function of the w/cm and the ASTM C 1240<sup>11</sup> silica fume, ASTM C 618<sup>12</sup> Class F fly ash and ASTM C 989<sup>13</sup> ground granulated blast furnace slag (GGBFS) content as shown in Equations 6, 7 and 8:

$$m = 0.26 + 0.4 \left( \frac{FA}{50} + \frac{SG}{70} \right) \quad (6)$$

$$D_{PC-28} = 2.17 \times 10^{-12} e^{(3.584 \cdot W/CM)} \quad (7)$$

$$\frac{D_{SF}}{D_{PC}} = 0.206 + 0.794 e^{(-SF/2.51)} \quad (8)$$

where SF, FA and SG are the percent replacement of portland cement by silica fume, Class F fly ash and GGBFS, respectively.<sup>14</sup> The effects of portland cement replacement with Class C fly ash binary and ternary mixture blends on diffusivity have not been determined. This study aims to quantify the effect of binary Class C fly ash concrete and ternary blend concrete containing silica fume, Class C and Class F fly ash and GGBFS on the diffusivity and decay coefficient of concrete.

Several software packages have been developed to aid in the prediction of concrete structure service lives. These programs calculate the expected life of a structure based on many different variables, including w/cm, supplementary cementitious material mixtures, curing compounds, reinforcement type, climate, predicted chloride exposure and depth of the reinforcement. In order to predict the service life of a structure, these programs use diffusion coefficients and decay coefficients established in literature to determine the time it will take for a critical chloride ion concentration to reach the depth of the steel, allowing for a more comprehensive view of the differences between mixtures than what comparing diffusion coefficients provides. These values have only been established for mixtures containing Class F fly ash, silica fume and GGBFS and are unable to model mixtures containing Class C fly ash, which is commonly used in the western United States. Creation of a model analyzing Class C fly

ash would help engineers in states using Class C fly ash to model and create low-cost, durable concrete mixtures.

Deterioration due to freezing and thawing is prolific in concrete structures in cold climates, such as the Midwestern United States. This deterioration occurs when the tensile forces developed from the freezing of water in concrete exceeds the tensile capacity of the concrete. Past studies have come to mixed conclusions regarding the effect supplementary cementitious materials have on the freeze-thaw durability of concrete structures. Use of supplementary cementitious materials is believed to affect concrete's resistance to freezing and thawing in two capacities. Infilling of the void spaces and reduction in diffusivity is believed to reduce durability by decreasing water's ability to diffuse through the concrete into open pore spaces to relieve the pressure created by moisture's expansion during freezing.<sup>15-18</sup> At the same time, infilling of the concrete's pores creates a stronger concrete matrix, enhancing the tensile capacity of the concrete and increasing the concrete's freeze thaw durability.<sup>4,5</sup> Additionally, the freezing and thawing behavior of concrete is known to be affected by the saturation level of the pores, with a critical saturation level needed to induce damage, even in non-air entrained concrete.<sup>18</sup> As a much greater length of time is required to reach the critical saturation level in lower diffusivity concrete, use of lower diffusivity concrete may result in greater freeze-thaw durability. This study documents the effect of two replacement rates of Class C fly ash, silica fume and a ternary blend of Class C fly ash and silica fume on freeze-thaw deterioration. The performance of concrete containing SCMs was also investigated to determine if the change in concrete transport properties affected the freeze-thaw behavior.

## **Research Significance**

Service life modeling software is often used by engineers to determine the best SCM mixtures for their intended structures, yet these models do not currently have diffusivity information for Class C fly ash, which is a readily available low-cost material in many western United States. Additionally, service life models currently assume a linear superposition of material effects on the concrete diffusivity of ternary blends, an assumption that has not been verified by research. This research will establish diffusivity values for Class C fly ash, ternary

blend concrete mixtures and will also ascertain the effects of reduced diffusivity on freeze-thaw durability.



## Chapter 2 - Materials, Mixture Proportioning and Specimen Casting

Thirteen combinations of cementitious materials, including binary and ternary blends, were used in this study. An ASTM C 150<sup>19</sup> Type I cement was used in all concrete mixtures, with the chemical and physical properties listed in Table 2.1. One ASTM C 618<sup>12</sup> Class C fly ash, one ASTM C 618<sup>12</sup> Class F fly ash, one silica fume, and one ASTM C 989<sup>13</sup> ground-granulated blast-furnace GGBFS were used in this study. Their chemical compositions are shown in Table 2.2.

**Table 2.1 - Chemical composition and physical properties of cement, %**

Oxides (%)							
SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O
21.34	4.74	3.29	62.94	1.69	2.68	0.14	0.53

Bogue Calculations (%)				Reitveld XRD (%)				Blaine Fineness (m <sup>2</sup> /kg)
C <sub>3</sub> S	C <sub>2</sub> S	C <sub>3</sub> A	C <sub>4</sub> AF	C <sub>3</sub> S	C <sub>2</sub> S	C <sub>3</sub> A	C <sub>4</sub> AF	
49.85	23.57	6.99	10.01	66.96	16.49	2.92	9.29	360.1

**Table 2.2 - Chemical composition of SCMs, %**

Material	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O
<b>Class F Fly Ash</b>	47.35	17.32	5.67	20.13	2.94	2.09	0.59	0.95
<b>Class C Fly Ash</b>	30.5	17.69	5.93	28.64	7.49	2.85	2.2	0.35
<b>Silica Fume</b>	95.3	0.22	0.08	0.45	0.33	0.03	0.07	0.41
<b>GGBFS</b>	33.59	10.03	0.95	40.98	10.96	2.68	0.24	0.4

A 12.5 mm (0.5 in.) nominal maximum size pavement class 0 coarse aggregate, obtained from a Desoto, Kansas quarry, and a 4.75 mm (0.187 in.) natural siliceous river sand were used in all test specimens. Specific gravity and absorption were measured using ASTM C 127<sup>20</sup> for the coarse aggregate and ASTM C 128<sup>21</sup> for the fine aggregate. Particle size distributions for both coarse and fine aggregate were measured using ASTM C 136<sup>22</sup> and are shown in Table 2.3. The coarse aggregate meets ASTM C 33<sup>23</sup> requirements for a size 67 gradation. An ASTM C

494<sup>24</sup> Class F, high-range water reducing polycarboxylate based admixture and a vinsol resin based air-entraining admixture were used in the concrete mixtures.

**Table 2.3 - Sieve analysis and physical properties of fine and coarse aggregates**

<b>Sieve Size (mm)</b>	<b>Fine aggregate % passing</b>	<b>Coarse aggregate % passing</b>
<b>¾" (19)</b>	<b>100</b>	<b>100</b>
<b>½" (12.5)</b>	<b>100</b>	<b>81.41</b>
<b>3/8" (9.5)</b>	<b>100</b>	<b>57.39</b>
<b>No. 4 (4.75)</b>	<b>95.43</b>	<b>9.98</b>
<b>No. 8 (2.36)</b>	<b>78.27</b>	<b>1.55</b>
<b>No. 16 (1.18)</b>	<b>52.40</b>	<b>0.24</b>
<b>No. 30 (0.595)</b>	<b>27.66</b>	<b>0.04</b>
<b>No. 50 (0.3)</b>	<b>4.62</b>	<b>0.01</b>
<b>No. 100 (0.1485)</b>	<b>0.65</b>	<b>0</b>
<b>Fineness modulus</b>	<b>3.41</b>	<b>5.88</b>
<b>Specific gravity</b>	<b>2.63</b>	<b>2.65</b>
<b>Absorption, %</b>	<b>0.5</b>	<b>1.35</b>

For the mixtures that contained SCMs, a percentage of portland cement was replaced by weight with a binary or ternary cementitious blend. Mixtures for chloride profile test specimens were designed to have a w/cm of 0.34, slump of 6±1 inches and 6.5±1% entrained air. Freezing and thawing specimens were made with a w/cm of 0.34 and 0.47, a slump of 6±1 inches and 6.5±1% entrained air. The concrete specimens made for the concrete apparent diffusion testing and the freezing and thawing tests were made from different batches of concrete, but using the same mixture proportions for the 0.34 w/cm mixtures. The concrete mixture proportions for each mixture are shown in Table 2.4. Concrete mixture fresh properties are shown in Tables 2.5 and 2.6.

**Table 2.4 - Concrete mixture proportions**

Mixture	Water kg/m <sup>3</sup>	OPC kg/m <sup>3</sup>	C kg/m <sup>3</sup>	F kg/m <sup>3</sup>	S kg/m <sup>3</sup>	G kg/m <sup>3</sup>	Coarse Agg kg/m <sup>3</sup>	Fine Agg kg/m <sup>3</sup>	HRWR mL/m <sup>3</sup>	AEA mL/m <sup>3</sup>
OPC-0.34	181	532	0	0	0	0	953	587	406	164
10C-0.34	181	479	53	0	0	0	953	565	71	326
25C-0.34	181	399	133	0	0	0	953	531	0	186
10F-0.34	181	479	0	53	0	0	953	565	1034	671
25F-0.34	181	399	0	133	0	0	953	531	562	414
5S-0.34	181	505	0	0	27	0	953	577	899	336
25G-0.34	181	399	0	0	0	133	953	543	1182	621
10C 5S- 0.34	181	452	53	0	27	0	953	559	1075	394
25C 5S- 0.34	181	372	133	0	27	0	953	522	1075	276
10F 5S- 0.34	181	452	0	53	27	0	953	559	811	205
25F 5S- 0.34	181	372	0	133	27	0	953	522	527	369
25C 25G- 0.34	181	266	133	0	0	133	953	487	862	744
25F 25G- 0.34	181	266	0	133	0	133	953	487	507	697
OPC-0.47	181	385	0	0	0	0	953	709	205	109
10C-0.47	181	346	38	0	0	0	953	693	205	113
25C-0.47	181	289	96	0	0	0	953	669	0	168
5S-0.47	181	366	0	0	19	0	953	702	496	111
10C 5S- 0.47	181	327	38	0	19	0	953	686	249	116

Note: OPC-ordinary portland cement, C-Class C fly ash, F-Class F fly ash, S-Silica Fume, G-GGBFS

**Table 2.5 - Fresh concrete properties of diffusivity specimens**

Mixture	Slump mm	% Air
OPC-0.34	5	5.5
10C-0.34	5.5	6
25C-0.34	6	6
10F-0.34	5.25	7.5
25F-0.34	6.25	6
5S-0.34	5	5.75
25G-0.34	5.5	6
10C 5S-0.34	6.25	7.5
25C 5S-0.34	5.25	5.5
10F 5S-0.34	7.25	8
25F 5S-0.34	6	5
25C 25G-0.34	7	6
25F 25G-0.34	5.5	6

**Table 2.6 - Fresh concrete properties of freeze-thaw specimens**

<b>Mixture</b>	<b>Slump mm</b>	<b>% Air</b>
OPC-0.34	5	5.75
10C-0.34	6	6.25
25C-0.34	6	5.5
5S-0.34	5.5	7
10C 5S-0.34	6.25	7.25
OPC-0.47	8.25	7.5
10C-0.47	8.5	6.75
25C-0.47	9	7.25
5S-0.47	8.5	8
10C 5S-0.47	8	6.5

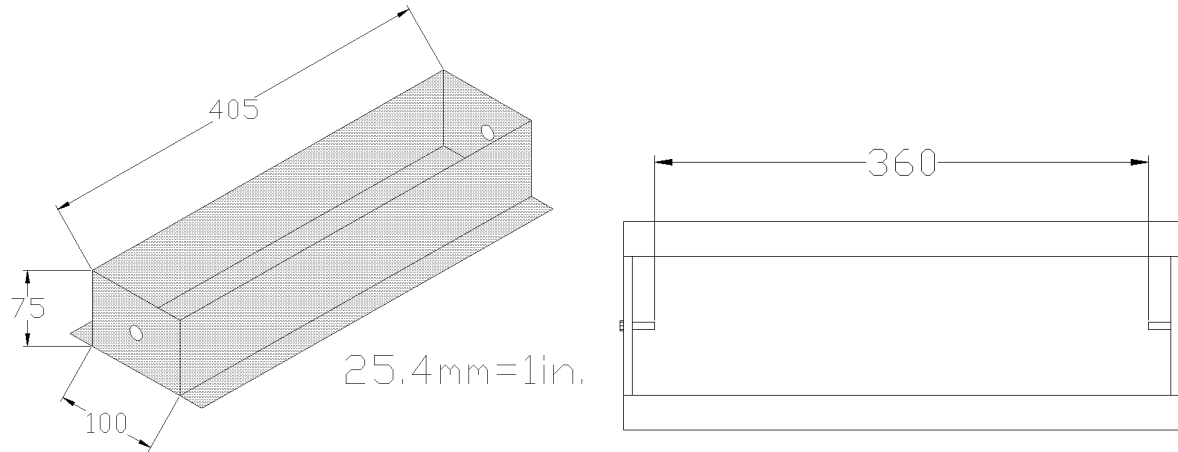
## Chapter 3 - Methodology

This section details the methods used to create and test concrete specimens for diffusivity, concrete electrical conductivity, deterioration due to freezing and thawing, and compressive strength.

### Concrete Mixing

Concrete batching was completed using a procedure similar to the Silica Fume Association's laboratory batching guidelines.<sup>25</sup> Admixture quantities for each mixture were determined through trial and error using small (0.5 cubic foot) batches. Aggregate moisture contents were calculated prior to batching and accounted for in the mixture proportions. Coarse and fine aggregates, 75% of the total mixture water, SCMs if called for, and 75% of the superplasticizing admixture (mixed with water) were added to the pan and mixed for 1½ minutes to allow aggregates and SCMs to absorb some of the water. After this initial mixing, the cement, followed by the air entraining agent, mixed with most of the remaining water, were added slowly into the mixture and mixed for an additional three minutes, allowed to rest for three minutes and mixed a final time for two minutes. A small amount of water and 25% of the superplasticizing admixture were held back until the three minute rest phase. If the mixture's slump did not appear to be high enough the remainder of the water and admixture were added, if the slump appeared to be close to the target value only the remaining water was added.

Concrete slump and air content were tested in accordance with ASTM C 143<sup>26</sup> and ASTM C 231.<sup>27</sup> 4"x8" concrete cylinders for compressive strength testing and chloride profiling were made according to the ASTM C 31<sup>28</sup> procedure. Concrete freeze-thaw specimen dimensions were 3"x4"x16" (75mm x100mm x405mm) with stainless steel pins embedded in the ends for measuring the concrete prism length change. Figures 3.1 and 3.2 show the specimen dimension, gage length and pin setup. To cast the specimens, molds were filled with concrete, vibrated with a pencil immersion vibrator, leveled, and covered with plastic to prevent moisture loss. After 24 hours, specimens were de-molded, labeled and placed in a 100% relative humidity moist room meeting ASTM C 192<sup>29</sup> for curing.



**Figure 3.1 - Freeze-thaw specimen mold with dimensions and mold gage length in mm**



**Figure 3.2 - Freeze thaw mold and stainless steel pin setup**

Fourteen 4 x 8 in. (100 x 200 mm) cylinder specimens were made for each mixture to quantify the chloride diffusivity with time under laboratory curing conditions. Concrete cylinders for each mixture were cured for different amounts of time and conditions. Two cylinders were cured in the moist room for 28 days after which they were cut, sealed and immersed in a sodium chloride solution (165g/L) for 35 days following ASTM C 1556.<sup>30</sup> The remaining twelve cylinders were cured for 91 days, after which they were cut, sealed, and ponded. Of the specimens that were placed in the salt solution at 91 days, two were removed from the salt solution for profile grinding after 35 days of soaking, two were removed after 126 days of soaking and the remaining concrete specimens will be removed from the exposure solution at later ages for additional testing. Removal of the specimens at 126 days corresponds

to six months of curing followed by 35 days of salt bath immersion. Soak times of future specimens will follow this model.

In addition to the 14 laboratory cured specimens, four cylinders for each mixture were cast and cured outdoors to determine the influence of curing on the concrete chloride apparent diffusivity. Two of the outdoor specimens were cast and capped while the other two were sealed with wax based concrete curing compound. After 24 hours the concrete cylinders were removed from their molds and were placed at Kansas Outdoor Concrete Exposure site for 215 days of bold field exposure. After curing, the cylinders were cut and sealed following the same procedures as previous diffusivity specimens. The cylinders were then saturated for four days in a calcium hydroxide bath until the change in mass over a 24 hour period was less than 0.1%. The cylinders were rinsed and ponded in the sodium chloride salt solution for 35 days, and profile ground using the same procedures as previous diffusivity specimens.

### **Concrete Strength, Electrical Conductivity, and Apparent Diffusivity**

The concrete compressive strength was tested according to ASTM C 39<sup>31</sup> using 4"x 8" (100mm x200 mm) concrete cylinders at 28, 91, and 180 days after casting and curing in the moist room.

The concrete electrical conductivity was measured at 91 days on uncut 4"x8" (100mm x200mm) concrete cylinders using a simplified rapid chloride permeability testing procedure. In this method, the uncut cylinders were continuously cured in a moist room after demolding. At 91 days the cylinders were tested using the rapid chloride permeability cells, except with longer bolts and sleeves to accommodate an 8 in. (200 mm) long specimen instead of the 2 in. (50 mm) specimens called for by ASTM C 1202.<sup>32</sup> The charge passed on the sample was measured and recorded at 5 minutes.<sup>33</sup> It is assumed that higher electrical conductivity readings correspond to higher concrete diffusivity, so the recorded amperages at 5 minutes were used to compare with the diffusivity values.

Upon removal from the salt solution, chloride concentration profiles were measured first by grinding off layers parallel to the exposed surface and collecting the powder. Eight layer depths, designated by ASTM C 1556,<sup>30</sup> were used to obtain a 10 g powder sample for each layer of each specimen. Concrete specimen layer depths used are shown in Table 3.1. Chloride analysis was performed on each powder sample following the procedures outlined in ASTM C

1152.<sup>34</sup> Chlorides were disassociated from the concrete using dilute nitric acid and then titrated to find the percent chlorides present using a silver-sulfide ion selective electrode. The percent chlorides for each sample were determined by using the Berman method of equivalence point analysis.<sup>35</sup> A more thorough description of profile grinding and titration procedures can be found in Appendixes A and B.

**Table 3.1 - Recommended depth intervals (in mm) for powder grinding**

w/cm	Depth 1	Depth 2	Depth 3	Depth 4	Depth 5	Depth 6	Depth 7	Depth 8
0.25	0-1	1-2	2-3	3-4	4-5	5-6	6-8	8-10

Two methods of analysis were used to interpret chloride profiling results. The first method calculates the average diffusion coefficient of a specimen using the error function shown in Equation 4. Chloride profiles were also analyzed through a finite difference approximation of Fick's second law of diffusion described in Equations 1 and 4-8. Diffusion coefficients, decay coefficients and chloride coefficients at the specimen's surface were calculated for 28 day, 91 day and 6 month specimens as well as fitting the curve over all time periods at the same time for the finite difference analysis method. Decay coefficients were calculated for each mixture by solving for the closest fit to the experimental data assuming the diffusion coefficient to be equal to the OPC-0.34 28 day diffusion coefficient for all mixtures not containing silica fume and equal to the 5SF-0.34 28 day diffusion coefficient for all mixtures containing silica fume. Diffusion coefficient numerical fit methods are described in more depth in Appendix C.

### **Service Life Modeling**

Service life modeling was performed using Life365<sup>36</sup> and another recently developed finite difference analysis based software program.<sup>14</sup> All analyses were modeled for a concrete wall with 51mm of concrete covering the steel reinforcement, in a splash zone in Key West, Florida. An initial estimate of the concrete service life was created using the using the recently developed finite difference analysis based software program's default diffusion and decay coefficient values based on Equations 4-6 for the w/cm and SCM replacement rates for each of the experimental mixtures. Equations used by the Life-365 software differed somewhat from the equations shown in Equations 6-8 and are shown below in Equations 9-11:



$$D_{28} = 1 \times 10^{(-12.06 + 2.40w/cm)} \quad (9)$$

$$m = 0.2 + 0.4 \left( \frac{FA}{50} + \frac{SG}{70} \right) \quad (10)$$

$$D_{SF} = D_{PC} \cdot e^{-0.165 \cdot SF} \quad (11)$$

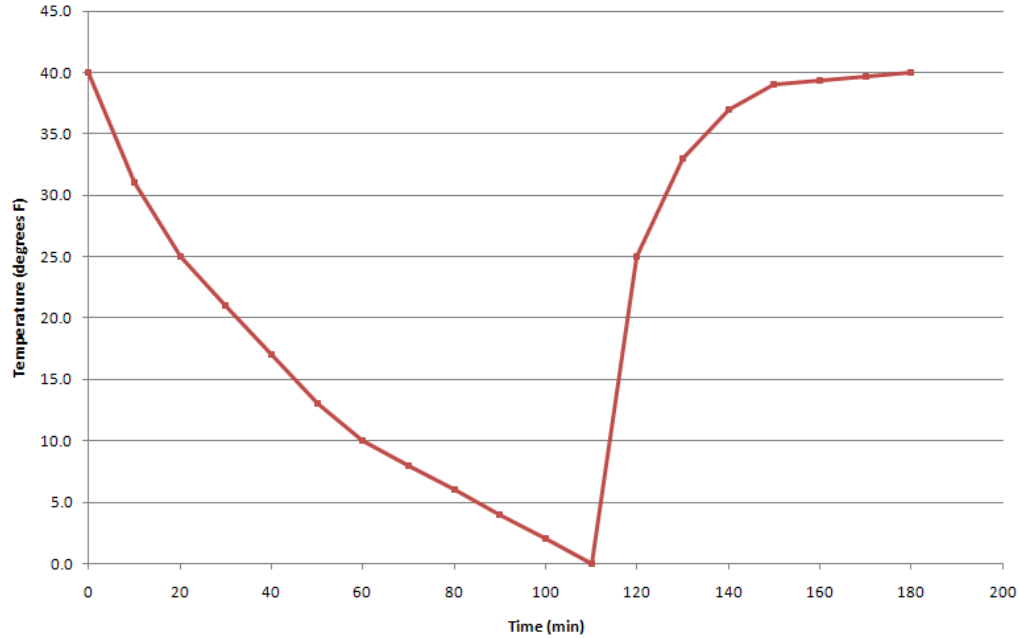
Further analyses were run by manually overriding the software's values and using the diffusion coefficients and decay values found from the experimental chloride profiles. Models were created for the calculated decay coefficients, diffusion coefficients for 28 day, 91 day and 6 month specimens as well as for the values determined from fitting the data to all three profiled times at once.

### Testing for Deterioration due to Freezing and Thawing

Curing of freeze thaw specimens was conducted for 90 days according to Kansas Department of Transportation Materials and Research Bureau Test Method KTMR-22,<sup>37</sup> which is a modified version of ASTM C 666<sup>38</sup> method B. Beams were cured in 100% relative humidity for 67 days followed by 21 days of curing in a room at 72 ± 3 °F (22.8 ± 2 °C) and 50 ± 4 % relative humidity. Beams were then tempered in water maintained at 70 °F (21.1 °C) for 24 hours and placed in a freezer maintained at 40 °F (4.4 °C) for 24 hours. Beams were then subjected to cyclical freezing and thawing cycles following ASTM C 666 Procedure B,<sup>38</sup> which calls for beams to be surrounded by air while freezing and thawed in tempered water. The temperature profile used is shown in Table 3.2 and Figure 3.3.

**Table 3.2 - Freezing and thawing cycle temperatures**

Segment #	Time (minutes)	Setpoint (degrees F)	Mode
1	0	31	Freeze
2	10	25	Freeze
3	20	13	Freeze
4	50	10	Freeze
5	60	0	Freeze
6	110	25	Thaw
7	120	33	Thaw
8	130	37	Thaw
9	140	39	Drain
10	150	40	Drain



**Figure 3.3 - Freezing and Thawing Cycle Temperature Profile**

The mass, length and resonant frequency of the beams were measured using the methods specified in ASTM C 490<sup>39</sup> and ASTM C 215.<sup>40</sup> The transverse resonant frequency for each beam was determined using an impact hammer and accelerometer with a 4 Hz resolution. The impact resonance test setup is shown in Figure 3.4.

Laboratory testing of freeze-thaw deterioration was evaluated by tracking the changes in the length and the relative dynamic modulus of elasticity of the specimens undergoing continuous freezing and thawing cycles. The percent change in length and relative modulus of elasticity are calculated according to ASTM C 666,<sup>38</sup> shown in Equations 12 and 13. Each specimen's durability factor was also calculated according to Equation 14:

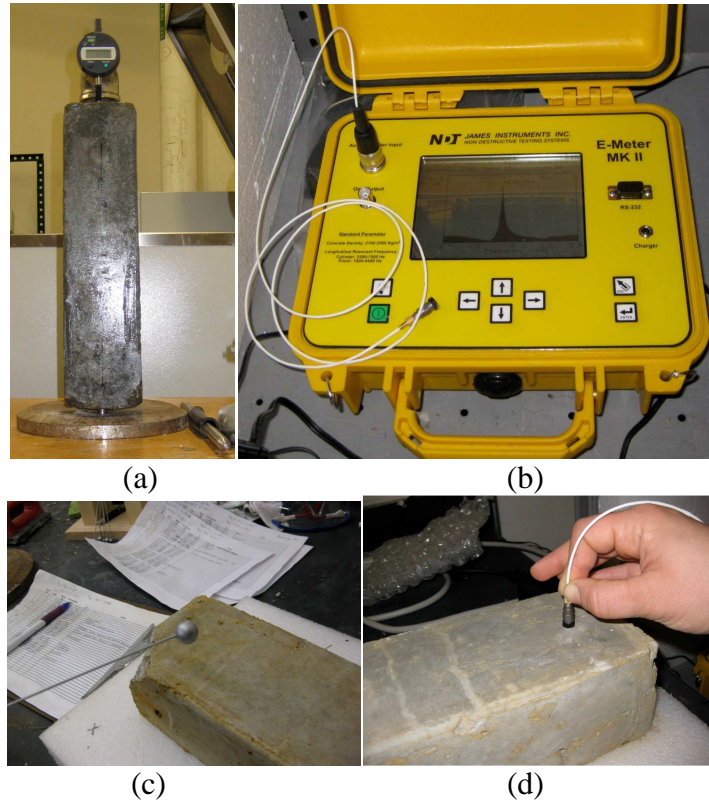
$$L_c = \frac{(l_2 - l_1)}{L_g} \times 100 \quad (12)$$

$$P_c = \left( \frac{n_1^2}{n^2} \right) \times 100 \quad (13)$$

$$DF = PN/M \quad (14)$$

where  $L_c$  is the length change of the test specimen after  $C$  cycles of testing,  $l_2$  and  $l_1$  are the length comparator readings after  $C$  cycles and at 0 cycles, respectively,  $L_g$  is the distance between the inner surfaces of the gage studs,  $P_c$  is the relative dynamic modulus of elasticity after  $c$  cycles of freezing and thawing and  $n$  and  $n_1$  are the fundamental transverse frequencies of the specimen at 0 and after  $c$  cycles of freezing and thawing, respectively.  $DF$  is the durability

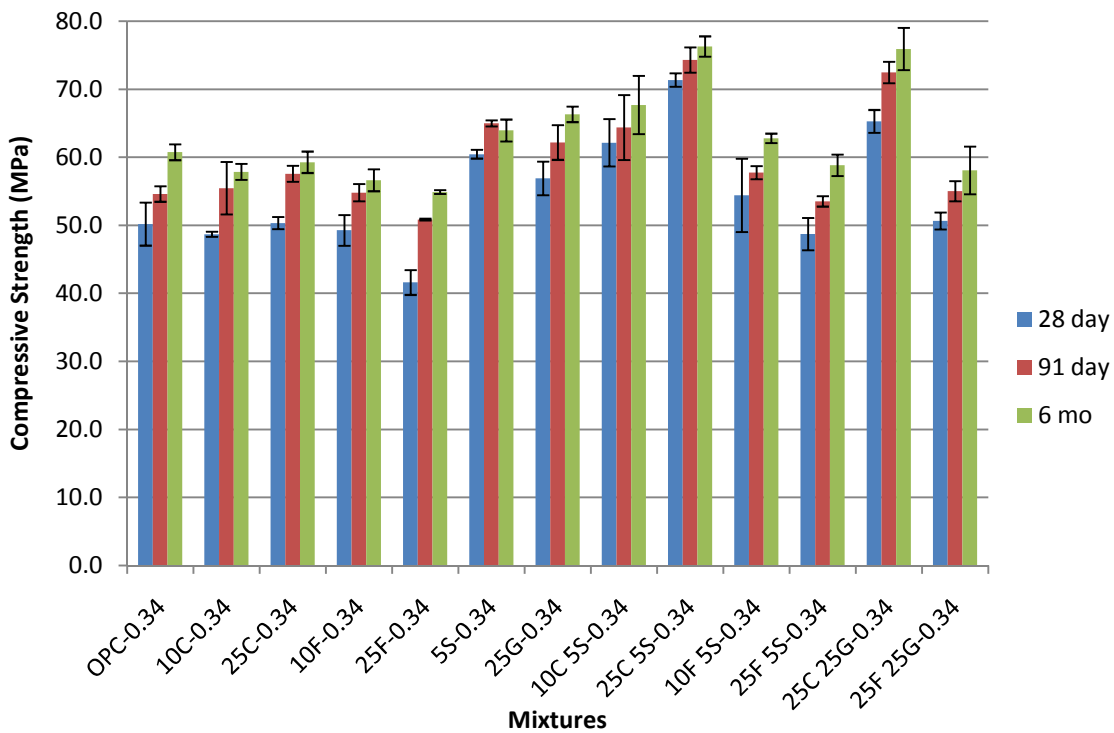
factor and  $P$  is the relative dynamic modulus of elasticity in percent at the number of cycles,  $N$  at which the exposure is to be terminated, in this case 300.



**Figure 3.4 - Freeze - Thaw Deterioration Specimen Test Setup. (a) Length comparator (b) E-meter MK II transverse frequency measuring device and accelerometer, (c) impactor, (d) accelerometer placement**

## Chapter 4 - Results and Discussion

Concrete compressive strength test results are shown in Figures 4.1 and 4.2. The compressive strengths relative to the control mixture are shown in Figure 4.2. In general, mixtures using silica fume or GGBFS obtained higher strengths than the control mixture, while both Class C and Class F fly ash binary mixtures showed reduced strengths as compared to the control mixture. With the exception of the 25% Class F fly ash 5% silica fume and the 25% Class F fly ash 25% GGBFS mixtures, all ternary mixture blends obtained higher strengths than the control mixtures. The lower strengths with the mixtures containing fly ash were most likely due to the slower reaction rate of the fly ash. A comparison of the 91 day strengths of the two freeze-thaw specimen mixtures is shown in Figure 4.3. Predictably, strengths were, on average, 30% higher for the 0.34 w/cm specimens than for the 0.47 w/cm specimens.



**Figure 4.1 - Compressive strengths for all diffusivity mixtures at 28, 91 and 180 days**

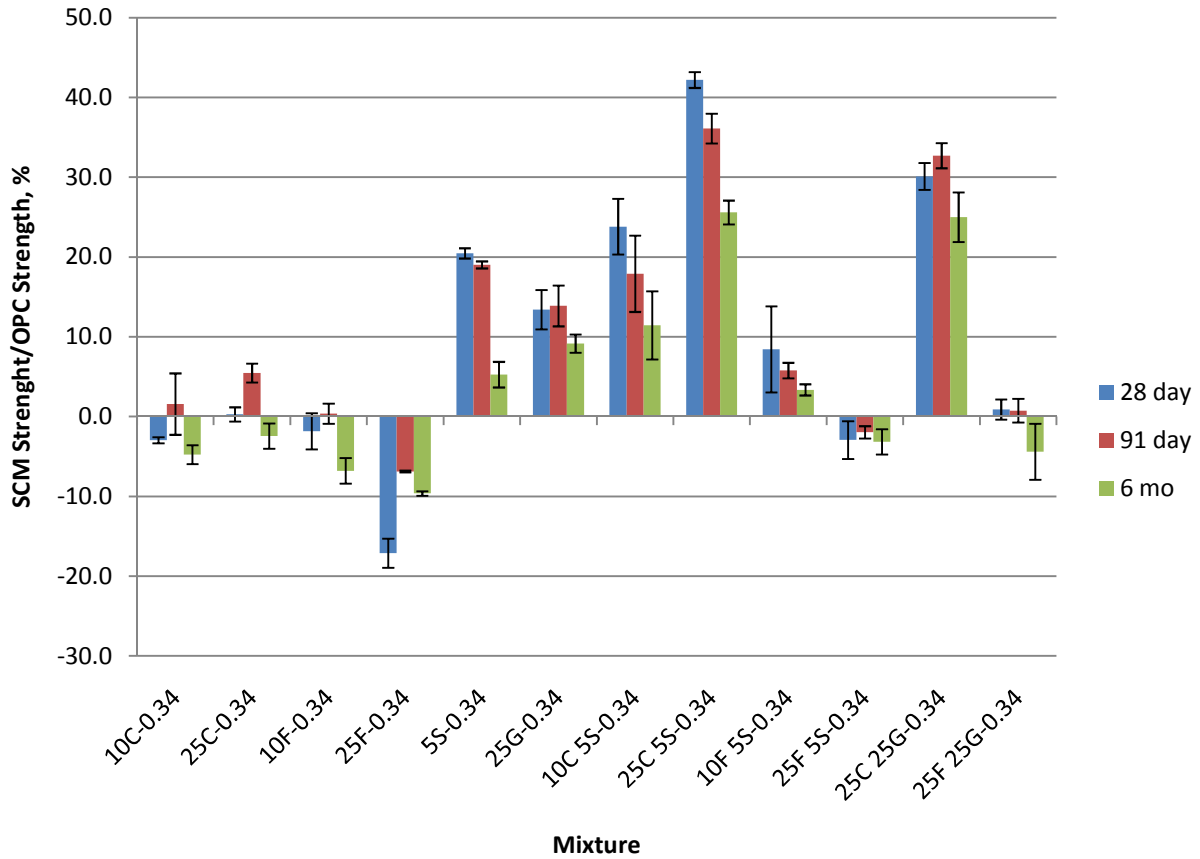


Figure 4.2 - Compressive strength normalized with respect to the control mixture

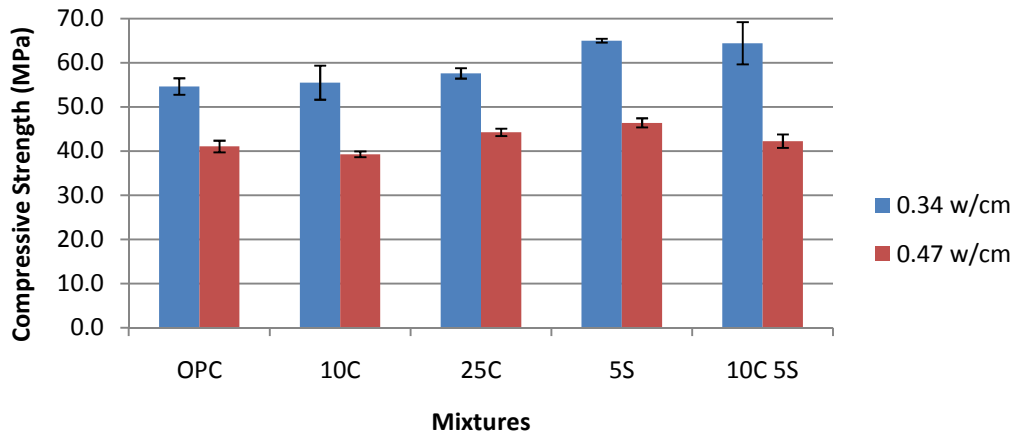


Figure 4.3 – 91 day compressive strengths for freeze-thaw specimen mixtures

## Diffusivity Test Results

Diffusion coefficients and chloride concentration at the specimen's surface are calculated using the error function method and shown in Table 4.1, with the finite difference results shown in Tables 4.2 and 4.3. The error function method and finite difference analysis diffusion coefficients for the individual time chloride profiles are shown in Figures 4.4 and 4.5. 28 day apparent diffusion coefficients were also calculated by fitting the three chloride profiles obtained for each mixture to one diffusion coefficient and decay coefficient. The 28 day apparent diffusion coefficients and m values fit to all three chloride profiles are shown in Table 4.3.

**Table 4.1 - Error function method average diffusion coefficients and surface concentrations**

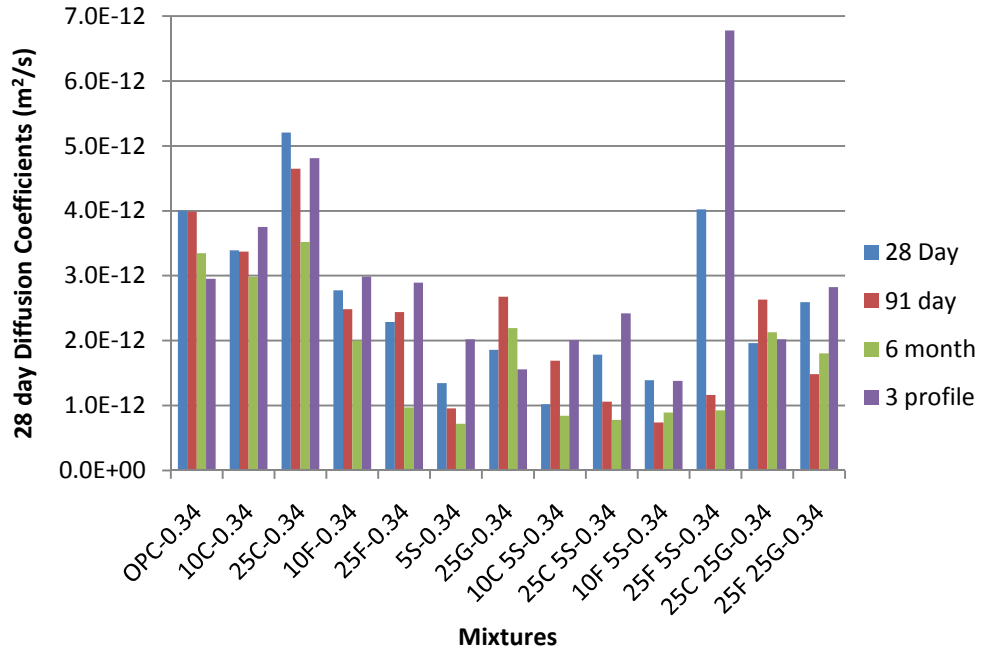
Mixture	Error Function					
	28 day		91 day		6 mo	
	$D_c \times 10^{-12}$ (m <sup>2</sup> /s)	$C_s$ (mass %)	$D_c \times 10^{-12}$ (m <sup>2</sup> /s)	$C_s$ (mass %)	$D_c \times 10^{-12}$ (m <sup>2</sup> /s)	$C_s$ (mass %)
<b>Control</b>	4.370	0.550	3.850	0.300	2.263	0.626
<b>10C-0.34</b>	3.130	0.498	2.504	0.878	1.965	0.647
<b>25C-0.34</b>	4.336	0.563	2.859	0.649	1.807	0.830
<b>10F-0.34</b>	2.496	0.646	1.810	0.757	1.309	0.750
<b>25F-0.34</b>	2.299	0.679	1.111	0.939	0.428	1.039
<b>5S-0.34</b>	1.316	0.508	0.783	0.578	0.483	0.554
<b>25G-0.34</b>	1.754	0.635	1.650	0.850	0.847	0.779
<b>10C 5S-0.34</b>	0.674	0.687	0.65	1.25	0.560	0.754
<b>25C 5S-0.34</b>	1.485	0.901	0.558	1.123	0.334	1.083
<b>10F 5S-0.34</b>	1.261	0.789	0.548	1.409	0.499	1.110
<b>25F 5S-0.34</b>	3.644	0.738	0.666	0.777	0.457	1.179
<b>25C 25G-0.34</b>	1.753	0.790	1.394	0.626	0.522	0.984
<b>25F 25G-0.34</b>	2.110	0.992	0.782	1.559	0.703	1.211

**Table 4.2 - Finite difference method determined 28 day apparent chloride diffusion coefficients and surface concentrations**

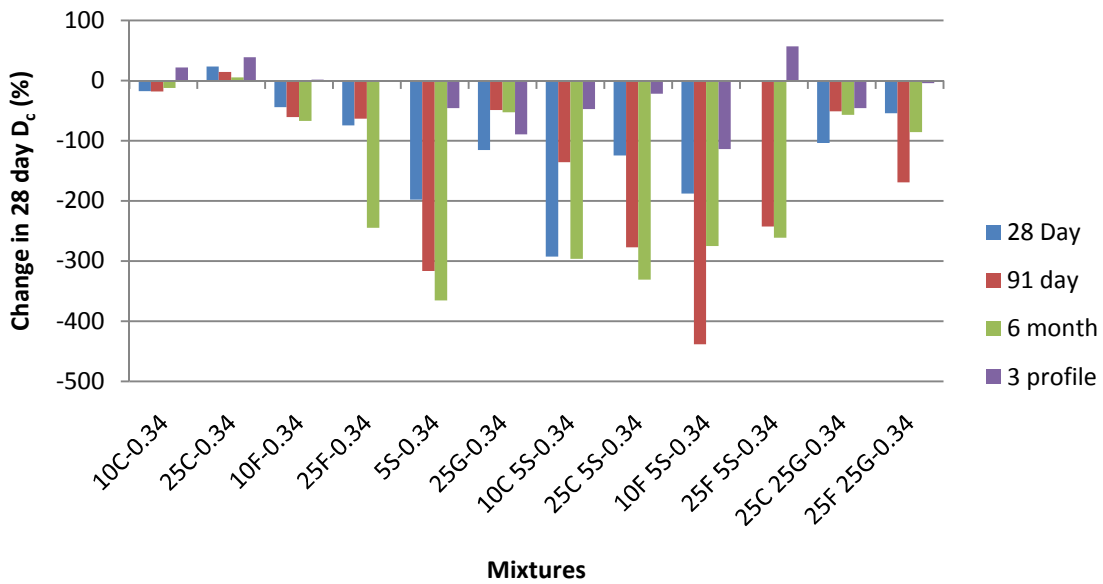
Mixture	28 Day		91 day		6 month	
	$D_{28} \times 10^{-12}$ (m <sup>2</sup> /s)	$C_s$ (mass %)	$D_{28} \times 10^{-12}$ (m <sup>2</sup> /s)	$C_s$ (mass %)	$D_{28} \times 10^{-12}$ (m <sup>2</sup> /s)	$C_s$ (mass %)
<b>OPC-0.34</b>	4.003	0.537	3.988	0.329	3.347	0.580
<b>10C-0.34</b>	3.392	0.485	3.372	0.935	2.982	0.668
<b>25C-0.34</b>	5.207	0.525	4.651	0.666	3.518	0.815
<b>10 F-0.34</b>	2.774	0.648	2.482	0.808	1.999	0.742
<b>25 F-0.34</b>	2.289	0.708	2.441	0.765	0.971	1.036
<b>5S-0.34</b>	1.344	0.525	0.957	0.568	0.719	0.547
<b>25G-0.34</b>	1.857	0.622	2.675	0.838	2.192	0.656
<b>10C 5S-0.34</b>	1.020	0.595	1.690	0.629	0.844	0.785
<b>25C 5S-0.34</b>	1.782	0.899	1.058	1.012	0.776	1.036
<b>10F 5S-0.34</b>	1.390	0.784	0.740	1.405	0.892	1.069
<b>25F 5S-0.34</b>	4.021	0.759	1.163	0.765	0.927	1.166
<b>25C 25G-0.34</b>	1.962	0.845	2.634	0.649	2.131	0.772
<b>25F 25G-0.34</b>	2.591	0.982	1.481	1.571	1.803	1.226

**Table 4.3 - 28 day Apparent diffusion coefficients calculated using all chloride profiles from all three specimen sets for each mixture**

Mixture	3 profile 28 day $D_c \times 10^{-12}$ (m <sup>2</sup> /s)	M
<b>OPC-0.34</b>	2.951	0.000
<b>10C-0.34</b>	3.750	0.383
<b>25C-0.34</b>	4.811	0.525
<b>10F-0.34</b>	2.989	0.490
<b>25F-0.34</b>	2.893	0.979
<b>5S-0.34</b>	2.022	1.207
<b>25G-0.34</b>	1.556	0.020
<b>10C 5S-0.34</b>	2.003	0.645
<b>25C 5S-0.34</b>	2.420	1.147
<b>10F 5S-0.34</b>	1.378	0.608
<b>25F 5S-0.34</b>	6.782	1.696
<b>25C 25G-0.34</b>	2.021	0.534
<b>25F 25G-0.34</b>	2.824	0.946



**Figure 4.4 - Finite difference analysis apparent chloride diffusion coefficients**



**Figure 4.5 - Change in diffusion coefficient in comparison to the control mixture**

In comparison with the control mixture, the largest reduction of diffusion coefficients occurred in the mixtures containing silica fume, while the mixtures containing Class C fly ash did not significantly reduce the 28 day concrete diffusivity relative to the OPC mixture. Specimen diffusivity was greater, at all times analyzed, for the 25% Class C fly ash mixture than



for the OPC control specimen, while 10% Class C fly ash mixture showed much smaller improvements in diffusivity than all of the other mixtures. The specimens containing Class F fly ash and GGBFS had a reduction in their 28 day diffusivity coefficients of between 50-100% for most curing times compared to the control specimen.

The values of the decay coefficient,  $m$ , from equation 2, were determined during the analysis fitting the data over all time periods at the same time for the finite difference analysis method. In order to determine these values it was assumed that the diffusion coefficient for mixtures not containing silica fume would be equal to the 28 day apparent diffusion coefficient for the control mixture that was ponded at 28 days and the diffusion coefficient for mixtures containing silica fume would be equal to the 28 day apparent diffusion coefficient for the 5% silica fume mixture that was ponded at 28 days. Decay coefficient values are shown in Table 4.4. The experimentally determined decay coefficients are, in most cases, higher than the values predicted by Equation 7, suggesting that service life models which use the theoretical values may yield very conservative results. It can also be seen that the decay coefficients for all ternary mixtures were higher than for either material alone, suggesting that use of ternary blends results in a synergistic effect from both of the incorporated materials on the reduction in concrete diffusivity over time.

**Table 4.4 - Decay coefficient values**

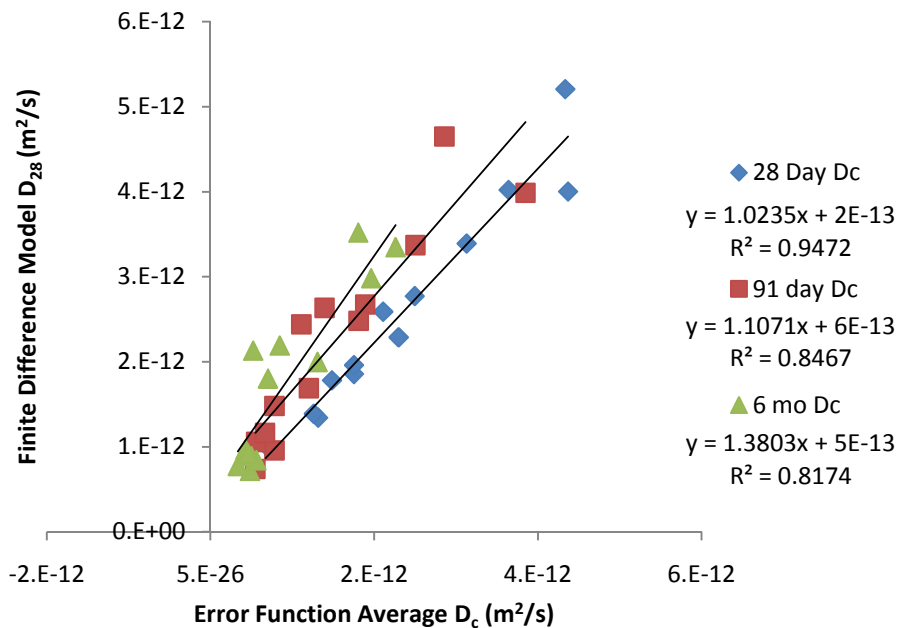
Mixture	Experimental $m$	$m$ predicted by Eqn. 7
OPC-0.34	0.33	0.26
10C-0.34	0.39	0.34
25C-0.34	0.27	0.46
10F-0.34	0.70	0.34
25F-0.34	1.31	0.46
5S-0.34	0.56	0.26
25G-0.34	0.67	0.40
10C 5S-0.34	0.59	0.34
25C 5S-0.34	0.76	0.46
10F 5S-0.34	0.57	0.34
25F 5S-0.34	0.66	0.46
25C 25G-0.34	0.98	0.60
25F 25G-0.34	1.14	0.60

Precision for the chloride profiling tests was determined using six powder samples obtained from unpounded samples of 10% Class C fly ash and 25% Class C fly ash concrete that had not been exposed to the salt water solution. Chloride contents for the samples are shown in Table 4.5.

**Table 4.5 - Chloride Titration Precision**

Mixture	Chloride Concentration (%)	Standard Deviation (%)
10C-0.34	-0.035	0.0152
	-0.010	
	-0.008	
25C-0.34	-0.007	0.0015
	-0.006	
	-0.009	

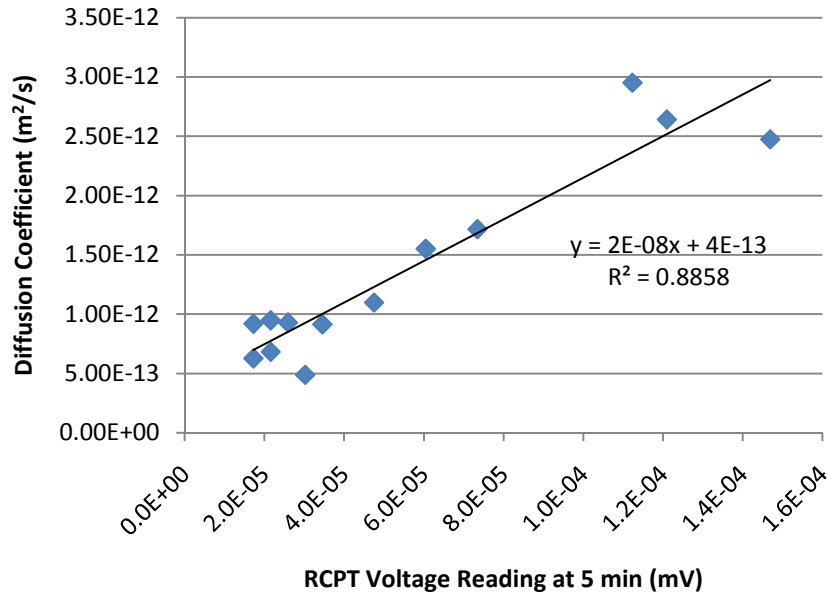
Results of precision tests show the repeatability of samples to be very good, with two standard deviations, representing 95% of the possible chloride concentration values of the 10% Class C fly ash mixture, still within 0.0304% of the average value. The relationship between the error function and finite difference method of diffusion coefficient calculation is shown in Figure 4.6.



**Figure 4.6 - Comparison of error function and finite difference coefficient analysis methods**

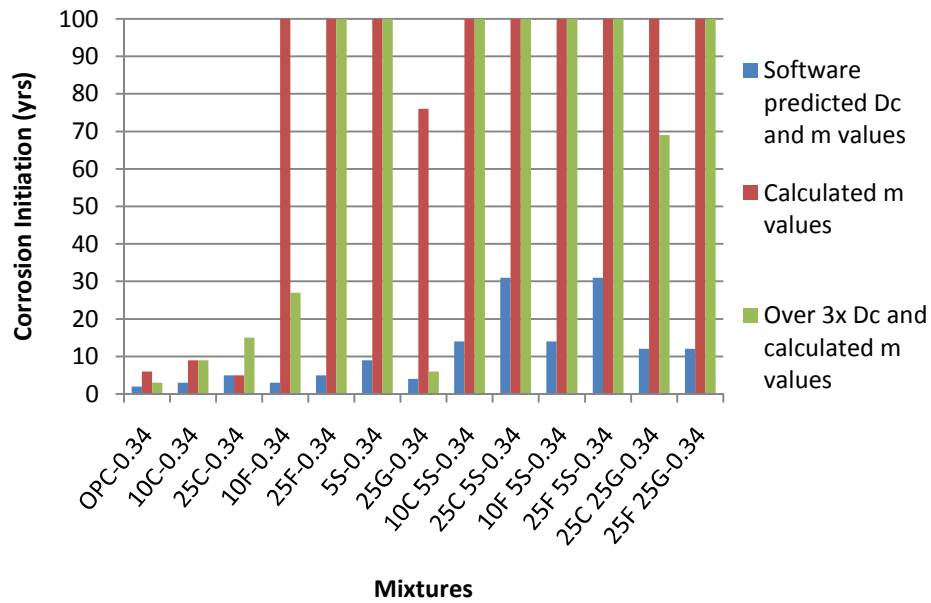
Differences occur due to the way each method calculates the diffusion coefficient. The finite difference model, regardless of the curing or ponding time, calculates the diffusion coefficient of the specimen at 28 days. In contrast, the error function method calculates an average diffusion coefficient over the time the specimen was ponded. Thus the diffusion coefficients calculated using both methods for the specimens ponded at 28 days are very similar. However, because the 91 day and 6 month specimens were not ponded until after 91 days of curing and the 6 month specimens were ponded for 126 days, results for the two diffusion coefficient calculation methods diverge noticeably. For the 91 day specimens the finite difference model calculated the diffusion coefficient of all specimens at 28 days, while the error function method found an average diffusion coefficient value for the specimen over days 91-126, the time the specimen was ponded. For the 6 month specimens, the finite difference model again determine the  $D_{28}$  value while the error function found an average diffusion coefficient value over days 91-217. Due to this long time period, the diffusion coefficients calculated using the error function method tended to be lower than those found by the finite difference method. The error function method not only yields incorrect low values but using these values to calculate service life conditions will result in service life increases that are not conservative.

Concrete electrical conductivity tests were conducted on all mixtures at 91 days of curing. These values were compared with the diffusion coefficients at 91 days calculated from the three profile 28 day diffusion coefficients and decay coefficient values using Equations 4 and 5. Although not directly comparable, these results show good agreement with the 91 day diffusion coefficients, as shown in Figure 4.7. Discrepancies most likely occurred between the methods due to differences in the conductivity of each mixture's pore solution.

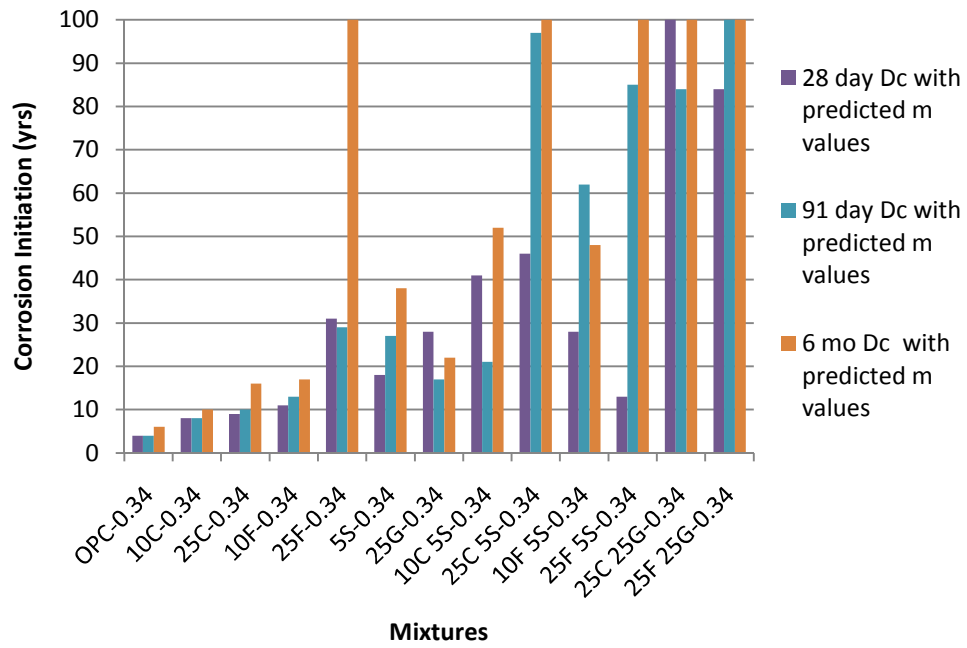


**Figure 4.7 - Rapid chloride permeability and chloride profiling results comparison**

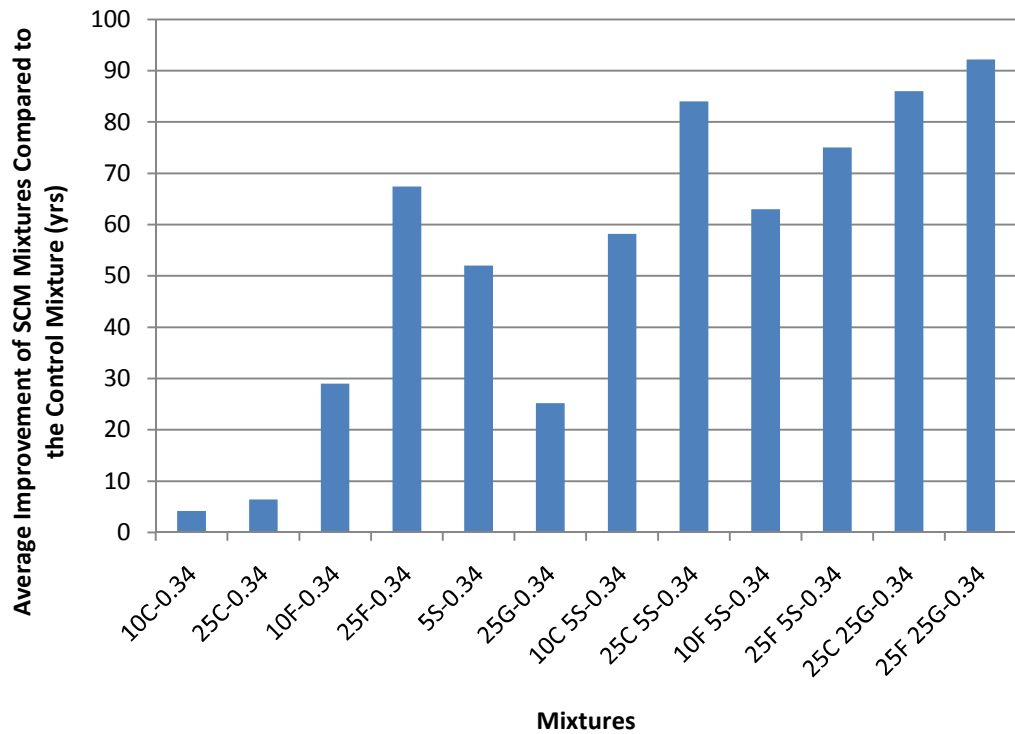
Results of the service life modeling analysis are shown in Figures 4.8 and 4.9 and the average service life increases for SCM mixtures compared to the control mixture are shown in Figure 4.10. The average service life increases were calculated by averaging the time to corrosion initiation for all of the different methods investigated.



**Figure 4.8 – Predicted service life corrosion initiation times**



**Figure 4.9 - Service life modeling predicted corrosion times**



**Figure 4.10 - Average service life increases relative to the control mixture**

Figures 4.8 and 4.9 show that, for all mixtures, the time to initiation of corrosion found using the software's preset values is much less than for those determined from the measured values. Thus the times obtained by using the software's values to model service life will be conservative for cases where diffusion is the main mechanism of chloride ingress, especially for ternary blend mixtures. Figure 4.10 shows the average service life increase for each mixture. These values were computed by averaging the difference between the OPC-0.34 mixture service life and the SCM mixtures for all service life calculations methods shown in Figures 4.8 and 4.9. The default service life program default values were not included in the average. Based on the service life models, the Class C fly ash mixtures were consistently predicted to have the lowest service lives. The Class C fly ash mixtures show an average 4.2 year increase in service life at the 10% replacement level and an average 6.4 year increase in service life at the 25% replacement level compared with the control, however this improvement was much less than the service life improvements shown by the other SCMs which ranged from an average 25.2 year increase in service life for the 25% GGBFS replacement levels to a 92.2 year service life increase for the 25% Class F fly ash 25% GGBFS ternary blend. The predicted time to corrosion initiation was consistently higher for the ternary mixture blends than the binary blends, suggesting that a synergistic effect is occurring between the SCMs, especially in the case of the Class C ternary blends. Figure 4.11 is a comparison of the two software packages used in the service life calculations. For all SCM mixtures the Life-365 software gave more conservative service life predictions than the alternate finite difference modeling program used. The reduced service lives calculated by to the Life-365 model are most likely a result of differences in the prediction of higher diffusion and decay coefficients and increased chloride loading over time.

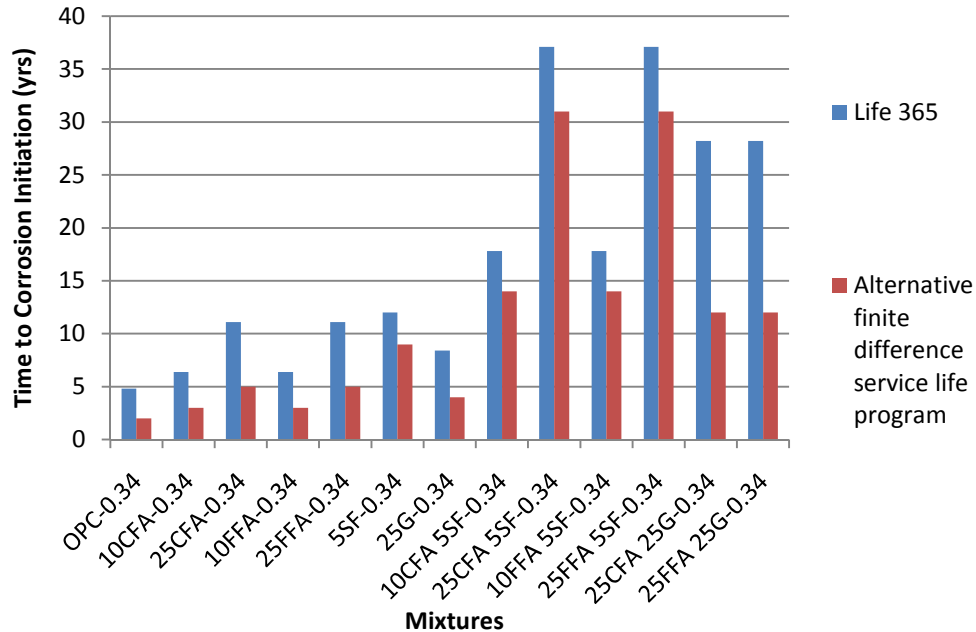


Figure 4.11 - Comparison of the two software packages used to calculate service life

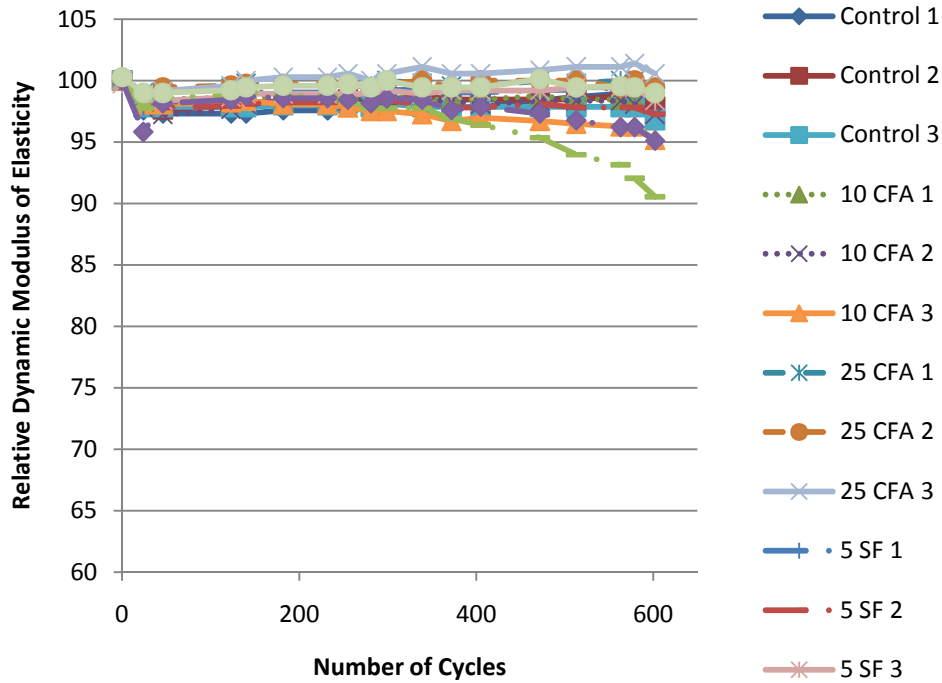
### Freeze-Thaw Durability Test Results

The change in length and resonant frequency were measured for both sets of specimens to determine the resistance to freezing and thawing deterioration of the concrete mixtures. All 0.34 w/cm specimens showed greater than 98% durability factors at 300 cycles and greater than 96% durability factor at 550 cycles. The 0.47 w/cm specimens showed greater than 100% durability factor at 300 cycles and greater than 98% durability factor at 550 cycles. These results show that SCM replacements of portland cement do not adversely affect freeze-thaw durability if there is adequate air entrainment. Dynamic modulus ( $P_c$ ) and length change ( $L_c$ ) results are shown in

Table 4.6 and dynamic modulus results are shown in Figures 4.12 and 4.13 for both the lower and higher w/cm sets of specimens. Results are averaged for three specimens from the same mixture for the 0.34 w/cm mixtures and two specimens from the same mixture for the 0.47 w/cm mixtures.

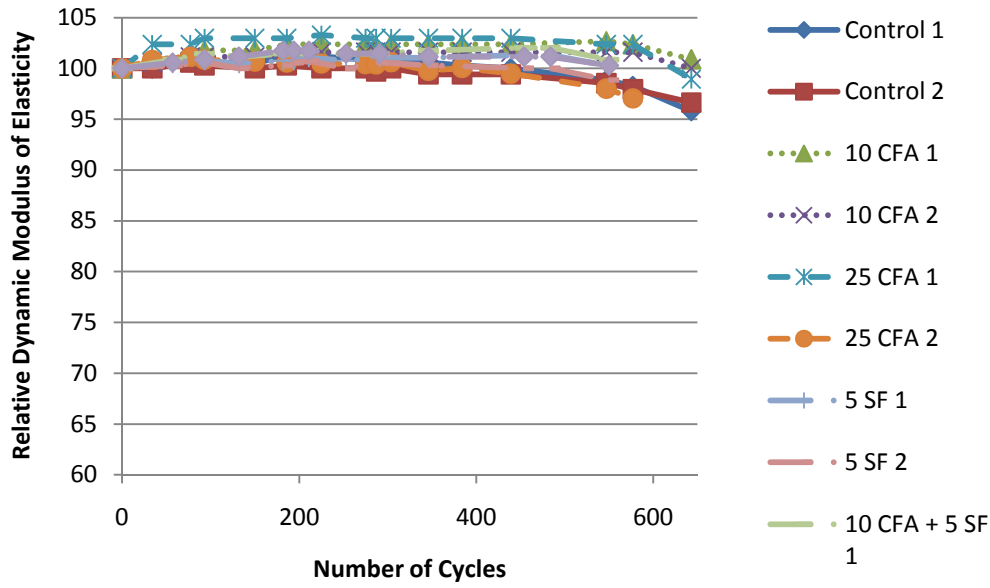
**Table 4.6- Percent change in dynamic modulus and length for freeze-thaw durability specimens**

Mixture	No. of F/T Cycles	300 cycles		550 cycles		
		w/cm	P <sub>c</sub> (%)	L <sub>c</sub> (%)	P <sub>c</sub> (%)	L <sub>c</sub> (%)
OPC-0.34	0.34		98.23	0.02	98.50	0.02
10C-0.34	0.34		98.11	0.02	97.69	0.01
25C-0.34	0.34		100.09	0.01	100.19	0.00
5S-0.34	0.34		98.92	0.01	98.90	0.01
10C 5S-0.34	0.34		98.76	0.01	96.30	0.01
OPC-0.47	0.47		100.29	0.02	98.69	0.02
10C-0.47	0.47		101.99	0.01	101.99	0.02
25C-0.47	0.47		101.79	0.02	99.71	0.03
5S-0.47	0.47		100.66	-0.02	99.55	-0.01
10C 5S-0.47	0.47		101.59	-0.01	100.58	0.00



**Figure 4.12 – Change in relative dynamic modulus of elasticity – w/cm = 0.34**





**Figure 4.13 - Change in relative dynamic modulus of elasticity -  $w/cm = 0.47$**

The resonant frequency values of some of the 0.34  $w/cm$  specimens began to decline near the end of testing, however those results were not repeated with the 0.47  $w/cm$  beams and could be due to normal variations in the concrete. All specimens, for both  $w/cm$ , showed comparable and excellent durability with respect to the control specimen. Results show that as long as adequate air entrainment is provided, there is no evidence that mixtures replacing a portion of portland cement with supplementary cementitious materials are less durable than portland cement concrete mixtures, as has been suggested in literature.<sup>12-14</sup>

## Chapter 5 - Conclusions

Based on the findings of this study, the following conclusions can be drawn:

1. Class C fly ash binary blends improve the diffusivity and increase concrete service life compared to mixtures containing only portland cement, however diffusivity improvements for Class C fly ash binary blends are much less than the improvements seen with Class F fly ash, silica fume and GGBFS binary replacements.
2. Ternary mixture blends demonstrate synergistic diffusivity effects, showing improvements in diffusivity and decay coefficients greater than the improvements shown by either binary blend materials. Class C fly ash showed especially remarkable improvements when incorporated in ternary blends, with only small improvements compared to the control mixture in the binary mixtures, while the diffusivity, decay coefficients and service life improvements of Class C fly ash ternary blends were comparable to or greater than the improvements of other binary and ternary blends.
3. As the reduction in diffusivity of Class C fly ash concrete is much less than the reduction that occurs with the use of Class F fly ash, it is not adequate to use the same model for these two materials in service life calculations. Diffusion and decay coefficients should be developed for Class C fly ash concrete for use in service life models.
4. Similarly, ternary mixture blends exhibit much different traits than either binary blend materials. Due to the synergistic effects shown by the ternary blends, they should neither be modeled as the better of the included materials nor as a simple addition of components, but rather, as a different material, using different diffusion and decay coefficients.
5. The ASTM C 1556<sup>30</sup> error function method of determining average diffusion coefficients may not be a good predictor of 28 day apparent diffusivity for curing greater than 28 days and/or ponding times greater than 35 days. Values calculated by the error function method match closely for specimens with short curing and ponding times, as shown for this study's specimens which were cured for 28 days and ponded for 35. However, for longer curing and ponding times, the average diffusion coefficient values computed by the error function method diverge from the 28 day diffusion coefficient as calculated using finite difference methods. For specimens with longer ponding and/or curing times

the average diffusion coefficient will be lower than the predicted 28 day apparent diffusion coefficient and will result in higher than expected service life predictions.

6. Concrete diffusivity, found through the chloride profiling method, and conductivity, as determined using the modified ASTM C 1202<sup>32</sup> setup, are closely correlated. Differences in the conductivity of pore solution ions from the use of SCMs results in discrepancies between the two methods irrespective of the similarities in specimen porosity and chloride diffusivity.
7. Current service life models calculate higher concrete diffusivity than what this research suggests will actually occur. This results in conservative service life predictions. Of the two software packages, Life-365 gives much lower service life predictions than the other finite difference model program.
8. As long as adequate air entrainment is provided, this research shows no evidence that SCM mixtures are less durable than portland cement concrete when subjected to freezing and thawing.

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## Appendix A - ASTM C 1556 Chloride Profiling Procedures

After casting and curing, specimens were first cut 3" from the finished face using a concrete saw. The specimen surface was allowed to dry, after which a ring of duck tape was applied around the outer circumference of the cylinder on the finished face as shown in Figure A.1. The specimen was placed with the finished face towards the table and covered in two-part epoxy paint. The epoxy was cured for 24 hours and then labeled with their mixture number, as shown in Figure A.2.



**Figure A.1 - Three inch concrete specimen with protective duck tape**



**Figure A.2 - Cured and labeled diffusivity specimens**

The specimens were immersed in a saturated calcium hydroxide solution (3g/L) for 24 hours, rinsed and then moved to the NaCl exposure solution. The specimens were stored in the ponding salt solution in 5 gallon buckets, with plastic louvers separating each layer, allowing the salt solution to be in contact with the exposed concrete surface of all specimens.



After the specified immersion period, the specimens were removed from the ponding solution, rinsed with tap water and allowed to dry in the shrinkage room, with the air maintained at  $23 \pm 2^{\circ}\text{C}$  and  $50 \pm 3\%$  relative humidity. After 24 hours the specimens were stored in watertight resealable bags until the time of grinding.

Powdered concrete samples were obtained using the profile grinding machine shown in Figure A.3. The machine consisted of a drill press equipped with a 1" core bit and a moveable base. Layers of concrete were removed by drilling a small amount into the concrete and then cranking the base across while holding the height of the drill steady. The concrete specimen was removed from the drill press after each pass of the current layer. The dust for each layer was shaken off and collected in a resealable plastic bag and measurements were taken and recorded at five locations across the ground face of the cylinder using a micrometer.



**Figure A.3 - Profile grinder with specimen**

## Appendix B - 1152 Titration Procedures

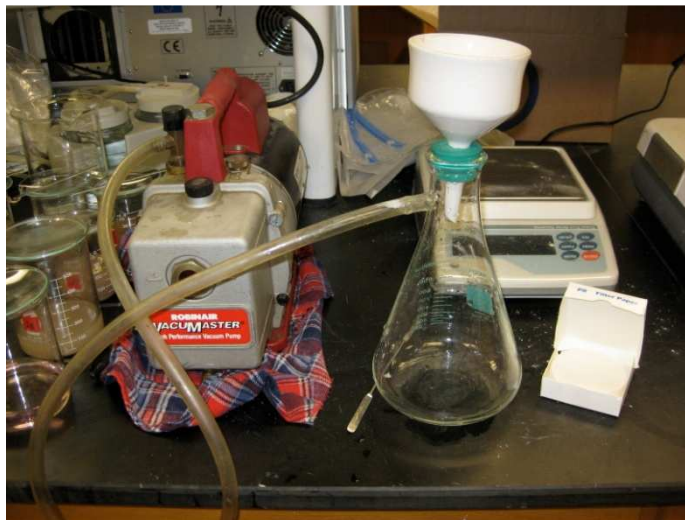
In order to determine the chloride content of a sample of concrete powder, 10 g of the sample was weighed and the mass was recorded to the nearest 0.01 g. The sample was then transferred to a 250 mL beaker as shown in Figure B.1 and dispersed in 75 mL of distilled water. Dilute nitric acid was then created by combining equal parts distilled water and nitric acid. 25 mL of the diluted acid was slowly added to the dispersed concrete powder in order to disassociate the powder's chloride ions and cement particles. If the sample used included GGBFS, 3 mL of 30% hydrogen peroxide was added to oxidize excessive sulfur in the mixture which can interfere with chloride measurements performed by titration. Three to four drops of methyl orange indicator were added to the beaker while the mixture was stirred with a glass stirring rod to make sure that the sample and acid were thoroughly combined. The beaker was then heated and allowed to boil for ten seconds before being removed from heat. A blank sample was created for each group of specimens following all of the same steps but without the added powder sample. A blank sample was titrated with every set of titration specimens in order to establish a baseline chloride concentration resulting from the chemicals used during the disassociation of the concrete powder and chlorides. The blank sample's chloride concentration was subtracted from each sample's chloride concentration during data analysis.



**Figure B.1 - Powdered sample**

After cooling to room temperature, the samples were filtered using a 6-cm diameter coarse-textured filter paper and a 250 mL Buchner funnel and filtration flask as shown in Figure

B.2. The filter paper and beaker were rinsed twice, after which the solution was then transferred back to the original beaker. A new filter paper was used for each sample.



**Figure B.2 - Buchner funnel setup**

Distilled water was added to bring the sample to 158 mL after 3 mL of a 5 N sodium nitrate ( $\text{NaNO}_3$ ) ion strength adjustor (ISA) solution was added to the sample. Several milliliters of 0.05 N sodium chloride ( $\text{NaCl}$ ) were added to the beaker depending on the projected chloride level of the solution in order to give the sample a beginning chloride concentration. Sodium chloride was added to samples in order to avoid the complications and error inherent in low-level chloride titration. For the blank sample and other samples expected to have very low chloride levels 4 mL of  $\text{NaCl}$  were added, while 2 mL were added to samples expected to have a mid-range level of chlorides. Sodium chloride was not added to samples that were expected to have high chloride levels.

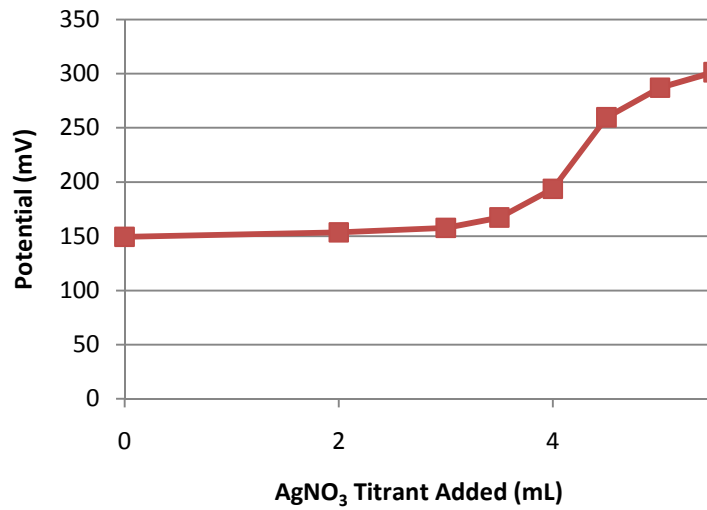
After adding  $\text{NaCl}$  and  $\text{NaNO}_3$ , the sample was stirred continuously using a TFE-fluorocarbon coated magnetic stir bar. The silver-sulfide electrode was then immersed in the solution as shown in Figure B.3, taking care to immerse the electrode up to the white reference mark on the side of the electrode cylinder. The electrode was allowed to sit for several minutes to obtain a stable reading before beginning the titration.



**Figure B.3 - Electrode, burette and sample titration setup**

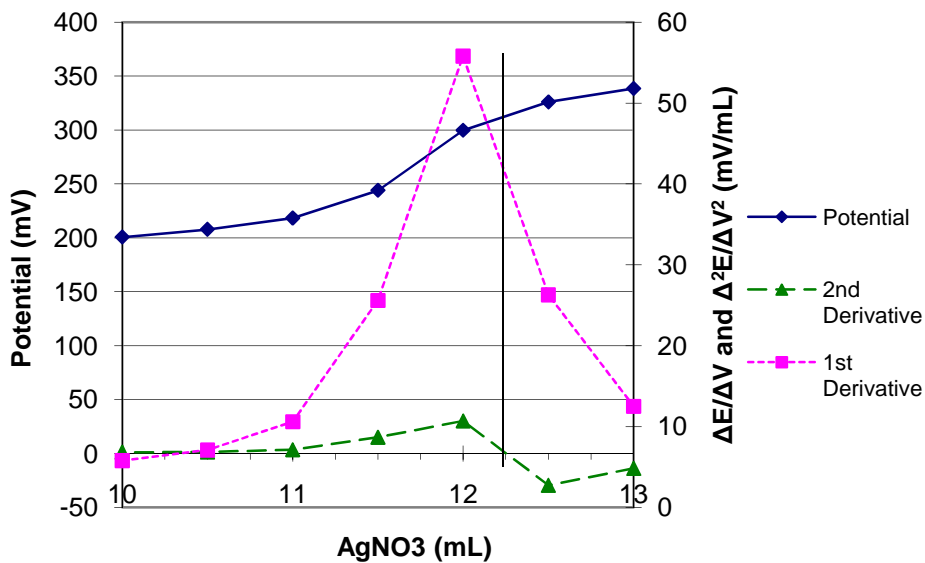
The titration was conducted using a 0.05 N  $\text{AgNO}_3$  solution. The tip of the titration burette was placed just into the surface of the water and titrant was added 1-2 mL at a time. The amount of titrant added to the solution and the corresponding electrode potential was recorded for each addition of  $\text{AgNO}_3$ . The electrode reading was allowed to stabilize before adding additional titrant to the solution. The chloride concentration for each sample was determined by the finding the solution's equivalence point. The equivalence point was reached when the amount of  $\text{AgNO}_3$  added to the mixture equals the amount of chloride in the mixture. When the solution was far from the equivalence point the change in potential with added titrant was very small, but as the solution was titrated further the changes in potential increased until the equivalence point was reached. After the equivalence point was passed the change in potential with added titrant became increasingly smaller. The equivalence point of the solution was found at the point where the greatest change in potential occurred during this process.

Plotting the potential (E) versus the amount of titrant added (V) during the titration resulted in an S-shaped curve, and the equivalence point was found at the midpoint of the most steeply rising portion of the S shape. The equivalence point was sometimes difficult to determine from the S-curve like the curve shown in Figure B.4.



**Figure B.4 - Titration S-curve**

Derivative methods were used to more easily and accurately determine the equivalence point. Plotting the first derivative,  $\Delta E/\Delta V$  against  $V$ , yielded a steep peak at the point of inflection in the S curve. A second derivative plot of  $\Delta^2 E/\Delta V^2$  versus  $V$ , was equal to zero at the point of greatest slope in the original S curve, or the equivalence point.<sup>35</sup> The 28 day 25% Class C fly ash specimen's potential curve and its first two derivatives are shown in Figure B.5.



**Figure B.5 - Titration potential and derivative curves**

After determining at what amount of added titrant the equivalence point occurred, the percent chloride present in the sample was calculated according to ASTM C 1152<sup>34</sup> using equation 8:

$$Cl, \% = 3.545 \frac{[(V_1 - V_2)N]}{W} \quad (8)$$

Where  $V_1$  is the amount of titrant added, in milliliters, at the sample's equivalence point,  $V_2$  is the amount of titrant added to reach the equivalence point of the blank sample,  $N$  is the exact normality of the 0.05 N AgNO<sub>3</sub> titration solution and  $W$  is the mass of the sample in grams.

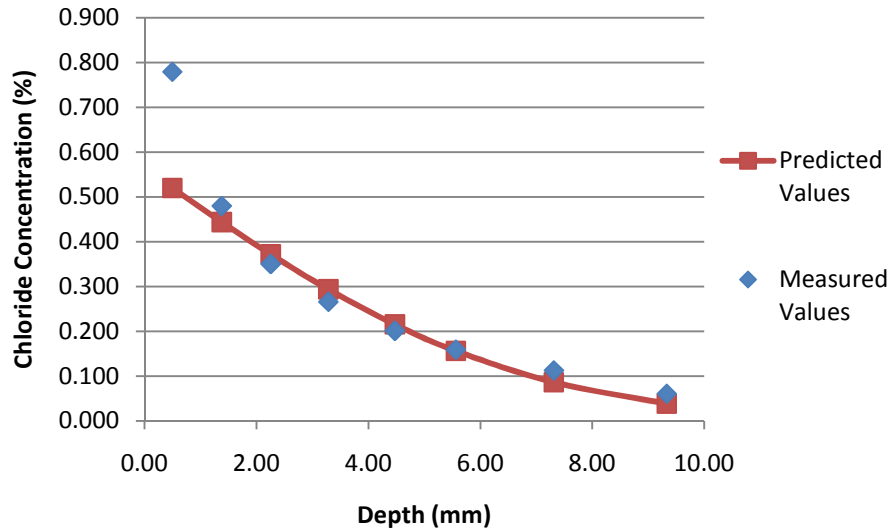
## Appendix C - Chloride Profile Data Analysis

Two methods of analysis were used to interpret chloride profiling results. The first method determined the diffusion coefficients the error function using Equation 4. For this method a spreadsheet was built to create a chloride profile based upon the specimen's exposure time in seconds,  $t$ , projected chloride concentration at the specimen's surface,  $C_s$ , the apparent diffusion coefficient,  $D_a$  and depth of the layer. The error between the predicted and experimentally measured values was calculated for each layer and the values were optimized to find the solution yielding the least error. The diffusion coefficient calculations for the 28 day 25C-0.34 specimen are shown in Table C.1 and then fitted curve is shown in Figure C.1.

**Table C.1 - Error function calculations**

Cs (mass %)	Ci (mass %)	Da (m <sup>2</sup> /s)	t (yrs)	Sum (Error) <sup>2</sup>
0.563	0	4.34E-12	0.0958	3.910E-03

x (mm)	Measured Values	Predicted Values	Error, ΔC(n) (Meas.-Pred.)	(Error) <sup>2</sup>
0.50	0.779	0.520		
1.38	0.479	0.444	0.036	1.28E-03
2.26	0.350	0.372	-0.022	4.65E-04
3.29	0.266	0.294	-0.028	7.82E-04
4.47	0.201	0.215	-0.015	2.11E-04
5.56	0.159	0.156	0.003	6.42E-06
7.31	0.112	0.086	0.026	6.80E-04
9.33	0.061	0.039	0.022	4.87E-04



**Figure C.1 - Error function method graph of least error fit**

Chloride profiles were also analyzed through a finite difference model applying Fick’s second law of diffusion. A finite difference model was built using a spreadsheet to model the chloride diffusion with time in the chloride ponding samples. In the spreadsheet, the change in chloride concentration was calculated at every 0.5 mm for 0.1 day time steps from the time when the specimen was ponded using Equations 1 and 2. The modeled values at the end of the ponding period were compared to the measured values with the diffusion coefficients, decay coefficients and  $C_s$  values changed using the solver until the modeled values fit the measured values. The fit variables, measured and calculated values are shown in Table C.2 and the fit curve is shown in Figure C.2.

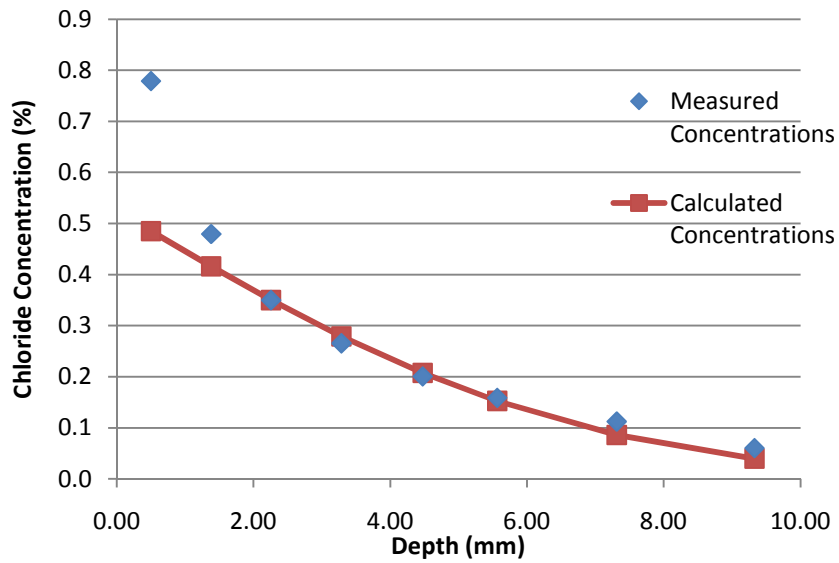
**Table C.2 - Finite difference model calculations for 28 day 25C-0.34 specimen**

Mixture Variables:		
D28 =	5.207E-12	m <sup>2</sup> /s
m =	0.46	
C <sub>s</sub> =	0.5246	%



Measured values:		Calculated Values:	
Depth	Concentration	Concentration at Measured Value Depth	Error
0.500	0.779	0.485	
1.381	0.479	0.416	0.063
2.256	0.350	0.350	0.000
3.286	0.266	0.279	0.013
4.474	0.201	0.208	0.007
5.564	0.159	0.153	0.006
7.313	0.112	0.086	0.026
9.327	0.061	0.040	0.021

AAE = 0.020



**Figure C.2 - Finite difference method best fit graph**

## Appendix D - Chloride Profile Data

**Table D.1 - Finite difference model diffusion coefficients, decay coefficients and surface chloride concentration**

Mixture	28 Day			91 day			6 month			3 profile	
	$D_{28} \times 10^{-12}$	m	$C_s$	$D_{28} \times 10^{-12}$	m	$C_s$	$D_{28} \times 10^{-12}$	m	$C_s$	$D_{28} \times 10^{-12}$	m
<b>OPC-0.34</b>	4.003	0.260	0.537	3.988	0.260	0.329	3.347	0.260	0.580	5.280	0.494
<b>10C-0.34</b>	3.392	0.340	0.485	3.372	0.340	0.935	2.982	0.340	0.668	3.488	0.303
<b>25C-0.34</b>	5.207	0.460	0.525	4.651	0.460	0.666	3.518	0.460	0.815	6.283	0.574
<b>10F-0.34</b>	2.774	0.340	0.648	2.482	0.340	0.808	1.999	0.340	0.742	3.070	0.543
<b>25F-0.34</b>	2.289	0.460	0.708	2.441	0.460	0.765	0.971	0.460	1.036	3.186	1.166
<b>5S-0.34</b>	1.344	0.260	0.525	0.957	0.260	0.568	0.719	0.260	0.547	1.692	0.731
<b>25G-0.34</b>	1.857	0.403	0.622	2.675	0.403	0.838	2.192	0.403	0.656	1.946	0.271
<b>10C 5S-0.34</b>	1.020	0.340	0.595	1.690	0.340	0.629	0.844	0.340	0.785	1.136	0.509
<b>25C 5S-0.34</b>	1.782	0.460	0.899	1.058	0.460	1.012	0.776	0.460	1.036	2.405	1.129
<b>10F 5S-0.34</b>	1.390	0.340	0.784	0.740	0.340	1.405	0.892	0.340	1.069	1.700	0.701
<b>25C 5S-0.34</b>	4.021	0.460	0.759	1.163	0.460	0.765	0.927	0.460	1.166	6.890	1.667
<b>25C 5S-0.34</b>	1.962	0.603	0.845	2.634	0.603	0.649	2.131	0.603	0.772	1.861	0.500
<b>25F 5S-0.34</b>	2.591	0.603	0.982	1.481	0.603	1.571	1.803	0.603	1.226	2.974	0.899

**Table D.2 - Error function average diffusion coefficients and surface chloride concentration**

Mixture	28 day		91 day		6 mo	
	$D_a$	$C_s$	$D_a$	$C_s$	$D_a$	$C_s$
<b>OPC-0.34</b>	4.370	0.550	3.850	0.300	2.263	0.626
<b>10C-0.34</b>	3.130	0.498	2.504	0.878	1.965	0.647
<b>25C-0.34</b>	4.336	0.563	2.859	0.649	1.807	0.830
<b>10F-0.34</b>	2.496	0.646	1.810	0.757	1.309	0.659
<b>25F-0.34</b>	2.299	0.679	1.111	0.939	0.428	1.039
<b>5S-0.34</b>	1.316	0.508	0.783	0.578	0.483	0.554
<b>25G-0.34</b>	1.754	0.635	1.890	0.797	0.847	0.779
<b>10C 5S-0.34</b>	0.674	0.687	1.204	0.628	0.560	0.754
<b>25C 5S-0.34</b>	1.485	0.901	0.558	1.123	0.334	1.083
<b>10F 5S-0.34</b>	1.261	0.789	0.548	1.409	0.499	1.110
<b>25C 5S-0.34</b>	3.644	0.738	0.666	0.777	0.457	1.179
<b>25C 5S-0.34</b>	1.753	0.790	1.394	0.626	0.522	0.984
<b>25F 5S-0.34</b>	2.110	0.992	0.782	1.559	0.703	1.211

**Table D.3 – OPC-0.34 measured and predicted chloride profiles for diffusion coefficient calculation**

OPC - 0.34											
28 day				91 day				6 mo			
Depth	Chloride Concentration (%)			Depth	Chloride Concentration (%)			Depth	Chloride Concentration (%)		
	Measured	Predicted			Measured	Predicted			Measured	Predicted	
		Finite Difference	Error function			Finite Difference	Error function			Finite Difference	Error function
0.57	0.4910	0.4864	0.5014	0.62	0.4043	0.2914	0.2692	0.61	0.9636	0.5405	0.5825
1.58	0.4285	0.3989	0.4173	1.65	0.2683	0.2319	0.2196	1.73	0.5710	0.4702	0.5045
2.50	0.3127	0.3240	0.3448	2.56	0.1794	0.1833	0.1786	2.68	0.4115	0.4118	0.4399
3.59	0.2446	0.2446	0.2667	3.61	0.1346	0.1346	0.1364	3.71	0.3386	0.3522	0.3741
4.68	0.1978	0.1776	0.1993	4.68	0.0856	0.0935	0.0995	4.71	0.2772	0.2982	0.3147
5.62	0.1298	0.1307	0.1511	5.73	0.0666	0.0627	0.0706	5.70	0.2644	0.2489	0.2609
7.01	0.1238	0.0758	0.0950	7.11	0.0439	0.0332	0.0422	7.24	0.1871	0.1839	0.1895
9.09	0.0975	0.0306	0.0424	9.12	-0.0002	0.0117	0.0176	9.21	0.1178	0.1178	0.1188
AAE/Error <sup>2</sup> =		0.0253	0.0060	AAE/Error <sup>2</sup> =		0.0107	0.0029	11.75	0.0954	0.0004	0.0589
								14.72	0.0889	0.0004	0.0225
								AAE/Error <sup>2</sup> =		0.0375	-0.0049

**Table D.4 – OPC-0.34 measured and predicted chloride profiles for diffusion coefficient calculation**

3 Profile OPC - 0.34								
28 day			91 day			6 mo		
Depth	Chloride Conc (%)		Depth	Chloride Conc (%)		Depth	Chloride Conc (%)	
	Measured	Predicted		Measured	Predicted		Measured	Predicted
		Finite Difference			Finite Difference			Finite Difference
0.57	0.4910	0.5356	0.62	0.4043	0.2931	0.61	0.9636	0.5169
1.58	0.4285	0.4285	1.65	0.2683	0.2329	1.73	0.5710	0.4571
2.50	0.3127	0.3380	2.56	0.1794	0.1838	2.68	0.4115	0.4072
3.59	0.2446	0.2446	3.61	0.1346	0.1346	3.71	0.3386	0.3557
4.68	0.1978	0.1686	4.68	0.0856	0.0932	4.71	0.2772	0.3084
5.62	0.1298	0.1177	5.73	0.0666	0.0623	5.70	0.2644	0.2644
7.01	0.1238	0.0668	7.11	0.0439	0.0328	7.24	0.1871	0.2045
9.09	0.0975	0.0210	9.12	-0.0002	0.0115	9.21	0.1178	0.1408
AAE =		0.0286	AAE =		0.0106	AAE =		0.0296

**Table D.5 – OPC-0.34 measured and predicted chloride profiles for decay coefficient calculation**

m value calculation OPC - 0.34								
28 day			91 day			6 mo		
Depth	Chloride Conc (%)		Depth	Chloride Conc (%)		Depth	Chloride Conc (%)	
	Measured	Predicted		Measured	Predicted		Measured	Predicted
		Finite Difference			Finite Difference			Finite Difference
0.57	0.4910	0.4854	0.62	0.4043	0.2894	0.61	0.9636	0.5415
1.58	0.4285	0.3965	1.65	0.2683	0.2271	1.73	0.5710	0.4729
2.50	0.3127	0.3204	2.56	0.1794	0.1766	2.68	0.4115	0.4158
3.59	0.2446	0.2402	3.61	0.1346	0.1268	3.71	0.3386	0.3574
4.68	0.1978	0.1729	4.68	0.0856	0.0856	4.71	0.2772	0.3043
5.62	0.1298	0.1261	5.73	0.0666	0.0555	5.70	0.2644	0.2556
7.01	0.1238	0.0764	7.11	0.0439	0.0277	7.24	0.1871	0.1909
9.09	0.0975	0.0282	9.12	-0.0002	0.0089	9.21	0.1178	0.1244
AAE =		0.0253	AAE =		0.0107	AAE =		0.0375

**Table D.6 – 10C-0.34 measured and predicted chloride profiles for diffusion coefficient calculation**

<b>10C-0.34</b>											
<b>28 day</b>				<b>91 day</b>				<b>6 mo</b>			
<b>Depth</b>	<b>Chloride Concentration (%)</b>			<b>Depth</b>	<b>Chloride Concentration (%)</b>			<b>Depth</b>	<b>Chloride Concentration (%)</b>		
	<b>Measured</b>	<b>Predicted</b>			<b>Measured</b>	<b>Predicted</b>			<b>Measured</b>	<b>Predicted</b>	
		<b>Finite Difference</b>	<b>Error function</b>			<b>Finite Difference</b>	<b>Error function</b>			<b>Finite Difference</b>	<b>Error function</b>
0.51	0.5579	0.4402	0.4511	0.54	0.9258	0.8287	0.4511	0.53	0.5818	0.6227	0.7511
1.59	0.3495	0.3479	0.3557	1.52	0.6432	0.6432	0.3557	1.54	0.5621	0.5385	0.6340
2.60	0.3118	0.2683	0.2734	2.47	0.4229	0.4795	0.2734	2.51	0.4597	0.4597	0.5383
3.56	0.1717	0.2026	0.2058	3.53	0.2893	0.3278	0.2058	3.50	0.3491	0.3853	0.4478
4.57	0.1330	0.1444	0.1459	4.55	0.2269	0.2150	0.1459	4.49	0.2757	0.3166	0.3750
5.72	0.1004	0.0938	0.0940	5.52	0.1717	0.1352	0.0940	5.60	0.2436	0.2485	0.3030
6.99	0.0540	0.0519	0.0539	7.01	0.0613	0.0565	0.0539	7.07	0.1896	0.1719	0.2121
				9.02	0.0239	0.0149		8.96	0.1652	0.1004	0.1231
AAE/Error <sup>2</sup> =		0.0260	0.0029	AAE/Error <sup>2</sup> =		0.0225	0.0029	AAE/Error <sup>2</sup> =		0.0269	0.0032

**Table D.7 – 10C-0.34 measured and predicted chloride profiles for diffusion coefficient calculation**

<b>3 Profile 10C-0.34</b>								
<b>28 day</b>			<b>91 day</b>			<b>6 mo</b>		
<b>Depth</b>	<b>Chloride Conc (%)</b>		<b>Depth</b>	<b>Chloride Conc (%)</b>		<b>Depth</b>	<b>Chloride Conc (%)</b>	
	<b>Measured</b>	<b>Predicted</b>		<b>Measured</b>	<b>Predicted</b>		<b>Measured</b>	<b>Predicted</b>
		<b>Finite Difference</b>			<b>Finite Difference</b>			<b>Finite Difference</b>
0.51	0.5579	0.4242	0.54	0.9258	0.8173	0.53	0.5818	0.6069
1.59	0.3495	0.3398	1.52	0.6432	0.6382	1.54	0.5621	0.5312
2.60	0.3118	0.2663	2.47	0.4229	0.4795	2.51	0.4597	0.4600
3.56	0.1717	0.2050	3.53	0.2893	0.3314	3.50	0.3491	0.3922
4.57	0.1330	0.1497	4.55	0.2269	0.2201	4.49	0.2757	0.3288
5.72	0.1004	0.1004	5.52	0.1717	0.1405	5.60	0.2436	0.2648
6.99	0.0540	0.0626	7.01	0.0613	0.0605	7.07	0.1896	0.1940
			9.02	0.0239	0.0167	8.96	0.1652	0.1221
	AAE =	0.0190		AAE =	0.0214		AAE =	0.0280



**Table D.8 – 10C-0.34 measured and predicted chloride profiles for decay coefficient calculation**

m value calculation 10C-0.34								
28 day			91 day			6 mo		
Depth	Chloride Conc (%)		Depth	Chloride Conc (%)		Depth	Chloride Conc (%)	
	Measured	Predicted		Measured	Predicted		Measured	Predicted
		Finite Difference			Finite Difference			Finite Difference
0.51	0.5579	0.4436	0.54	0.9258	0.8259	0.53	0.5818	0.6269
1.59	0.3495	0.3581	1.52	0.6432	0.5703	1.54	0.5621	0.5504
2.60	0.3118	0.2833	2.47	0.4229	0.4229	2.51	0.4597	0.4783
3.56	0.1717	0.2204	3.53	0.2893	0.2885	3.50	0.3491	0.4095
4.57	0.1330	0.1631	4.55	0.2269	0.1897	4.49	0.2757	0.3449
5.72	0.1004	0.1115	5.52	0.1717	0.1201	5.60	0.2436	0.2794
6.99	0.0540	0.0709	7.01	0.0613	0.0682	7.07	0.1896	0.2066
			9.02	0.0239	0.0199	8.96	0.1652	0.1320
	AAE =	0.0240		AAE =	0.0248		AAE =	0.0351

**Table D.9 – 25C-0.34 measured and predicted chloride profiles for diffusion coefficient calculation**

25C-0.34											
28 day				91 day				6 mo			
Depth	Chloride Concentration (%)			Depth	Chloride Concentration (%)			Depth	Chloride Concentration (%)		
	Measured	Predicted			Measured	Predicted			Measured	Predicted	
		Finite Difference	Error function			Finite Difference	Error function			Finite Difference	Error function
0.50	0.7786	0.4850	0.5197	0.49	0.7117	0.6016	0.7808	0.75	0.9259	0.7362	0.3389
1.38	0.4795	0.4160	0.4437	1.47	0.4777	0.4777	0.6112	1.88	0.6821	0.6180	0.2224
2.26	0.3501	0.3501	0.3717	2.56	0.3451	0.3520	0.4609	2.86	0.5217	0.5217	0.1359
3.29	0.2657	0.2789	0.2937	3.58	0.2519	0.2517	0.3196	3.85	0.4104	0.4310	0.0763
4.47	0.2009	0.2075	0.2154	4.51	0.1655	0.1775	0.2132	4.72	0.3512	0.3585	0.0421
5.56	0.1588	0.1527	0.1563	5.48	0.1177	0.1177	0.1369	5.68	0.2870	0.2871	0.0152
7.31	0.1124	0.0861	0.0864	6.96	0.0815	0.0546	0.0630	7.13	0.2191	0.1960	0.0027
9.33	0.0607	0.0399	0.0386	9.03	0.0362	0.0164	0.0180	9.07	0.1839	0.1103	0.0000
AAE/Error <sup>2</sup> =		0.0195	0.0039	AAE/Error <sup>2</sup> =		0.0094	0.0048	AAE/Error <sup>2</sup> =		0.0270	-0.0035

**Table D.10 – 25C-0.34 measured and predicted chloride profiles for diffusion coefficient calculation**

<b>3 Profile 25C-0.34</b>								
<b>28 day</b>			<b>91 day</b>			<b>6 mo</b>		
<b>Depth</b>	<b>Chloride Conc (%)</b>		<b>Depth</b>	<b>Chloride Conc (%)</b>		<b>Depth</b>	<b>Chloride Conc (%)</b>	
	<b>Measured</b>	<b>Predicted</b>		<b>Measured</b>	<b>Predicted</b>		<b>Measured</b>	<b>Predicted</b>
		<b>Finite Difference</b>			<b>Finite Difference</b>			<b>Finite Difference</b>
0.50	0.7786	0.4961	0.49	0.7117	0.6054	0.75	0.9259	0.6783
1.38	0.4795	0.4212	1.47	0.4777	0.4765	1.88	0.6821	0.5801
2.26	0.3501	0.3501	2.56	0.3451	0.3466	2.86	0.5217	0.4993
3.29	0.2657	0.2740	3.58	0.2519	0.2441	3.85	0.4104	0.4222
4.47	0.2009	0.1989	4.51	0.1655	0.1692	4.72	0.3512	0.3595
5.56	0.1588	0.1425	5.48	0.1177	0.1099	5.68	0.2870	0.2966
7.31	0.1124	0.0777	6.96	0.0815	0.0488	7.13	0.2191	0.2167
9.33	0.0607	0.0327	9.03	0.0362	0.0137	9.07	0.1839	0.1338
AAE =		0.0211	AAE =		0.0111	AAE =		0.0295

**Table D.11 – 25C-0.34 measured and predicted chloride profiles for decay coefficient calculation**

m value calculation 25C-0.34								
28 day			91 day			6 mo		
Depth	Chloride Conc (%)		Depth	Chloride Conc (%)		Depth	Chloride Conc (%)	
	Measured	Predicted		Measured	Predicted		Measured	Predicted
		Finite Difference			Finite Difference			Finite Difference
0.50	0.7786	0.4815	0.49	0.7117	0.6067	0.75	0.9259	0.7529
1.38	0.4795	0.4068	1.47	0.4777	0.4329	1.88	0.6821	0.6589
2.26	0.3501	0.3360	2.56	0.3451	0.3204	2.86	0.5217	0.5807
3.29	0.2657	0.2606	3.58	0.2519	0.2314	3.85	0.4104	0.5051
4.47	0.2009	0.1869	4.51	0.1655	0.1655	4.72	0.3512	0.4423
5.56	0.1588	0.1321	5.48	0.1177	0.1119	5.68	0.2870	0.3777
7.31	0.1124	0.0703	6.96	0.0815	0.0695	7.13	0.2191	0.2923
9.33	0.0607	0.0284	9.03	0.0362	0.0238	9.07	0.1839	0.1983
AAE =		0.0291	AAE =		0.0172	AAE =		0.0638

**Table D.12 – 10F-0.34 measured and predicted chloride profiles for diffusion coefficient calculation**

<b>10F-0.34</b>											
<b>28 day</b>				<b>91 day</b>				<b>6 mo</b>			
<b>Depth</b>	<b>Chloride Concentration (%)</b>			<b>Depth</b>	<b>Chloride Concentration (%)</b>			<b>Depth</b>	<b>Chloride Concentration (%)</b>		
	<b>Measured</b>	<b>Predicted</b>			<b>Measured</b>	<b>Predicted</b>			<b>Measured</b>	<b>Predicted</b>	
		<b>Finite Difference</b>	<b>Error function</b>			<b>Finite Difference</b>	<b>Error function</b>			<b>Finite Difference</b>	<b>Error function</b>
0.50	0.7108	0.5815	0.5799	0.61	0.7669	0.6873	0.6464	0.54	1.1119	0.6807	0.6060
1.47	0.4580	0.4580	0.4557	1.67	0.4911	0.4910	0.4650	1.64	0.5633	0.5588	0.5006
2.74	0.3218	0.3146	0.3110	2.56	0.2942	0.3473	0.3320	2.73	0.3267	0.4450	0.4017
3.81	0.1879	0.2153	0.2116	3.53	0.2071	0.2234	0.2162	3.75	0.2758	0.3491	0.3180
4.61	0.1471	0.1555	0.1521	4.55	0.1304	0.1304	0.1280	4.74	0.2684	0.2684	0.2469
5.56	0.1014	0.1014	0.0985	5.53	0.0889	0.0718	0.0717	5.74	0.2114	0.2000	0.1862
7.08	0.0674	0.0440	0.0441	6.96	0.0579	0.0233	0.0268	7.20	0.1341	0.1250	0.1170
9.23	0.0190	0.0117	0.0113	8.91	0.0055	0.0042	0.0053	9.12	0.0606	0.0606	0.0578
AAE/Error <sup>2</sup> =		0.0105	0.0060	AAE/Error <sup>2</sup> =		0.0175	0.0035	AAE/Error <sup>2</sup> =		0.0310	0.0017

**Table D.13 – 10F-0.34 measured and predicted chloride profiles for diffusion coefficient calculation**

3 Profile 10F-0.34								
28 day			91 day			6 mo		
Depth	Chloride Conc (%)		Depth	Chloride Conc (%)		Depth	Chloride Conc (%)	
	Measured	Predicted		Measured	Predicted		Measured	Predicted
		Finite Difference			Finite Difference			Finite Difference
0.50	0.7108	0.5817	0.61	0.7669	0.6933	0.54	1.1119	0.6324
1.47	0.4580	0.4581	1.67	0.4911	0.4911	1.64	0.5633	0.5263
2.74	0.3218	0.3145	2.56	0.2942	0.3439	2.73	0.3267	0.4264
3.81	0.1879	0.2152	3.53	0.2071	0.2182	3.75	0.2758	0.3413
4.61	0.1471	0.1554	4.55	0.1304	0.1252	4.74	0.2684	0.2684
5.56	0.1014	0.1012	5.53	0.0889	0.0676	5.74	0.2114	0.2054
7.08	0.0674	0.0487	6.96	0.0579	0.0211	7.20	0.1341	0.1340
9.23	0.0190	0.0116	8.91	0.0055	0.0036	9.12	0.0606	0.0696
AAE =		0.0099	AAE =		0.0180	AAE =		0.0311

**Table D.14 – 10F-0.34 measured and predicted chloride profiles for decay coefficient calculation**

m value calculation 10F-0.34								
28 day			91 day			6 mo		
Depth	Chloride Conc (%)		Depth	Chloride Conc (%)		Depth	Chloride Conc (%)	
	Measured	Predicted		Measured	Predicted		Measured	Predicted
		Finite Difference			Finite Difference			Finite Difference
0.50	0.7108	0.5877	0.61	0.7669	0.6642	0.54	1.1119	0.6824
1.47	0.4580	0.4749	1.67	0.4911	0.4006	1.64	0.5633	0.5639
2.74	0.3218	0.3412	2.56	0.2942	0.2710	2.73	0.3267	0.4528
3.81	0.1879	0.2455	3.53	0.2071	0.1654	3.75	0.2758	0.3586
4.61	0.1471	0.1854	4.55	0.1304	0.0910	4.74	0.2684	0.2787
5.56	0.1014	0.1285	5.53	0.0889	0.0471	5.74	0.2114	0.2103
7.08	0.0674	0.0683	6.96	0.0579	0.0207	7.20	0.1341	0.1341
9.23	0.0190	0.0206	8.91	0.0055	0.0035	9.12	0.0606	0.0672
AAE =		0.0231	AAE =		0.0394	AAE =		0.0325

**Table D.15 – 25F-0.34 measured and predicted chloride profiles for diffusion coefficient calculation**

<b>25F-0.34</b>											
<b>28 day</b>				<b>91 day</b>				<b>6 mo</b>			
<b>Depth</b>	<b>Chloride Concentration (%)</b>			<b>Depth</b>	<b>Chloride Concentration (%)</b>			<b>Depth</b>	<b>Chloride Concentration (%)</b>		
	<b>Measured</b>	<b>Predicted</b>			<b>Measured</b>	<b>Predicted</b>			<b>Measured</b>	<b>Predicted</b>	
		<b>Finite Difference</b>	<b>Error function</b>			<b>Finite Difference</b>	<b>Error function</b>			<b>Finite Difference</b>	<b>Error function</b>
0.70	0.8552	0.5971	0.5782	0.60	0.6613	0.6416	0.7678	0.63	1.0058	0.8739	0.8679
1.75	0.4399	0.4393	0.4337	1.64	0.5019	0.4427	0.4961	1.80	0.5951	0.5951	0.5761
2.56	0.3319	0.3320	0.3345	2.56	0.2934	0.2934	0.3030	2.74	0.3591	0.4077	0.3834
3.56	0.2225	0.2225	0.2311	3.58	0.1524	0.1712	0.1567	3.66	0.2158	0.2639	0.2395
4.56	0.1527	0.1397	0.1505	4.59	0.0730	0.0917	0.0721	4.78	0.1420	0.1420	0.1217
5.53	0.0815	0.0835	0.0939	5.60	0.0475	0.0443	0.0289	5.83	0.0807	0.0725	0.0582
7.05	0.0613	0.0306	0.0399	7.05	0.0188	0.0115	0.0062	7.26	0.0314	0.0275	0.0182
9.02	0.0270	0.0069	0.0106	8.91	-0.0021	0.0016	0.0006	9.20	0.0320	0.0054	0.0027
AAE/Error <sup>2</sup> =		0.0095	0.0060	AAE/Error <sup>2</sup> =		0.0158	0.0007	AAE/Error <sup>2</sup> =		0.0193	0.0080



**Table D.16 – 25F-0.34 measured and predicted chloride profiles for diffusion coefficient calculation**

3 Profile 25F-0.34								
28 day			91 day			6 mo		
Depth	Chloride Conc (%)		Depth	Chloride Conc (%)		Depth	Chloride Conc (%)	
	Measured	Predicted		Measured	Predicted		Measured	Predicted
		Finite Difference			Finite Difference			Finite Difference
0.70	0.8552	0.6000	0.60	0.6613	0.8609	0.63	1.0058	0.6973
1.75	0.4399	0.4405	1.64	0.5019	0.5061	1.80	0.5951	0.4972
2.56	0.3319	0.3322	2.56	0.2934	0.2727	2.74	0.3591	0.3583
3.56	0.2225	0.2219	3.58	0.1524	0.1186	3.66	0.2158	0.2468
4.56	0.1527	0.1387	4.59	0.0730	0.0443	4.78	0.1420	0.1457
5.53	0.0815	0.0826	5.60	0.0475	0.0139	5.83	0.0807	0.0826
7.05	0.0613	0.0353	7.05	0.0188	0.0015	7.26	0.0314	0.0361
9.02	0.0270	0.0067	8.91	-0.0021	0.0001	9.20	0.0320	0.0091
AAE =		0.0090	AAE =		0.0201	AAE =		0.0233

**Table D.17 – 25F-0.34 measured and predicted chloride profiles for decay coefficient calculation**

m value calculation 25F-0.34								
28 day			91 day			6 mo		
Depth	Chloride Conc (%)		Depth	Chloride Conc (%)		Depth	Chloride Conc (%)	
	Measured	Predicted		Measured	Predicted		Measured	Predicted
		Finite Difference			Finite Difference			Finite Difference
0.70	0.8552	0.6061	0.60	0.6613	0.5928	0.63	1.0058	0.8739
1.75	0.4399	0.4599	1.64	0.5019	0.3335	1.80	0.5951	0.5951
2.56	0.3319	0.3585	2.56	0.2934	0.1695	2.74	0.3591	0.4077
3.56	0.2225	0.2519	3.58	0.1524	0.0678	3.66	0.2158	0.2639
4.56	0.1527	0.1676	4.59	0.0730	0.0229	4.78	0.1420	0.1420
5.53	0.0815	0.1071	5.60	0.0475	0.0064	5.83	0.0807	0.0725
7.05	0.0613	0.0509	7.05	0.0188	0.0005	7.26	0.0314	0.0275
9.02	0.0270	0.0126	8.91	-0.0021	0.0000	9.20	0.0320	0.0054
AAE =		0.0202	AAE =		0.0698	AAE =		0.0193

**Table D.18 – 5S-0.34 measured and predicted chloride profiles for diffusion coefficient calculation**

5S-0.34											
28 day				91 day				6 mo			
Depth	Chloride Concentration (%)			Depth	Chloride Concentration (%)			Depth	Chloride Concentration (%)		
	Measured	Predicted			Measured	Predicted			Measured	Predicted	
		Finite Difference	Error function			Finite Difference	Error function			Finite Difference	Error function
0.60	0.5319	0.4349	0.4216	0.54	0.3924	0.4571	0.4653	1.64	0.5567	0.3365	0.3389
1.62	0.2949	0.2949	0.2873	1.61	0.2617	0.2617	0.2661	2.72	0.2188	0.2188	0.2224
2.67	0.1604	0.1785	0.1749	2.60	0.1478	0.1322	0.1339	3.77	0.1443	0.1309	0.1359
3.68	0.0987	0.0987	0.0973	3.54	0.0496	0.0594	0.0600	4.81	0.0680	0.0703	0.0763
4.57	0.0510	0.0535	0.0534	4.53	0.0217	0.0217	0.0216	5.75	0.0539	0.0382	0.0421
5.59	0.0312	0.0241	0.0242	5.54	-0.0063	0.0066	0.0063	7.15	0.0043	0.0059	0.0152
6.92	0.0182	0.0058	0.0072	7.03	0.0055	0.0006	0.0007	9.11	-0.0159	-0.0006	0.0027
8.19	0.0488	0.0009	0.0019	8.99	0.0006	0.0000	0.0000				
AAE/Error <sup>2</sup> =		0.0126	0.0026	AAE/Error <sup>2</sup> =		0.0063	0.0005	AAE/Error <sup>2</sup> =		0.0081	-0.0035

**Table D.19 – 5S-0.34 measured and predicted chloride profiles for diffusion coefficient calculation**

3 Profile 5S-0.34								
28 day			91 day			6 mo		
Depth	Chloride Conc (%)		Depth	Chloride Conc (%)		Depth	Chloride Conc (%)	
	Measured	Predicted		Measured	Predicted		Measured	Predicted
		Finite Difference			Finite Difference			Finite Difference
0.60	0.5319	0.4377	0.54	0.3924	0.6009	1.64	0.5567	1.0859
1.62	0.2949	0.2949	1.61	0.2617	0.2617	2.72	0.2188	0.5567
2.67	0.1604	0.1768	2.60	0.1478	0.0897	3.77	0.1443	0.3017
3.68	0.0987	0.0966	3.54	0.0496	0.0247	4.81	0.0680	0.1444
4.57	0.0510	0.0517	4.53	0.0217	0.0049	5.75	0.0539	0.0599
5.59	0.0312	0.0229	5.54	-0.0063	0.0007	7.15	0.0043	0.0241
6.92	0.0182	0.0083	7.03	0.0055	0.0000	9.11	-0.0159	0.0066
8.19	0.0488	0.0008	8.99	0.0006	0.0000			
AAE =		0.0122	AAE =		0.0161	AAE =		0.0200

**Table D.20 – 5S-0.34 measured and predicted chloride profiles for decay coefficient calculation**

m value calculation 5S-0.34								
28 day			91 day			6 mo		
Depth	Chloride Conc (%)		Depth	Chloride Conc (%)		Depth	Chloride Conc (%)	
	Measured	Predicted		Measured	Predicted		Measured	Predicted
		Finite Difference			Finite Difference			Finite Difference
0.60	0.5319	0.4280	0.54	0.3924	0.4440	1.64	0.5567	0.5461
1.62	0.2949	0.2790	1.61	0.2617	0.1743	2.72	0.2188	0.3482
2.67	0.1604	0.1594	2.60	0.1478	0.0757	3.77	0.1443	0.2376
3.68	0.0987	0.0819	3.54	0.0496	0.0288	4.81	0.0680	0.1527
4.57	0.0510	0.0410	4.53	0.0217	0.0087	5.75	0.0539	0.0912
5.59	0.0312	0.0166	5.54	-0.0063	0.0021	7.15	0.0043	0.0539
6.92	0.0182	0.0055	7.03	0.0055	0.0003	9.11	-0.0159	0.0238
8.19	0.0488	0.0004	8.99	0.0006	0.0000			
	AAE =	0.0171		AAE =	0.0296		AAE =	0.0429

**Table D.21 – 25G-0.34 measured and predicted chloride profiles for diffusion coefficient calculation**

<b>25G-0.34</b>											
<b>28 day</b>				<b>91 day</b>				<b>6 mo</b>			
<b>Depth</b>	<b>Chloride Concentration (%)</b>			<b>Depth</b>	<b>Chloride Concentration (%)</b>			<b>Depth</b>	<b>Chloride Concentration (%)</b>		
	<b>Measured</b>	<b>Predicted</b>			<b>Measured</b>	<b>Predicted</b>			<b>Measured</b>	<b>Predicted</b>	
		<b>Finite Difference</b>	<b>Error function</b>			<b>Finite Difference</b>	<b>Error function</b>			<b>Finite Difference</b>	<b>Error function</b>
0.50	0.6231	0.5454	0.5573	0.62	0.7400	0.7127	0.7174	0.59	1.3577	0.5946	0.6935
1.50	0.4181	0.3993	0.4095	1.71	0.5070	0.5070	0.5007	1.62	0.6307	0.4912	0.5496
2.50	0.2728	0.2728	0.2810	2.65	0.3176	0.3541	0.3420	2.60	0.3170	0.3988	0.4243
3.50	0.1692	0.1731	0.1793	3.67	0.2189	0.2234	0.2089	3.66	0.2836	0.3090	0.3073
4.50	0.1018	0.1018	0.1060	4.68	0.1324	0.1312	0.1178	5.50	0.1824	0.1824	0.1558
5.50	0.0675	0.0553	0.0579	5.67	0.0913	0.0721	0.0617	7.23	0.1208	0.1029	0.0718
7.00	0.0405	0.0171	0.0201	7.11	0.0466	0.0243	0.0208	9.11	0.0472	0.0494	0.0264
9.00	0.0239	0.0030	0.0036	9.11	-0.0086	0.0044	0.0033				
AAE/Error <sup>2</sup> =		0.0097	0.0012	AAE/Error <sup>2</sup> =		0.0138	0.0026	AAE/Error <sup>2</sup> =		0.0445	0.0077

**Table D.22 – 25G-0.34 measured and predicted chloride profiles for diffusion coefficient calculation**

<b>3 Profile 25G-0.34</b>								
<b>28 day</b>			<b>91 day</b>			<b>6 mo</b>		
<b>Depth</b>	<b>Chloride Conc (%)</b>		<b>Depth</b>	<b>Chloride Conc (%)</b>		<b>Depth</b>	<b>Chloride Conc (%)</b>	
	<b>Measured</b>	<b>Predicted</b>		<b>Measured</b>	<b>Predicted</b>		<b>Measured</b>	<b>Predicted</b>
		<b>Finite Difference</b>			<b>Finite Difference</b>			<b>Finite Difference</b>
0.50	0.6231	0.5439	0.62	0.7400	0.7180	0.59	1.3577	0.4922
1.50	0.4181	0.3987	1.71	0.5070	0.5070	1.62	0.6307	0.4179
2.50	0.2728	0.2728	2.65	0.3176	0.3510	2.60	0.3170	0.3506
3.50	0.1692	0.1735	3.67	0.2189	0.2187	3.66	0.2836	0.2836
4.50	0.1018	0.1022	4.68	0.1324	0.1266	5.50	0.1824	0.1840
5.50	0.0675	0.0557	5.67	0.0913	0.0683	7.23	0.1208	0.1155
7.00	0.0405	0.0219	7.11	0.0466	0.0223	9.11	0.0472	0.0640
9.00	0.0239	0.0030	9.11	-0.0086	0.0038			
	AAE =	0.0108		AAE =	0.0142		AAE =	0.0450

**Table D.23 – 25G-0.34 measured and predicted chloride profiles for decay coefficient calculation**

m value calculation 25G-0.34								
28 day			91 day			6 mo		
Depth	Chloride Conc (%)		Depth	Chloride Conc (%)		Depth	Chloride Conc (%)	
	Measured	Predicted		Measured	Predicted		Measured	Predicted
		Finite Difference			Finite Difference			Finite Difference
0.50	0.6231	0.5661	0.62	0.7400	0.6906	0.59	1.3577	0.5984
1.50	0.4181	0.4572	1.71	0.5070	0.4243	1.62	0.6307	0.5011
2.50	0.2728	0.3563	2.65	0.3176	0.2878	2.60	0.3170	0.4136
3.50	0.1692	0.2674	3.67	0.2189	0.1757	3.66	0.2836	0.3275
4.50	0.1018	0.1929	4.68	0.1324	0.1000	5.50	0.1824	0.2028
5.50	0.0675	0.1337	5.67	0.0913	0.0532	7.23	0.1208	0.1208
7.00	0.0405	0.0742	7.11	0.0466	0.0252	9.11	0.0472	0.0624
9.00	0.0239	0.0251	9.11	-0.0086	0.0047			
AAE =		0.0686	AAE =		0.0373	AAE =		0.0509



**Table D.24 – 10C 5S-0.34 measured and predicted chloride profiles for diffusion coefficient calculation**

10C 5S											
28 day				91 day				6 mo			
Depth	Chloride Concentration (%)			Depth	Chloride Concentration (%)			Depth	Chloride Concentration (%)		
	Measured	Predicted			Measured	Predicted			Measured	Predicted	
		Finite Difference	Error function			Finite Difference	Error function			Finite Difference	Error function
0.57	0.5548	0.4838	0.5342	0.61	0.5879	0.5157	0.9472	0.67	0.7238	0.6599	0.6396
1.59	0.3038	0.3038	0.2968	1.66	0.3372	0.3372	0.5022	1.71	0.4782	0.4782	0.4705
2.67	0.1040	0.1607	0.1283	2.59	0.2201	0.2110	0.2403	2.58	0.3453	0.3448	0.3468
3.87	0.0605	0.0432	0.0379	3.50	0.1030	0.1206	0.0971	3.59	0.2143	0.2215	0.2291
4.95	0.0243	0.0243	0.0097	4.46	0.0728	0.0632	0.0305	4.70	0.1199	0.1257	0.1346
6.03	0.0202	0.0075	0.0019	5.51	0.0265	0.0253	0.0068	5.71	0.0985	0.0691	0.0769
7.75	0.0257	0.0009	0.0001	6.97	0.0190	0.0050	0.0005	7.10	0.0500	0.0247	0.0317
9.78	0.0067	0.0000	0.0000	8.98	0.0049	0.0004	0.0000	9.10	0.0126	0.0047	0.0070
AAE/Error <sup>2</sup> =		0.0169	0.0024	AAE/Error <sup>2</sup> =		0.0080	0.0302	AAE/Error <sup>2</sup> =		0.0109	0.0032

**Table D.25 – 10C 5S-0.34 measured and predicted chloride profiles for diffusion coefficient calculation**

<b>3 Profile 10C 5S-0.34</b>								
<b>28 day</b>			<b>91 day</b>			<b>6 mo</b>		
<b>Depth</b>	<b>Chloride Conc (%)</b>		<b>Depth</b>	<b>Chloride Conc (%)</b>		<b>Depth</b>	<b>Chloride Conc (%)</b>	
	<b>Measured</b>	<b>Predicted</b>		<b>Measured</b>	<b>Predicted</b>		<b>Measured</b>	<b>Predicted</b>
		<b>Finite Difference</b>			<b>Finite Difference</b>			<b>Finite Difference</b>
0.57	0.5548	0.3040	0.61	0.5879	0.5606	0.67	0.7238	0.5832
1.59	0.3038	0.2175	1.66	0.3372	0.3372	1.71	0.4782	0.4466
2.67	0.1040	0.1403	2.59	0.2201	0.1898	2.58	0.3453	0.3437
3.87	0.0605	0.0769	3.50	0.1030	0.0945	3.59	0.2143	0.2420
4.95	0.0243	0.0404	4.46	0.0728	0.0395	4.70	0.1199	0.1554
6.03	0.0202	0.0191	5.51	0.0265	0.0133	5.71	0.0985	0.0978
7.75	0.0257	0.0037	6.97	0.0190	0.0016	7.10	0.0500	0.0499
9.78	0.0067	0.0007	8.98	0.0049	0.0001	9.10	0.0126	0.0151
AAE =		0.0263	AAE =		0.0153	AAE =		0.0142

**Table D.26 – 10C 5S-0.34 measured and predicted chloride profiles for decay coefficient calculation**

m value calculation 10C 5S-0.34								
28 day			91 day			6 mo		
Depth	Chloride Conc (%)		Depth	Chloride Conc (%)		Depth	Chloride Conc (%)	
	Measured	Predicted		Measured	Predicted		Measured	Predicted
		Finite Difference			Finite Difference			Finite Difference
0.57	0.5548	0.4916	0.61	0.5879	0.4770	0.67	0.7238	0.6604
1.59	0.3038	0.3220	1.66	0.3372	0.2540	1.71	0.4782	0.4782
2.67	0.1040	0.1817	2.59	0.2201	0.1220	2.58	0.3453	0.3461
3.87	0.0605	0.0814	3.50	0.1030	0.0494	3.59	0.2143	0.2228
4.95	0.0243	0.0339	4.46	0.0728	0.0158	4.70	0.1199	0.1269
6.03	0.0202	0.0121	5.51	0.0265	0.0038	5.71	0.0985	0.0700
7.75	0.0257	0.0008	6.97	0.0190	0.0002	7.10	0.0500	0.0301
9.78	0.0067	0.0001	8.98	0.0049	0.0000	9.10	0.0126	0.0064
AAE =		0.0237	AAE =		0.0483	AAE =		0.0101

**Table D.27 – 25C 5S-0.34 measured and predicted chloride profiles for diffusion coefficient calculation**

25C 5S											
28 day				91 day				6 mo			
Depth	Chloride Concentration (%)			Depth	Chloride Concentration (%)			Depth	Chloride Concentration (%)		
	Measured	Predicted			Measured	Predicted			Measured	Predicted	
		Finite Difference	Error function			Finite Difference	Error function			Finite Difference	Error function
0.64	0.6761	0.7510	0.7499	0.57	0.7804	0.7802	0.8513	0.67	0.9503	0.8446	0.8704
1.65	0.5294	0.5294	0.5242	1.59	0.4389	0.4178	0.4337	1.80	0.5493	0.5493	0.5457
2.79	0.2932	0.3243	0.3164	2.51	0.1766	0.1981	0.1932	2.72	0.3434	0.3570	0.3398
3.81	0.2117	0.1913	0.1834	3.49	0.0736	0.0736	0.0646	3.66	0.1609	0.2110	0.1898
4.56	0.1215	0.1215	0.1151	4.52	0.0385	0.0206	0.0156	4.72	0.1054	0.1051	0.0868
5.57	0.0325	0.0615	0.0567	5.56	0.0147	0.0049	0.0028	5.79	0.0496	0.0466	0.0346
7.35	0.0165	0.0142	0.0128	7.02	-0.0178	0.0003	0.0001	7.26	0.0245	0.0115	0.0077
				8.93	0.0002	0.0000	0.0000	9.18	0.0245	0.0014	0.0000
AAE/Error <sup>2</sup> =		0.0138	0.0020	AAE/Error <sup>2</sup> =		0.0127	0.0014	AAE/Error <sup>2</sup> =		0.0148	0.0048

**Table D.28 – 25C 5S-0.34 measured and predicted chloride profiles for diffusion coefficient calculation**

3 Profile 25C 5S-0.34								
28 day			91 day			6 mo		
Depth	Chloride Conc (%)		Depth	Chloride Conc (%)		Depth	Chloride Conc (%)	
	Measured	Predicted		Measured	Predicted		Measured	Predicted
		Finite Difference			Finite Difference			Finite Difference
0.64	0.6761	0.7520	0.57	0.7804	0.8329	0.67	0.9503	0.8379
1.65	0.5294	0.5300	1.59	0.4389	0.4211	1.80	0.5493	0.5420
2.79	0.2932	0.3245	2.51	0.1766	0.1845	2.72	0.3434	0.3500
3.81	0.2117	0.1914	3.49	0.0736	0.0614	3.66	0.1609	0.2052
4.56	0.1215	0.1215	4.52	0.0385	0.0154	4.72	0.1054	0.1010
5.57	0.0325	0.0614	5.56	0.0147	0.0030	5.79	0.0496	0.0442
7.35	0.0165	0.0159	7.02	-0.0178	0.0001	7.26	0.0245	0.0133
			8.93	0.0002	0.0000	9.18	0.0245	0.0019
AAE =		0.0136	AAE =		0.0130	AAE =		0.0146

**Table D.29 – 25C 5S-0.34 measured and predicted chloride profiles for decay coefficient calculation**

m value calculation 25C 5S-0.34								
28 day			91 day			6 mo		
Depth	Chloride Conc (%)		Depth	Chloride Conc (%)		Depth	Chloride Conc (%)	
	Measured	Predicted		Measured	Predicted		Measured	Predicted
		Finite Difference			Finite Difference			Finite Difference
0.64	0.6761	0.7170	0.57	0.7804	0.7580	0.67	0.9503	0.8472
1.65	0.5294	0.4539	1.59	0.4389	0.3730	1.80	0.5493	0.5552
2.79	0.2932	0.2337	2.51	0.1766	0.1575	2.72	0.3434	0.3639
3.81	0.2117	0.1124	3.49	0.0736	0.0498	3.66	0.1609	0.2175
4.56	0.1215	0.0591	4.52	0.0385	0.0117	4.72	0.1054	0.1100
5.57	0.0325	0.0225	5.56	0.0147	0.0021	5.79	0.0496	0.0496
7.35	0.0165	0.0035	7.02	-0.0178	0.0001	7.26	0.0245	0.0156
			8.93	0.0002	0.0000	9.18	0.0245	0.0024
	AAE =	0.0533		AAE =	0.0238		AAE =	0.0170

**Table D.30 – 10F 5S-0.34 measured and predicted chloride profiles for diffusion coefficient calculation**

10F 5S											
28 day				91 day				6 mo			
Depth	Chloride Concentration (%)			Depth	Chloride Concentration (%)			Depth	Chloride Concentration (%)		
	Measured	Predicted			Measured	Predicted			Measured	Predicted	
		Finite Difference	Error function			Finite Difference	Error function			Finite Difference	Error function
0.57	0.5517	0.6562	0.6598	0.66	0.7724	1.0108	1.0116	0.64	1.0850	0.9116	0.9398
1.63	0.4367	0.4367	0.4374	1.68	0.5032	0.5032	0.5000	1.82	0.6369	0.6374	0.6445
2.58	0.2814	0.2764	0.2758	2.53	0.2213	0.2336	0.2325	2.83	0.4389	0.4387	0.4334
3.53	0.1470	0.1601	0.1591	3.46	0.0919	0.0815	0.0806	3.80	0.2885	0.2878	0.2762
4.59	0.0854	0.0779	0.0762	4.48	0.0208	0.0209	0.0194	4.76	0.1778	0.1779	0.1647
5.62	0.0346	0.0346	0.0332	5.54	0.0126	0.0040	0.0033	5.73	0.0619	0.1029	0.0912
7.00	0.0039	0.0080	0.0089	7.04	-0.0061	0.0002	0.0002	7.23	0.0193	0.0413	0.0314
9.18	0.0113	0.0007	0.0007	8.99	-0.0123	0.0000	0.0000	9.20	0.0064	0.0093	0.0058
AAE/Error <sup>2</sup> =		0.0057	0.0004	AAE/Error <sup>2</sup> =		0.0071	0.0005	AAE/Error <sup>2</sup> =		0.0096	-0.0025

**Table D.31 – 10F 5S-0.34 measured and predicted chloride profiles for diffusion coefficient calculation**

<b>3 Profile 10F 5S-0.34</b>								
<b>28 day</b>			<b>91 day</b>			<b>6 mo</b>		
<b>Depth</b>	<b>Chloride Conc (%)</b>		<b>Depth</b>	<b>Chloride Conc (%)</b>		<b>Depth</b>	<b>Chloride Conc (%)</b>	
	<b>Measured</b>	<b>Predicted</b>		<b>Measured</b>	<b>Predicted</b>		<b>Measured</b>	<b>Predicted</b>
		<b>Finite Difference</b>			<b>Finite Difference</b>			<b>Finite Difference</b>
0.57	0.5517	0.6991	0.66	0.7724	0.8943	0.64	1.0850	0.9176
1.63	0.4367	0.4479	1.68	0.5032	0.4903	1.82	0.6369	0.6344
2.58	0.2814	0.2700	2.53	0.2213	0.2565	2.83	0.4389	0.4309
3.53	0.1470	0.1468	3.46	0.0919	0.1062	3.80	0.2885	0.2782
4.59	0.0854	0.0655	4.48	0.0208	0.0339	4.76	0.1778	0.1687
5.62	0.0346	0.0263	5.54	0.0126	0.0086	5.73	0.0619	0.0954
7.00	0.0039	0.0081	7.04	-0.0061	0.0006	7.23	0.0193	0.0370
9.18	0.0113	0.0003	8.99	-0.0123	0.0000	9.20	0.0064	0.0078
AAE =		0.0094	AAE =		0.0141	AAE =		0.0118



**Table D.32 – 10F 5S-0.34 measured and predicted chloride profiles for decay coefficient calculation**

m value calculation 10F 5S-0.34								
28 day			91 day			6 mo		
Depth	Chloride Conc (%)		Depth	Chloride Conc (%)		Depth	Chloride Conc (%)	
	Measured	Predicted Finite Difference		Measured	Predicted Finite Difference		Measured	Predicted Finite Difference
0.57	0.5517	0.6467	0.66	0.7724	1.0560	0.64	1.0850	0.9114
1.63	0.4367	0.4137	1.68	0.5032	0.5870	1.82	0.6369	0.6369
2.58	0.2814	0.2489	2.53	0.2213	0.3124	2.83	0.4389	0.4381
3.53	0.1470	0.1350	3.46	0.0919	0.1325	3.80	0.2885	0.2873
4.59	0.0854	0.0601	4.48	0.0208	0.0437	4.76	0.1778	0.1774
5.62	0.0346	0.0240	5.54	0.0126	0.0115	5.73	0.0619	0.1025
7.00	0.0039	0.0074	7.04	-0.0061	0.0008	7.23	0.0193	0.0411
9.18	0.0113	0.0003	8.99	-0.0123	0.0000	9.20	0.0064	0.0092
AAE =		0.0168	AAE =		0.0370	AAE =		0.0097

**Table D.33 – 25F 5S-0.34 measured and predicted chloride profiles for diffusion coefficient calculation**

25F 5S											
28 day				91 day				6 mo			
Depth	Chloride Concentration (%)			Depth	Chloride Concentration (%)			Depth	Chloride Concentration (%)		
	Measured	Predicted			Measured	Predicted			Measured	Predicted	
		Finite Difference	Error function			Finite Difference	Error function			Finite Difference	Error function
0.55	0.4489	0.6870	0.6696	0.57	0.4775	0.5954	0.6023	0.67	0.8769	0.9688	0.9804
1.04	0.5980	0.6206	0.6086	1.63	0.3249	0.3242	0.3234	1.84	0.6499	0.6508	0.6596
2.51	0.4512	0.4433	0.4380	2.63	0.1422	0.1517	0.1477	2.81	0.4595	0.4350	0.4411
3.50	0.3433	0.3374	0.3365	3.60	0.0613	0.0603	0.0567	3.76	0.2763	0.2710	0.2749
4.52	0.2459	0.2459	0.2480	4.54	0.0202	0.0204	0.0183	4.81	0.1415	0.1486	0.1505
5.56	0.1753	0.1709	0.1747	5.58	0.0067	0.0052	0.0042	5.80	0.0672	0.0774	0.0781
7.04	0.0883	0.0916	0.0988	7.10	0.0006	0.0003	0.0003	7.26	0.0277	0.0277	0.0253
8.97	0.0362	0.0362	0.0414	9.10	-0.0012	0.0000	0.0000	9.23	0.0189	0.0049	0.0041
AAE/Error <sup>2</sup> =		0.0063	0.0010	AAE/Error <sup>2</sup> =		0.0021	0.0001	AAE/Error <sup>2</sup> =		0.0089	0.0010

**Table D.34 – 25F 5S-0.34 measured and predicted chloride profiles for diffusion coefficient calculation**

<b>3 Profile 25F 5S-0.34</b>								
<b>28 day</b>			<b>91 day</b>			<b>6 mo</b>		
<b>Depth</b>	<b>Chloride Conc (%)</b>		<b>Depth</b>	<b>Chloride Conc (%)</b>		<b>Depth</b>	<b>Chloride Conc (%)</b>	
	<b>Measured</b>	<b>Predicted</b>		<b>Measured</b>	<b>Predicted</b>		<b>Measured</b>	<b>Predicted</b>
		<b>Finite Difference</b>			<b>Finite Difference</b>			<b>Finite Difference</b>
0.55	0.4489	0.6945	0.57	0.4775	0.5444	0.67	0.8769	0.9791
1.04	0.5980	0.6273	1.63	0.3249	0.3041	1.84	0.6499	0.6506
2.51	0.4512	0.4479	2.63	0.1422	0.1474	2.81	0.4595	0.4296
3.50	0.3433	0.3407	3.60	0.0613	0.0613	3.76	0.2763	0.2635
4.52	0.2459	0.2481	4.54	0.0202	0.0220	4.81	0.1415	0.1415
5.56	0.1753	0.1724	5.58	0.0067	0.0060	5.80	0.0672	0.0720
7.04	0.0883	0.0985	7.10	0.0006	0.0005	7.26	0.0277	0.0250
8.97	0.0362	0.0363	9.10	-0.0012	0.0000	9.23	0.0189	0.0042
AAE =		0.0073	AAE =		0.0043	AAE =		0.0094

**Table D.35 – 25F 5S-0.34 measured and predicted chloride profiles for decay coefficient calculation**

m value calculation 25F 5S-0.34								
28 day			91 day			6 mo		
Depth	Chloride Conc (%)		Depth	Chloride Conc (%)		Depth	Chloride Conc (%)	
	Measured	Predicted		Measured	Predicted		Measured	Predicted
		Finite Difference			Finite Difference			Finite Difference
0.55	0.4489	0.6289	0.57	0.4775	0.5831	0.67	0.8769	0.9706
1.04	0.5980	0.5053	1.63	0.3249	0.2987	1.84	0.6499	0.6552
2.51	0.4512	0.2433	2.63	0.1422	0.1281	2.81	0.4595	0.4404
3.50	0.3433	0.1259	3.60	0.0613	0.0456	3.76	0.2763	0.2763
4.52	0.2459	0.0565	4.54	0.0202	0.0135	4.81	0.1415	0.1529
5.56	0.1753	0.0218	5.58	0.0067	0.0029	5.80	0.0672	0.0805
7.04	0.0883	0.0059	7.10	0.0006	0.0001	7.26	0.0277	0.0293
8.97	0.0362	0.0002	9.10	-0.0012	0.0000	9.23	0.0189	0.0053
AAE =		0.1399	AAE =		0.0098	AAE =		0.0092

**Table D.36 – 25C 25G-0.34 measured and predicted chloride profiles for diffusion coefficient calculation**

<b>25C 25G</b>											
<b>28 day</b>				<b>91 day</b>				<b>6 mo</b>			
<b>Depth</b>	<b>Chloride Concentration (%)</b>			<b>Depth</b>	<b>Chloride Concentration (%)</b>			<b>Depth</b>	<b>Chloride Concentration (%)</b>		
	<b>Measured</b>	<b>Predicted</b>			<b>Measured</b>	<b>Predicted</b>			<b>Measured</b>	<b>Predicted</b>	
		<b>Finite Difference</b>	<b>Error function</b>			<b>Finite Difference</b>	<b>Error function</b>			<b>Finite Difference</b>	<b>Error function</b>
0.56	0.7868	0.7289	0.6828	0.61	0.6114	0.5367	0.5220	0.59	0.9758	0.6859	0.8467
1.58	0.5270	0.5270	0.4958	1.71	0.3534	0.3513	0.3486	1.67	0.6325	0.5338	0.6095
2.55	0.3015	0.3623	0.3430	2.69	0.2116	0.2176	0.2214	2.71	0.4019	0.4019	0.4150
3.54	0.1962	0.2297	0.2190	3.68	0.1328	0.1224	0.1286	3.77	0.1972	0.2866	0.2592
4.60	0.1324	0.1302	0.1249	4.70	0.0592	0.0605	0.0661	4.71	0.1724	0.2041	0.1601
5.60	0.0926	0.0699	0.0676	5.74	0.0421	0.0264	0.0301	5.74	0.1415	0.1338	0.0871
7.08	0.0662	0.0219	0.0235	7.16	0.0151	0.0062	0.0085	7.22	0.0525	0.0693	0.0317
9.05	0.0343	0.0038	0.0043	9.05	0.0025	0.0007	0.0011	9.11	0.0359	0.0254	0.0068
AAE/Error <sup>2</sup> =		0.0272	0.0066	AAE/Error <sup>2</sup> =		0.0066	0.0004	AAE/Error <sup>2</sup> =		0.0364	0.0092

**Table D.37 – 25C 25G-0.34 measured and predicted chloride profiles for diffusion coefficient calculation**

<b>3 Profile 25C 25G-0.34</b>								
<b>28 day</b>			<b>91 day</b>			<b>6 mo</b>		
<b>Depth</b>	<b>Chloride Conc (%)</b>		<b>Depth</b>	<b>Chloride Conc (%)</b>		<b>Depth</b>	<b>Chloride Conc (%)</b>	
	<b>Measured</b>	<b>Predicted</b>		<b>Measured</b>	<b>Predicted</b>		<b>Measured</b>	<b>Predicted</b>
		<b>Finite Difference</b>			<b>Finite Difference</b>			<b>Finite Difference</b>
0.56	0.7868	0.6850	0.61	0.6114	0.5814	0.59	0.9758	0.6709
1.58	0.5270	0.5016	1.71	0.3534	0.3631	1.67	0.6325	0.5273
2.55	0.3015	0.3505	2.69	0.2116	0.2116	2.71	0.4019	0.4021
3.54	0.1962	0.2271	3.68	0.1328	0.1100	3.77	0.1972	0.2913
4.60	0.1324	0.1324	4.70	0.0592	0.0492	4.71	0.1724	0.2110
5.60	0.0926	0.0734	5.74	0.0421	0.0190	5.74	0.1415	0.1415
7.08	0.0662	0.0297	7.16	0.0151	0.0035	7.22	0.0525	0.0757
9.05	0.0343	0.0047	9.05	0.0025	0.0003	9.11	0.0359	0.0293
AAE =		0.0272	AAE =		0.0113	AAE =		0.0383

**Table D.38 – 25C 25G-0.34 measured and predicted chloride profiles for decay coefficient calculation**

m value calculation 25C 25G-0.34								
28 day			91 day			6 mo		
Depth	Chloride Conc (%)		Depth	Chloride Conc (%)		Depth	Chloride Conc (%)	
	Measured	Predicted		Measured	Predicted		Measured	Predicted
		Finite Difference			Finite Difference			Finite Difference
0.56	0.7868	0.7559	0.61	0.6114	0.5117	0.59	0.9758	0.6860
1.58	0.5270	0.5975	1.71	0.3534	0.2634	1.67	0.6325	0.5338
2.55	0.3015	0.4601	2.69	0.2116	0.1488	2.71	0.4019	0.4019
3.54	0.1962	0.3380	3.68	0.1328	0.0754	3.77	0.1972	0.2866
4.60	0.1324	0.2320	4.70	0.0592	0.0330	4.71	0.1724	0.2041
5.60	0.0926	0.1549	5.74	0.0421	0.0126	5.74	0.1415	0.1338
7.08	0.0662	0.0816	7.16	0.0151	0.0041	7.22	0.0525	0.0693
9.05	0.0343	0.0251	9.05	0.0025	0.0004	9.11	0.0359	0.0254
AAE =		0.0796	AAE =		0.0398	AAE =		0.0364

**Table D.39 – 25F 25G-0.34 measured and predicted chloride profiles for diffusion coefficient calculation**

25F 25G											
28 day				91 day				6 mo			
Depth	Chloride Concentration (%)			Depth	Chloride Concentration (%)			Depth	Chloride Concentration (%)		
	Measured	Predicted			Measured	Predicted			Measured	Predicted	
		Finite Difference	Error function			Finite Difference	Error function			Finite Difference	Error function
0.56	0.5730	0.8618	0.8692	0.63	0.8100	1.2094	1.2046	0.76	1.0026	1.0347	1.0246
1.60	0.6467	0.6467	0.6487	1.71	0.6695	0.6695	0.6725	1.87	0.7817	0.7691	0.7660
2.56	0.4846	0.4719	0.4704	2.63	0.3624	0.3484	0.3538	2.77	0.5738	0.5793	0.5800
3.52	0.3071	0.3253	0.3217	3.55	0.1538	0.1549	0.1599	3.75	0.3788	0.4046	0.4082
4.60	0.1851	0.2015	0.1964	4.71	0.0466	0.0466	0.0472	4.74	0.2685	0.2685	0.2732
5.61	0.1202	0.1202	0.1154	5.83	0.0051	0.0116	0.0114	5.80	0.1870	0.1629	0.1675
7.03	0.0676	0.0484	0.0487	7.31	-0.0110	0.0011	0.0012	7.30	0.0956	0.0745	0.0753
9.14	0.0166	0.0109	0.0104	9.34	-0.0196	0.0000	0.0000	9.43	0.0184	0.0184	0.0193
AAE/Error <sup>2</sup> =		0.0103	0.0010	AAE/Error <sup>2</sup> =		0.0076	0.0007	12.25	0.0461	0.0001	0.0021
								15.16	0.0273	0.0001	0.0001
								AAE/Error <sup>2</sup> =		0.0180	0.0020



**Table D.40 – 25F 25G-0.34 measured and predicted chloride profiles for diffusion coefficient calculation**

3 Profile 25F 25G - 0.34								
28 day			91 day			6 mo		
Depth	Chloride Conc (%)		Depth	Chloride Conc (%)		Depth	Chloride Conc (%)	
	Measured	Predicted		Measured	Predicted		Measured	Predicted
		Finite Difference			Finite Difference			Finite Difference
0.56	0.5730	0.8728	0.63	0.8100	1.1387	0.76	1.0026	1.0777
1.60	0.6467	0.6466	1.71	0.6695	0.6695	1.87	0.7817	0.7817
2.56	0.4846	0.4644	2.63	0.3624	0.3754	2.77	0.5738	0.5736
3.52	0.3071	0.3136	3.55	0.1538	0.1843	3.75	0.3788	0.3867
4.60	0.1851	0.1890	4.71	0.0466	0.0642	4.74	0.2685	0.2459
5.61	0.1202	0.1092	5.83	0.0051	0.0189	5.80	0.1870	0.1413
7.03	0.0676	0.0491	7.31	-0.0110	0.0025	7.30	0.0956	0.0595
9.14	0.0166	0.0084	9.34	-0.0196	0.0001	9.43	0.0184	0.0125
AAE =		0.0253	AAE =		0.0107	AAE =		0.0375

**Table D.41 – 25F 25G-0.34 measured and predicted chloride profiles for decay coefficient calculation**

m value calculation 25F 25G - 0.34								
28 day			91 day			6 mo		
Depth	Chloride Conc (%)		Depth	Chloride Conc (%)		Depth	Chloride Conc (%)	
	Measured	Predicted		Measured	Predicted		Measured	Predicted
		Finite Difference			Finite Difference			Finite Difference
0.56	0.5730	0.8728	0.63	0.8100	1.2510	0.76	1.0026	1.0263
1.60	0.6467	0.6759	1.71	0.6695	0.7578	1.87	0.7817	0.7504
2.56	0.4846	0.5125	2.63	0.3624	0.4408	2.77	0.5738	0.5554
3.52	0.3071	0.3709	3.55	0.1538	0.2271	3.75	0.3788	0.3788
4.60	0.1851	0.2454	4.71	0.0466	0.0850	4.74	0.2685	0.2443
5.61	0.1202	0.1576	5.83	0.0051	0.0274	5.80	0.1870	0.1429
7.03	0.0676	0.0816	7.31	-0.0110	0.0042	7.30	0.0956	0.0618
9.14	0.0166	0.0207	9.34	-0.0196	0.0002	9.43	0.0184	0.0137
AAE =		0.0338	AAE =		0.0479	AAE =		0.0375