# Performance Evaluation and Economic Analysis of Combinations of Durability Enhancing Admixtures (Mineral and Chemical) in Structural Concrete for the Northeast U.S.A.

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**Prepared for**
**The New England Transportation Consortium**
**February 2003**
**NETCR36** **Project No. 97-2**

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**Technical Report Documentation Page**

| | | |
|---|---|---|
| 1. Report No. NETCR36 | 2. Government Accession No. N/A | 3. Recepient's Catalog No. N/A |
| 4. Title and Subtitle NETC 97-2 Performance Evaluation and Economic Analysis of Combinations of Durability Enhancing Admixtures (Mineral and Chemical) in Structural Concrete for the Northeast U.S.A. | | 5. Report Date 02/05/03 |
| | | 6. Performing Organization Code N/A |
| 7. Author(s) Civjan, S. A., LaFave, J. M., Lovett, D., Sund, D. J., and Trybulski, J. | | 8. Performing Organization Report No. NETCR36 |
| 9. Performing Organization Name and Address Department of Civil and Environmental Engineering<br>University of Massachusetts<br>224 Marston Hall<br>130 Natural Resources Road<br>Amherst, MA 01003-9293 | | 10 Work Unit No. (TRAIS) N/A |
| | | 11. Contract or Grant No. N/A |
| 12. Sponsoring Agency Name and Address New England Transportation Consortium<br>179 Middle Turnpike<br>University of Connecticut, U-202<br>Storrs, CT 06269-5202 | | 13. Type of Report and Period Covered Final<br>08/30/98 through 08/31/02 |
| | | 14. Sponsoring Agency Code NETC 97-2 |
| 15 Supplementary Notes N/A | | |

16. Abstract

The performance of single, double, and triple combinations of corrosion preventing admixtures was investigated. An extensive literature review, a survey of New England States mix design procedures, and 108 weeks of accelerated corrosion study results are presented. The experimental study included slab specimens subjected to severe salt water ponding conditions to evaluate corrosion inhibiting performance of each mix design. Both non-cracked and pre-cracked specimens were evaluated for fourteen mix designs (42 specimens). Admixtures studied were; calcium nitrite, silica fume, fly ash, ground blast furnace slag, and DSS. Corrosion was monitored through half-cell and macrocell potential readings, visual observation, and autopsies of specimens at the end of testing. Based on these results, mix designs including a triple combination of calcium nitrite, silica fume, and fly ash, or a double combination of calcium nitrite and slag are currently recommended. DSS alone or in combination with calcium nitrite provided the best performance of all mixes studied, but requires further study prior to widespread acceptance.

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|---|---|---|---|
| 17. Key Words corrosion, concrete, reinforcing steel, macrocell, half-cell, calcium nitrite, ground blast furnace slag, fly ash, silica fume, DSS, admixture combinations, corrosion inhibitor | 18. Distribution Statement No restrictions. This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161. | | |
| 19. Security Classif. (of this report) Unclassified | 20. Security Classif. (of this page) Unclassified | 21. No. of Pages 165 | 21. Price N/A |

**Form DOT F 1700.7** (8-72) Reproduction of completed page authorized

# TABLE OF CONTENTS


| | Page |
|---|---|
| TABLE OF CONTENTS | iii |
| LIST OF TABLES | vi |
| LIST OF FIGURES | vii |
| LIST OF SYMBOLS | ix |
| 1. INTRODUCTION | 1 |
| 1.1. DURABILITY ENHANCING CONCRETE ADMIXTURES | 1 |
| 1.2. OVERALL RESEARCH OBJECTIVES | 2 |
| 1.3. SCOPE OF RESEARCH | 3 |
| 2. BACKGROUND AND LITERATURE REVIEW | 4 |
| 2.1. INTRODUCTION | 4 |
| 2.2. CHEMICAL CORROSION INHIBITORS | 7 |
| 2.2.1. Calcium Nitrite | 7 |
| 2.2.2. Amines and Esters (Rheocrete 222 and Armatec 2000) | 11 |
| 2.2.3. Other Chemical Corrosion Inhibitors | 13 |
| 2.3. MINERAL CORROSION INHIBITORS | 16 |
| 2.3.1. Silica Fume | 16 |
| 2.3.2. Fly Ash | 20 |
| 2.3.3. Ground Granulated Blast Furnace Slag | 23 |
| 2.4. COMBINATIONS AND DIRECT COMPARISONS | 26 |
| 2.4.1. Combinations of Chemical and/or Mineral Admixtures | 26 |
| 2.4.2. Direct Comparisons of Chemical and/or Mineral Admixtures | 28 |
| 2.5. OPTIMUM DOSAGES OF INHIBITORS PER THE LITERATURE REVIEW | 31 |

3. SURVEY OF NEW ENGLAND STATES CORROSION INHIBITOR USE 42

4. TYPICAL TEST METHODS USED 45
4.1. MACROCELL CORROSION CURRENT (adaptation of ASTM G109) 45
4.2. MACROCELL ELECTRICAL RESISTANCE 45
4.3. HALF-CELL POTENTIAL, ASTM C876 46
4.4 LINEAR POLARIZATION RESISTANCE (LPR), ASTM G59 46
4.5. ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY (EIS) 46
4.6. CYCLIC POTENTIODYNAMIC POLARIZATION (CPP), ASTM G5 and G61 47
4.7. RAPID CHLORIDE PERMEABILITY (RCP), ASTM 1202, AASHTO T277 47
4.8. VISUAL INSPECTIONS AND AUTOPSIES 48
4.9. CHLORIDE INGRESS ANALYSIS, ASTM C114, AASHTO T259 48

5. EXPERIMENTAL PROGRAM 51
5.1. CONCRETE SPECIMENS 51
5.1.1 Specimen Details 51
5.1.2 Materials 53
5.1.3 Water-to-Cementitous (w/c) Ratio 54
5.1.4 Mix Designs 55
5.1.4.1 Basic Mix Design 55
5.1.4.2 Corrosion Inhibiting Admixture Batch Quantities 55
5.1.5 Mixing Procedure and Placement 57
5.2. PREPARATION OF CONCRETE SPECIMENS FOR PONDING 57
5.3. TEST PROCEDURE 58
5.3.1 Ponding Cycles 58
5.3.2 Corrosion Activity Monitoring 58

6. RESULTS 67
6.1. MACROCELL CORROSION CURRENT 67
6.1.1 Macrocell Activity 67
6.1.2 Cumulative Macrocell Data 68
6.2. HALF-CELL CORROSION CURRENT 70
6.3. VISUAL INSPECTIONS 70
6.3.1 Visible Cracking 70
6.3.2 Visible Corrosion on Reinforcement 71
6.4. REPLACED SPECIMENS 72
6.5. COMPARISON OF DATA 73
6.6. RESULTS SUMMARY 74

7. SUMMARY AND CONCLUSIONS 89

8. REFERENCES 92

APPENDIX A: LITERATURE REVIEW SUMMARIES 100

APPENDIX B: MACROCELL DATA 134

APPENDIX C: HALF-CELL DATA 150

## LIST OF TABLES


Page

Table 3.1: Chemical and Mineral Corrosion Inhibiting Admixtures Used by New England State DOTs 44

Table 3.2: Structures Using Chemical Corrosion Inhibiting Admixtures by New England State DOTs 44

Table 5.1: Specimens 60

Table 5.2: Mix Designs 61

Table 5.3: Specimen Summary 62

Table 5.4: Project Schedule 62

Table 6.1: Corrosion Activity - Non-Cracked Specimens 78

Table 6.2: Corrosion Activity - Pre-Cracked Specimens 79

Table 6.3: Percent Area Corroded – Non-Cracked Specimens 80

Table 6.4: Percent Area Corroded – Pre-Cracked Specimens 81

Table 6.5: Percent Area Corroded – Replaced Specimens 81

Table 6.6: Chloride Content of Replaced Specimens 82

Table 6.7: Rating of Non-Cracked Specimens 82

Table 6.8: Rating of Pre-Cracked Specimens 83

Table 6.9: Rating of Pre-Cracked Specimens to Non-Cracked Control 83

Table 6.10: Ranking of all Mix Designs 84

# LIST OF FIGURES

Page

Figure 2.1: Total Corrosion Vs. Time for Concrete with Calcium Nitrite (Berke & Weil, 1992) 33

Figure 2.2: Macrocell Corrosion Current Vs. Time using OCIA (non-cracked, w/c = 0.40, 1 gal/yd$^3$) (Nmai et al., 1992) 33

Figure 2.3: Half-Cell Potential Vs. Time using OCIA (non-cracked, w/c = 0.40, 1 gal/yd$^3$) (Nmai et al., 1992) 33

Figure 2.4: Chloride Concentration Vs. Depth using Silica Fume Cement Replacement (w/c = 0.50) (Gautefall & Havdahl, 1989) 34

Figure 2.5: Macrocell Corrosion Vs. Time using Silica Fume at 20% Addition by Weight of Cement (Wolsiefer, 1993) 34

Figure 2.6: Half-Cell Potentials Vs. Time using Fly Ash Concrete (Maslehuddin et al., 1989) 35

Figure 2.7: Corrosion Rates Vs. w/c for Fly Ash Concrete (Maslehuddin et al., 1989) 35

Figure 2.8: Chloride Content Vs. Depth Below Surface of Slag Concrete at 365 Days (w/c = 0.50) (Rose, 1987) 36

Figure 2.9: Total Corrosion as a Function of Calcium Nitrite and Silica Fume Content (Berke and Weil, 1992) 37

Figure 2.10: Corrosion Rate as a Function of Calcium Nitrite and Fly Ash (Berke and Weil, 1992) 38

Figure 2.11: Chloride Profile of Silica Fume with 10% Fly Ash Blended Cement (w/c = 0.50) (Gautefall & Havdahl, 1989) 38

Figure 2.12: Total Corrosion Vs. Time as a Function of Pozzolans (Berke et al., 1991) 39

Figure 2.13: Chloride Profile with Calcium Nitrite and OCIA at 1000 Days (Nmai, 1999) 39

Figure 2.14: Macrocell Corrosion Current (Non-Cracked) with Calcium Nitrite and OCIA (w/c = 0.50) (Nmai and Krauss, 1994) 40

Figure 2.15: Corrosion Rates for Calcium Nitrite and Butyl Ester (w/c = 0.40) (Berke et al., 1993) 40
Figure 2.16: Half-Cell Potentials for Silica Fume (10% Cement Replacement), Fly Ash (20% Cement Replacement), and Slag (60% Cement Replacement) Concrete (w/c = 0.50) (Al-Amoudi et al., 1994) 41
Figure 4.1: Non-Cracked Reinforced Concrete Slab Specimen (WJE, 1995) 48
Figure 4.2: Copper-Copper Sulfate Half-Cell Circuitry (ASTM C876, 1994) 49
Figure 4.3: Rapid Chloride Permeability Test Schematic (Rose, 1987; ASTM C1202, 1994) 50
Figure 4.4: Permeability Vs. Total Charge Passed of Silica Fume Concrete (Wee et al., 1999) 50
Figure 5.1: Geometry of Specimens 63
Figure 5.2: Wiring of Specimens 63
Figure 5.3: Typical Specimen 64
Figure 5.4: Temperature-Controlled Boxes 64
Figure 5.5: Heat Lamp and Thermostat in the Temperature-Controlled Boxes 65
Figure 5.6: Macrocell Reading 65
Figure 5.7: Half-Cell Reading 66
Figure 6.1: Iron Lost Data – Control and Single Admixtures 85
Figure 6.2: Iron Lost Data – Double Admixtures 85
Figure 6.3: Iron Lost Data – Triple Admixtures and Higher w/c 86
Figure 6.4: Iron Lost Data Detail– Control and Single Admixtures 86
Figure 6.5: Iron Lost Data Detail– Double Admixtures 87
Figure 6.6: Iron Lost Data Detail – Triple Admixtures and High w/c 87
Figure 6.7: Iron Lost Data – Pre-Cracked Specimens 88
Figure 6.8: Iron Lost Data – Replaced Specimens 88

# LIST OF SYMBOLS

| | |
|---|---|
| A2000 | Armatec 2000 |
| AASHTO | American Association of State Highway and Transportation Officials |
| AC | alternating current |
| ACI | American Concrete Institute |
| ASTM | American Society for Testing and Materials |
| BS | black steel |
| $C_3A$ | tricalcium aluminate |
| $Ca(NO_2)_2$ | calcium nitrite |
| CaO | calcium oxide |
| $Ca(OH)_2$ | calcium hydroxide |
| $Cl^-$ | chloride ion |
| $Cl^-/NO_2^-$ | chloride-to-nitrite ratio |
| $Cl^-/OH^-$ | chloride-to-hydroxide ratio |
| $cm^2$ | square centimeters |
| CNI | calcium nitrite inhibitor |
| CT | Connecticut |
| DC | direct current |
| DCI | Darex corrosion inhibitor (calcium nitrite) |
| DMEA | dimethylethanol amine |
| DOT | Department of Transportation |
| $e^-$ | electron |
| FA | fly ash |
| Fe | iron |
| $Fe^{2+}$ | ferrous iron |
| $gal/yd^3$ | gallons per cubic yard |
| GBFS | granulated blast furnace slag |
| GGBFS | ground granulated blast furnace slag |

| | |
|---|---|
| H | hydrogen |
| $H_2O$ | water |
| HRWR | high range water reducer |
| in. | inches |
| in/yr | inches per year |
| $kg/m^3$ | kilograms per cubic meter |
| kohm cm | kilo ohm centimeter |
| kΩ cm | kilo ohm centimeter |
| $lb/yd^3$ | pound per cubic yard |
| $l/m^3$ | liters per cubic meter |
| $L/m^3$ | liters per cubic meter |
| M | moles |
| MA | Massachusetts |
| $mA/cm^2$ | microamps per square centimeter |
| ME | Maine |
| $m^2/s$ | square meters per second |
| mm | millimeter |
| mM/l | millimoles per liter |
| mol/l | moles per liter |
| mV | millivolts |
| mV/s | millivolts per second |
| N | nitrogen |
| NaCl | sodium chloride |
| $Na_2PO_3F$ | MFP |
| NCHRP | National Cooperative Highway Research Program |
| NETC | New England Transportation Consortium |
| NH | New Hampshire |
| $NO_2^-$ | nitrite |
| No. | number |
| O | oxygen |

| | |
|---|---|
| OCIA | organic-based corrosion-inhibiting admixture |
| $OH^-$ | hydroxide |
| ohm $cm^2$ | ohm square centimeter |
| OPC | ordinary Portland cement |
| PC | Portland cement |
| R222 | Rheocrete 222 |
| REF | reference |
| R.H. | relative humidity |
| RI | Rhode Island |
| $R_p$ | polarization resistance (ohms $cm^2$) |
| SCE | saturated calomel electrode |
| SF | silica fume |
| $SiO_2$ | silicon dioxide |
| VT | Vermont |
| w/c | water-to-cement, or water-to-cementitious material ratio |
| WJE | Wiss, Janney, Elstner Associates, Inc. |
| μA | microamps |
| μm | microns |
| μohms/$cm^2$ | micro ohms per square centimeter |
| μS/$cm^2$ | micro ohms per square centimeter |

# Performance Evaluation and Economic Analysis of Combinations of Durability Enhancing Admixtures (Mineral and Chemical) in Structural Concrete for the Northeast U.S.A. (NETC 97-2)

## 1. INTRODUCTION

### 1.1. DURABILITY ENHANCING CONCRETE ADMIXTURES

Durability is an important consideration when structural reinforced concrete is used in harsh environments where it is exposed to the weather. One of the main durability problems in the harsh environment of New England, in the Northeast U.S.A., is corrosion of reinforcing steel in structural concrete, particularly in bridge structures. As a result, a variety of measures are often relied upon to improve the durability of structural concrete used in this part of the country. Some of these corrosion protection systems and materials include: low water-cement ratio concrete, epoxy-coated or stainless steel reinforcing steel, protective concrete surface sealers, chemical and mineral concrete admixtures (including silica fume, fly ash, ground granulated blast furnace slag, and chemical corrosion inhibitors), and cathodic protection. These systems and materials utilize a number of different corrosion protection mechanisms, and they are frequently used in combinations without specifically knowing to what extent they are improving concrete durability or what economic impact they have over the life cycle of a structure.

In the last fifteen years, a number of reinforced concrete test specimens and test methods have been developed and used to evaluate the available corrosion protection systems. The consulting engineering firm of Wiss, Janney, Elstner Associates, Inc. (WJE) developed many of these test specimens and methods. WJE, the Project Consultant for this NETC 97-2 study, has previously been selected by the National Cooperative Highway Research Program (NCHRP) and the Federal Highway Administration (FHWA) to undertake six major laboratory and field research projects on corrosion protection systems for bridge structures. In these projects, WJE has taken the lead in standardizing various laboratory test protocols. These testing procedures have been used in the past to characterize the benefits of various corrosion protection systems. However, in spite of the extensive testing to date, many possible combinations of the various potential corrosion protection systems have not been thoroughly investigated.

Only limited tests to determine the ability of mineral admixtures (silica fume, fly ash, and ground granulated blast furnace slag) in conjunction with chemical corrosion inhibitor admixtures to prevent corrosion of reinforcing steel in concrete have been performed under independent analyses to date. The purposes of this NETC 97-2 research program is to test how combinations of mineral and chemical admixtures might offer dual corrosion protection and therefore significantly enhance durability of structural reinforced concrete subjected to a corrosive environment, and to provide direct comparisons between admixtures. With this information in hand, the State Highway Departments in New England will be better able to make informed decisions about specifying chemical and mineral admixtures for structural reinforced concrete.

## 1.2. OVERALL RESEARCH OBJECTIVES

The objectives of Phase I of this project were to present the results of an exhaustive literature review of relevant previous research, to evaluate the current use of chemical and mineral durability enhancing admixtures in structural reinforced concrete by State Highway Departments in New England, and to develop an experimental research plan. Combinations of silica fume, fly ash, ground granulated blast furnace slag, and chemical corrosion inhibitors were considered. The results of this phase of the project are covered in Chapters 2 through 5 of this report.

The objective of Phase II of the research project was to implement the testing protocol on the series of single, double, and triple admixture combinations. Results of this research are included in Chapters 5 through 7 of this report and can be used for the formulation of guidelines for New England State Highway Departments on the specification and use of mineral and chemical admixtures. These guidelines address expected long-term durability enhancement of using various mineral and chemical admixtures in reinforced concrete structures.

## 1.3. SCOPE OF RESEARCH

This report completes the NETC 97-2 research project, and includes the following:

**Literature Review (Phase I):**

A thorough literature search of all information available on the use of durability enhancing admixtures has been performed. The relevant literature (more than sixty published papers and reports) concerning previous research findings and current construction practices were collected, reviewed, and summarized. In conjunction with this task, the Project Team surveyed the past and current use of durability enhancing concrete admixtures in the New England states.

**Research Plan (Phase I):**

Based on the results of the literature review and consultation with the Project Consultant (WJE), a laboratory investigation research plan was developed to test the durability enhancement of combinations of chemical and mineral admixtures in structural reinforced concrete. The research plan includes the rationale for selecting the various laboratory tests, the details of the tests themselves, and how the results will be interpreted.

**Laboratory Testing Program (Phase II):**

The research plan developed at the conclusion of Phase I of the project was implemented. Approximately 2 years of data was collected for 42 specimens. Macro-cell, half-cell, crack inspections, visual inspections, and autopsies of specimens were performed. Evaluations of performance for single, double, and triple combinations of admixtures were performed based on time to corrosion, relative values of iron lost, time to cracking, visual inspections, and qualitative measures.

**Interim and Final Reports:**

This NETC 97-2 final report summarizes the work completed in the project, inclusive of Phases I and II. An internal NETC 97-2 interim report was distributed in July 2000, which reported on the progress through Phase I of the project. All relevant information from that report is repeated in this final report.

## 2. BACKGROUND AND LITERATURE REVIEW

A summary of the reviewed literature is presented below. Complete summaries of the referenced papers and reports can be found in Appendix A.

### 2.1. INTRODUCTION

Since the early 1970s, corrosion has been recognized as a problem in reinforced concrete structures. The concern arose in the 1970s when bridge decks designed for 30 to 50 years of service began to deteriorate after only 10 years of use. In addition to bridge decks and their supporting members, parking garages are also subject to corrosion. In coastal environments, structures typically subject to corrosion are sea walls and piers, as well as bridge piles, girders, and decks. Corrosion in all of these types of structures is severe and widespread. Internal damage is caused by the corrosive action of external and internal chlorides on embedded reinforcing steel and prestressing strands in the concrete. The external chlorides are from de-icing salts, marine sea-spray, and immersion in water containing chlorides. Chlorides also enter concrete by means of construction materials: marine aggregates, chloride contaminated mixing water, and chloride containing admixtures such as calcium chloride. When iron is exposed to water and oxygen, it oxidizes and produces a corrosion by-product (rust). This steel corrosion by-product can expand in size to approximately four times its original volume, creating tensile stresses within the concrete and causing the concrete to crack and spall; this action allows chlorides to enter at an even faster rate. (Berke et al., 1988.) Even minimal amounts of corrosion can cause cracking in concrete specimens. McDonald et al (1996) reviewed several studies and determined that as little as 0.025 mm (0.001 in.) loss in bar diameter can be sufficient to cause cracking in concrete. This would be equivalent to a 0.6 percent steel weight loss in a 16 mm (#5) reinforcing bar if the corrosion were evenly distributed over the entire surface. However, actual corrosion will not be evenly distributed, indicating that a much lower average percentage loss could result in cracking.

It has been found that corrosion can begin with a chloride ion content in the concrete of only 1.0 to 1.6 lb/yd$^3$ at the level of the steel (Berke et al., 1988). For a group of bridges constructed with conventional concrete, after 11 to 30 years of exposure to chlorides from de-icing salts, the chloride content at 1-3/4 in. (approximately the level of the reinforcing

steel) had a median value of 6.4 lb/yd$^3$ (more than four times the "threshold" cited above) and corrosion was confirmed by half-cell potentials. This data indicates that ordinary concrete does not provide adequate resistance to chloride penetration or subsequent corrosion. (Ozyildirim, 1993.)

Corrosion of marine structures is typically a result of the wicking action that occurs during wetting and drying cycles. Piles in warmer climates deteriorate faster than their northern counterparts. (Berke et al., 1988.) After about 12 years of exposure, tests on a concrete fishing pier indicated chloride ion concentrations ranging from 34 to 58 lb/yd$^3$ in piles, and 20 to 41 lb/yd$^3$ in bent caps. Corrosion below the water line was not a problem because oxygen, which was needed for corrosion to occur, was not available. (Krauss & Nmai, 1996.)

The protection provided to embedded reinforcing steel by ordinary Portland cement is made up of three main components as follows: 1) the physical barrier of the concrete between the contaminants and the steel, 2) the thermodynamic stabilization of the steel provided by the high pH of concrete, and 3) the chemical stabilization provided by the formation of a mineral scale on the steel. The degree of corrosion protection provided by the concrete alone is dependent on: the quality of the concrete (curing, cement grade, water-to-cement ratio, permeability, etc.), the pH of the concrete at casting and throughout its service life (optimum pH is 12.5 to 13), and the chloride ion content at casting and throughout its service life (especially soluble chloride). (Incorvia, 1996.)

Corrosion of reinforcing steel embedded in concrete depends on the electrolytic conditions of the concrete as characterized by these three factors: 1) the passivity of embedded reinforcing steel, 2) the availability of oxygen, and 3) the electrical resistivity of the concrete (Gjorv, 1995). The chloride corrosion damage typically sustained by reinforcing steel embedded in concrete is a result of one or more of the following: chloride penetration and degradation of the protective oxide film on the steel, preferential adsorption of chloride (instead of a protective passivating species) onto the reinforcing steel, assistance to the removal of ferrous ions from the surface of the steel by the presence of chlorides, the bridging effect of chlorides facilitating the corrosion process, and the formation of a chloride/iron complex. Chloride ions are found in the following forms: free (non-bonded), bonded to calcium silicate hydrates, combined with tricalcium aluminate to form calcium

chloroaluminate hydrate (Friedel's salt), and as calcium ferrite chlorides or calcium oxychlorides. (Incorvia, 1996.) When chlorides and sulfates both reach the steel, the presence of the sulfates typically increases the corrosion current density. However, the time to initiation of corrosion is not influenced by the concomitant presence of chloride and sulfate ions. (Al-Amoudi et al., 1994.)

The typical mechanism of corrosion of embedded reinforcing steel is electrochemical, by galvanic action. Galvanic cells exist along the steel (microcell) or between embedded steel layers (macrocell). Macrocell corrosion occurs when the top reinforcing steel mat performs as an anode and the bottom mat performs as a cathode; such as, a bridge deck with top and bottom reinforcing steel where de-icing salt are applied to the surface. The anode steel deteriorates by losing electrons through conduction by connected steel rebar and ties to the cathode steel, where the electrons are consumed by oxidation. The corrosion cell circuit is completed by the diffusion of ions through moist concrete, acting as an electrolyte. For steel corrosion to begin, the chloride threshold level, of 1.1 to 1.3 $lb/yd^3$ (0.2% of chloride ion by weight of cement), must be exceeded in the concrete at the level of the anode steel. Chloride ions disrupt the normal passivation of the steel provided by the high pH of the cement paste. (Wolsiefer, 1993.)

Corrosion can be reduced or eliminated by one or more of the following: 1) reducing or eliminating chlorides at the anode, 2) decreasing oxygen at the cathode, and/or 3) increasing electrical resistance of the concrete that acts as the corrosion cell electrolyte (Wolsiefer, 1993).

It has been found that merely increasing the concrete cover over the reinforcing steel, lowering the water-to-cement ratio (to reduce permeability), and using epoxy coated rebar are typically not sufficient to provide long term protection of steel reinforced concrete structures; therefore, chemical and mineral corrosion inhibiting admixtures have often been incorporated into concrete to enhance durability. Cracks in concrete permit easier access of chloride ions, moisture, and oxygen to the reinforcing steel; therefore, an effective corrosion-inhibiting admixture would need to still be effective when concrete is cracked. Some inhibitors act by controlling either the anodic or cathodic reactions at the steel surface, while others prevent chloride ions from reaching the steel. Following is a literature review of various chemical and mineral admixtures that may provide enhanced corrosion resistance in

reinforced concrete structures. These admixtures include calcium nitrite, amines and esters, silica fume, fly ash, and granulated blast furnace slag.

## 2.2. CHEMICAL CORROSION INHIBITORS

### 2.2.1. Calcium Nitrite

**Product Description:**

Calcium nitrite, $Ca(NO_2)_2$, (sold commercially as DCI by W. R. Grace and Company) is a fine white powder that is usually mixed into concrete as a slurry.

**Mechanism of Protection:**

Calcium nitrite promotes the stabilization of the steel's natural passivating layer, increasing the time to corrosion initiation. Nitrite appears to be a nonspecific inhibitor that reduces the transport of ferrous ions to the electrolyte; in other words, the inhibiting reaction does not occur at the anode or cathode sites, but rather the nitrite blocks the current path between adjoining mats of reinforcing steel. (Gaidis & Rosenberg, 1987.)

The mechanism of protection can be described as follows. The initial reaction occurring when steel is placed in an alkaline environment, such as concrete, is:

$$Fe \rightarrow Fe^{2+} + 2e^- \qquad (1)$$

Then later reactions convert the ferrous ions ($Fe^{2+}$) to $Fe(OH)_2$, or $Fe_3O_4 \cdot nH_2O$, or γ-FeOOH, forming a passive oxide layer at the steel surface. All of the oxide phases are stable in alkaline environments when chlorides are not present. The oxide layers are only a few monolayers thick, but they are able to prevent further oxidation from occurring. γ-FeOOH is the most stable in the presence of chloride or other depassivating ions. (Berke & Weil, 1992.)

On the microscopic scale, there are regions on the reinforcing steel surface where the protective oxide is not present. At these locations, chloride ions can form a complex with $Fe^{2+}$. This complex can then migrate from the steel surface, subsequently becoming an expansive corrosion product. (Berke & Weil, 1992.)

The passivation chemical reaction of nitrite with ferrous ions ($Fe^{2+}$) blocks active corrosion centers by producing a passive ferric oxide protective film.

$$2Fe^{2+} + 2OH^- + 2NO_2^- \rightarrow 2NO\ (g) + Fe_2O_3 + H_2O \qquad (2a)$$

or

$$Fe^{2+} + OH^- + NO_2^- \rightarrow NO\ (g) + \gamma\text{-}FeOOH \qquad (2b)$$

If corrosion reaction (1) occurs, the ferrous ions produced are changed through calcium nitrite to a stable passive layer. The iron in the ferric state cannot then become a chloride complex, and therefore corrosion is reduced. Nitrite does not enter into anodic reactions, but reacts with the resulting products of the anode, so it does not affect the size of the anode. Essentially no nitrite or hydroxide is consumed in forming the initial protective oxides or hydroxide, as only monolayers of oxides are involved. Chlorides ($Cl^-$), nitrites ($NO_2^-$), and hydroxides ($OH^-$) compete at flaws in the protective oxide layer for $Fe^{2+}$. Over time, a nitrite and/or an alkaline environment, free of chloride, can reduce the number of sites where $Fe^{2+}$ ions are formed, through the formation of a protective coating $\gamma$-FeOOH or $Fe(OH)_2$. However, when chloride is present at very high $Cl^-/NO_2^-$ and/or $Cl^-/OH^-$ ratios, the probability of a $Cl^-$ and $Fe^{2+}$ complex forming is increased, and pitting is likely. The corrosion threshold ratio of $Cl^-/OH^-$ is typically between 0.3 and 0.6. The corrosion threshold ratio of $Cl^-/NO_2^-$ is approximately between 1 and 1.5. (Berke & Weil, 1992.)

**Experimental Results:**

A total of twenty papers and reports were found that included calcium nitrite as a corrosion inhibitor. Tests were typically performed on small reinforced concrete slabs and beams (both cracked and non-cracked) with two layers of reinforcing steel, and on concrete cylinders with embedded reinforcing steel. The concrete specimens, some with admixed chlorides, were typically subjected to continuous or cyclic ponding with sodium chloride, or to partial immersion in sodium chloride. A number of non-destructive and destructive electrochemical and physical tests, as well as visual surveys, were typically performed on the specimens over time to characterize their behavior. The calcium nitrite testing programs were performed on concretes with water-to-cement (w/c) ratios ranging from 0.32 to 0.64, and the calcium nitrite dosages ranged from 2 gallons to over 7 gallons of 30% calcium nitrite solution per cubic yard of concrete. There were also a few tests of mortars containing calcium nitrite and of reinforcing steel immersed directly into aggressive chloride solutions that also contained calcium nitrite. Finally, a few studies reported on field experience with concretes containing calcium nitrite. Studies of calcium nitrite used as a corrosion inhibitor in conjunction with mineral admixtures will be summarized in a later section.

Overall, the tests reported in the literature indicated that an adequate dose of calcium nitrite in good quality concrete was a low-cost, effective method to provide protection against

corrosion of reinforcing steel in an aggressive environment, with no detrimental effects on concrete strength or durability (El-Jazairi & Berke, 1990; Lee & Lee, 1997). Calcium nitrite was able to retard the onset of steel corrosion in chloride-laden environments, even offering protection when chlorides were present in concrete at the level of the reinforcing steel (Hartt & Rosenberg, 1980; Hope & Ip, 1989; Berke et al., 1993; Pyc et al., 1999). For example, calcium nitrite was able to substantially delay the onset of corrosion in reinforced concrete cylinders with admixed chlorides (Berke & Weil, 1992).

Calcium nitrite was also effective in reducing the rate of corrosion of reinforcing steel in concrete even after corrosion had begun (Berke, 1987; Pfeifer, 1989; Nmai & Krauss, 1994). In reinforced concrete beams and cylinders subjected to aggressive chloride environments, calcium nitrite reduced the total macrocell corrosion by two to four times in comparison with control concrete specimens (Pfeifer, 1989; Berke & Hicks, 1992).

All of the above improvements were possible because the calcium nitrite did not allow a large electrical potential difference to develop between adjoining mats of reinforcing steel. Also, a reservoir of calcium nitrite was typically still available at the reinforcement level to repassivate the steel, even after severe chloride exposure and corrosion initiation. (Virmani et al., 1983; Virmani, 1988; Virmani, 1990; Berke et al., 1988; Hope & Ip, 1989; Berke & Weil, 1992; Pyc et al., 1999.) There was some disagreement, however, as to whether the presence of calcium nitrite in concrete was capable of reducing the rate of diffusion of chlorides into the concrete (Berke & Rosenberg, 1989; Nmai et al., 1992; McDonald 1995; Incorvia, 1996; Pyc et al., 1999).

Calcium nitrite was most effective in improving the corrosion resistance of reinforcing steel when used in concrete with low w/c of less than 0.50, although it could still be an effective inhibitor at high w/c ratios (Berke, 1987; Berke et al., 1988; Berke & Weil, 1992). In one two-and-a-half year test of reinforced concrete cylinders subjected to an aggressive chloride environment, it was found that a 0.49 w/c concrete with 3 gal/yd$^3$ of calcium nitrite solution outperformed a 0.38 w/c concrete without calcium nitrite; therefore, low w/c alone did not determine the optimal concrete mix (Berke, 1987). For a particular w/c, calcium nitrite concrete typically had somewhat higher early strengths and slightly lower later strengths than the control (El-Jazairi & Berke, 1990; Lee & Lee, 1997). In concrete with water-reducing admixtures, calcium nitrite increased the time to corrosion by

even more than it did in concrete without water-reducing admixtures (Harrt & Rosenberg, 1980).

In cracked reinforced concrete test specimens, calcium nitrite also increased time to corrosion and reduced corrosion rates, with respect to a control (Berke & Rosenberg, 1989; Nmai et al., 1992; McDonald, 1995). In one test series, a fully cracked control specimen exhibited four times the corrosion of a similar fully cracked specimen with calcium nitrite, and a partially cracked specimen exhibited three times the corrosion of a similar partially cracked specimen with calcium nitrite (Figure 2.1) (Pfeifer, 1989; Berke & Weil, 1992).

The rate of corrosion of steel in a chloride-laden environment increased as the ratio of chloride to nitrite increased, and a critical chloride/nitrite threshold for corrosion appeared to exist, particularly in poor quality, chloride contaminated concrete (Virmani et al., 1983; Virmani, 1988; Hope & Ip, 1989; Virmani, 1990). Corrosion rates were reduced by a factor of ten for chloride/nitrite values less than 1.1, and the rates were reduced by at least a factor of two for chloride/nitrite values up to 2.5 (Virmani et al., 1983; Gaidis & Rosenberg, 1987; Virmani, 1988; Virmani, 1990; Berke & Weil, 1992). It was shown that for chloride/nitrite values less than 1.5, calcium nitrite was able to provide protection to reinforcing steel in concrete and inhibit corrosion. For example, reinforced concrete slab samples containing 4 gal/yd$^3$ of calcium nitrite solution had a threshold chloride concentration of approximately 14 lb/yd$^3$ for corrosion, which was equivalent to a chloride/nitrite ratio of about 1.6. (Gaidis & Rosenberg, 1987.) In control concrete without calcium nitrite, the threshold chloride concentration was about ten times lower (Berke & Rosenberg, 1989; McDonald, 1995).

A limited amount of field experience with calcium nitrite as a concrete admixture in aggressive environments has been reported. Core samples from bridge decks up to eight years old (constructed of 0.45 w/c concrete with 3 gal/yd$^3$ of calcium nitrite solution) have shown that calcium nitrite was still effective in maintaining concrete passivity and controlling reinforcing steel corrosion. An ocean fishing pier showed no sign of corrosion after eleven years, with calcium nitrite as the only corrosion protection system. Finally, parking garages in a severe environment, constructed with 0.45 w/c concrete with 3.5 gal/yd$^3$ of calcium nitrite solution, showed no signs of corrosion after ten years of service. (Berke & Weil, 1992.)

Based on the available literature, concrete mix design recommendations have been made for the use of calcium nitrite in order for it to provide long-term reinforcing steel corrosion protection in aggressive environments. For instance, a maximum w/c of 0.40 to 0.50, a minimum cement content of 500 lb/yd$^3$ to 600 lb/yd$^3$, and a minimum concrete cover of 1¼ in. to 1½ in. have been recommended (El-Jazairi & Berke, 1990). For concrete designed for a chloride content of approximately 6 lb/yd$^3$ at the level of the reinforcing steel, the recommended calcium nitrite dosage ranged from 2 gal/yd$^3$ to 3 gal/yd$^3$; for concrete designed for a chloride content of about 10 lb/yd$^3$ at the level of the reinforcing steel, the recommended calcium nitrite dosage ranged from 3 gal/yd$^3$ to 5 gal/yd$^3$ (Berke & Rosenberg, 1989; Nmai et al., 1992; McDonald, 1995).

### 2.2.2. Amines and Esters (Rheocrete 222 and Armatec 2000)

**Product Description:**

This type of inhibitor is a water based organic corrosion inhibitor consisting of amines and fatty acid esters (sold commercially as Rheocrete 222 by Master Builders Incorporated and Armatec 2000 by SIKA Corporation).

**Mechanism of Protection:**

The mechanism of protection provided by the amines and esters is the development of an organic protective coating on the reinforcing steel and a reduction of chloride penetration into the concrete. The inhibitor bonds to metals by adsorption, physically, and/or chemically, due to the polar or weakly polar characteristic of the organic compound. The film provides a chloride screening process that results in a reduction of the macrocell corrosion currents. (Nmai et al. 1992; Bobrowski & Youn, 1993.) In addition, the hydrophobic nature of the inhibitor reduces chloride permeability (Incorvia, 1996). X-ray photoelectron spectroscopy (XPS) indicates that amines can interact with the hydroxyl group on the steel surface that forms insoluble iron oxide complexes that stabilize the oxide surface and inhibit further corrosion. Also amines have the ability to diffuse considerable distances through concrete because of their vapor pressure, so they do not have to be initially in contact with the steel and may work well for rehabilitation. (Buerge, 1995.)

**Experimental Results:**

A total of eight papers and reports were found that included amines and esters as a corrosion inhibitor. The tests were typically performed on small reinforced concrete slabs and beams (both cracked and non-cracked) with two layers of reinforcing steel, and on concrete cylinders with embedded reinforcing steel. The concrete specimens were typically subjected to continuous or cyclic ponding with sodium chloride, or to partial immersion in sodium chloride. A number of non-destructive and destructive electrochemical and physical tests, as well as visual surveys, were typically performed on the specimens over time to characterize their behavior. The amines and esters testing programs were performed on concretes with water-to-cement ratios ranging from 0.34 to 0.50, and the amines and esters dosages ranged from 1 gallon to 3 gallons of solution per cubic yard of concrete. There were also a few tests of reinforcing steel immersed directly into aggressive chloride solutions that also contained amines and esters. Studies of amines and esters used as a corrosion inhibitor in conjunction with mineral admixtures will be summarized in a later section.

Butyl esters and amines reduced concrete permeability to chloride ions; as a result chloride content was reduced by up to 85% in comparison with a control (Nmai et al., 1992; Incorvia, 1996). Concrete with amines and esters delayed the onset of corrosion by 6 months in cracked reinforced concrete beams subjected to cyclic ponding (in comparison to untreated samples) (Bobrowski & Youn, 1993). Butyl ester emulsion reduced chloride ingress in concrete with w/c of 0.50, but it had little effect on concrete with w/c of 0.40. Also, butyl ester emulsion adversely affected concrete compressive strength and the ability to entrain air. (Nmai et al., 1992; Berke et al., 1993.)

Tests with both reinforced concrete cylinders and steel plates submerged in aggressive chloride solutions showed that amines protected steel from corrosion. In fact, the pitting potential of mortar containing amines could be shifted towards the positive side. (Buerge, 1995.) In non-cracked reinforced concrete beams subjected to chloride ponding, measurable corrosion was detected in the reference concrete after 9 weeks, compared to 36 weeks for the concrete treated with amines and esters (Figures 2.2 and 2.3).

There is some debate as to the ability of amines and esters (Rheocrete and Armatec) to provide any or minimal protection against chloride ingress and/or corrosion of reinforcing steel (Pyc et al., 1999; Nmai, 1999). For example, dimethylethanol amine (DMEA) did not

appear to be an effective corrosion inhibitor in alkaline or concrete environments when chloride was present at the reinforcing steel. (Berke et al., 1993).

The recommended dosage of amine and esters is 1 gal/yd$^3$ (Nmai et al., 1994).

### 2.2.3. Other Chemical Corrosion Inhibitors

**Experimental Results:**

A total of twelve papers and reports were found that included chemical corrosion inhibitors other than calcium nitrite and amines and esters. These included DSS (referred to as disodium tetrapropenyl succinate), sodium nitrite, sodium benzoate, iron oxide, formaldehyde, potassium dichromate, $Na_2PO_3F$, di-sodium β-glycerophosphate, superplasticizers, phosphonic acid, carboxylic acid, sodium chromate, polysiloxane, potassium chromate, stannic chloride, stannous chloride, and stannous tin. The tests were typically performed on small reinforced concrete slabs and beams with two layers of reinforcing steel, and on concrete cylinders with embedded reinforcing steel. The concrete specimens, some with admixed chlorides, were typically subjected to continuous or cyclic ponding with sodium chloride, or to partial immersion in sodium chloride. A number of non-destructive and destructive electrochemical and physical tests, as well as visual surveys, were typically performed on the specimens over time to characterize their behavior. There were also a few tests of mortars containing inhibitors and of reinforcing steel immersed directly into aggressive chloride solutions that contained inhibitors.

The DSS testing program was performed on concrete with a water-to-cement (w/c) ratio of 0.40, and the DSS dosages ranged from 1/4%-2% addition by weight of cement. Testing included lollipop and slab specimens, and included corrosion testing, absorption testing, freeze thaw testing, and strength testing. DSS provided dual protection against corrosion of reinforcing steel by reducing permeability and inhibiting corrosion. (Allyn et al., 1998; Allyn and Frantz, 2001a, 2001b.) Corrosion testing was performed at 1% and 2% DSS concentrations per weight of cement, however conversations with the researchers indicated that ½% dosages would likely be adequate. At the end of testing, no corrosion had initiated in the DSS specimens. It was noted that DSS had a detrimental effect on concrete strength. DSS is an experimental admixture that has promising potential.

The sodium nitrite testing programs were performed on concretes with water-to-cement (w/c) ratios ranging from 0.44 to 0.90, and the sodium nitrite dosages ranged from 1% to 5% addition by weight of cement. Sodium nitrite reduced corrosion in cracked specimens, even at higher than recommended w/c and at low dosage rates for the exposure conditions. (Berke et al., 1989; McDonald, 1995; Berke & Weil, 1992.) Sodium nitrite offered superior protection, lowering the steel mass loss after 8 months exposure by 47% to 55%, depending on the concentration (Batis et al., 1996). Sodium nitrite at 2% and 3% addition by weight of cement reduced the negative effect of carbonation on pH; however, this protection was not effective when concrete was under both carbonation and chloride attack. Sodium nitrites' inhibiting effects were enhanced in moist cured concrete. The higher the concentration of nitrites, the higher the protection level. (Alonso & Andrade, 1990.) However, in another study sodium nitrite had a tendency toward effective protection, but it was minimal (Loto, 1992).

The sodium benzoate testing programs were performed on mortars with w/c ranging from 0.50 to 0.90, and the sodium benzoate dosages ranged from 1% to 2% addition by weight of cement. Sodium benzoate had a protective effect on the steel, but overall, sodium benzoate did not perform well as an inhibitor (Batis et al., 1996; Berke & Weil, 1992.)

The iron oxide testing programs were performed on mortars with w/c ranging from 0.50 to 0.90, and the iron oxide dosages ranged from 5% to 10% addition by weight of cement. Iron oxide had a protective effect on the steel (Batis et al., 1996).

The formaldehyde and potassium dichromate testing programs were performed on concretes with w/c of 0.44; the formaldehyde dosages ranged from 0.5% to 1% addition by weight of cement and the potassium dichromate dosage was 1% addition by weight of cement. Formaldehyde and potassium dichromate, when mixed alone with the concrete, were not effective inhibitors. Potassium dichromate and formaldehyde together provided a passivating effect up to the seventh week of testing. Further investigation is required to determine the full extent of the effectiveness of the inhibitors, especially by varying the dosages. (Loto, 1992.)

The $Na_2PO_3F$ (MFP) testing programs were performed on concretes with a w/c of 0.50, and the $Na_2PO_3F$ dosages ranged from 0.05 to 0.5 M. $Na_2PO_3F$ seemed to act as an anodic inhibitor in the presence of NaCl when added in alkaline solutions to the mortar mix.

The inhibitor was more effective in the same proportions when added to the mortar mix than in the solutions. When MFP was added to the mortar mix, it was able to resist chloride attack when the ratio of concentrations of MFP to chloride was greater than one. The inhibitor was also effective when it penetrated through the pores of hardened concrete; this could reduce or stop corrosion. (Andrade et al., 1992.)

The di-sodium β-glycerophosphate testing programs were performed with a dosage of 0.05 M. Di-sodium β-glycerophosphate (GPH) had good inhibitor efficiency towards localized attack, nearly comparable to sodium nitrite. The GPH/sodium nitrite mixture at a concentration of 0.005 M of each inhibitor also efficiently inhibited localized attack. (Monticelli et al., 1993.)

The superplasticizer testing programs were performed on concretes with w/c ranging from 0.25 to 0.51. Superplasticizers reduced concrete porosity and chloride permeability, but not enough to provide protection against chloride induced corrosion. (Incorvia, 1996.)

The phosphonic acid testing programs were performed on concretes with dosages ranging from 0.005% to 5% addition by weight of cement. Phosphonic acid derivatives containing hydroxyl or amino groups provided some protection. (Incorvia, 1996.)

The carboxylic acid testing programs were performed on mortars with a dosage of 2.5% addition by weight of cement. Carboxylic acids provided corrosion protection; malonate was the most efficient acid of malonate, formate, acetate, and propionate. (Incorvia, 1996.) The acids remained soluble after curing in cement for up to 90 days. Malonic acid (malonate) was a very effective corrosion inhibitor, even in the presence of 2.5% chloride by weight of cement; however, it acted as a set retarder in the mortar. Soluble dicarboxylic acids inhibited corrosion more effectively than monofunctional acids. (Sagoe-Crentsil et al., 1993.)

The stannous chloride testing programs were performed in solution with dosages ranging from 0.1% to 0.3%. Stannic chloride and stannous chloride did not act as corrosion inhibitors. (Berke & Weil, 1992; Hope & Ip, 1989.)

The stannous tin testing programs were performed on concrete with w/c of 0.50 and stannous tin dosages of 200 mM/l. Stannous tin was a strong inhibitor of chloride induced corrosion of steel embedded in concrete; the mechanism was believed to be that tin stabilized the passivating layer on the steel. For cement pastes containing 0-1630 mM/l chloride, $Sn^{2+}$,

but not $Sn^{4+}$, was an effective inhibitor at an initial concentration of 200 mM/l. (Sagoe-Crentsil et al., 1994.)

Sodium chromate and polysiloxane did not provide reduced chloride penetration (Incorvia, 1996). Potassium chromate did not perform well as an inhibitor (Berke & Weil, 1992).

## 2.3. MINERAL CORROSION INHIBITORS

### 2.3.1. Silica Fume

**Product Description:**

Silica fume, or microsilica, is a light to dark gray, or bluish-green-gray, powdery product. It is a fine-grained material (30 to 100 times finer than cement) of particles with diameters less than 1 μm, with an average diameter of 0.1 μm. Its specific gravity is in the range of 2.10 to 2.55. Silica fume is the by-product of silicon-metal production, namely the reduction of high purity quartz with coal in an electric arc furnace. It rises as an oxidized vapor from the furnace, cools and condenses, and is collected in filter bags. Silicon dioxide ($SiO_2$) constitutes more than 90% of silica fume. Silica fume is usually sold in slurry form or powder. (Kosmatka & Panarese, 1988.)

**Mechanism of Protection:**

The silica reacts with free lime during hydration of cement. This chemical reaction creates a stronger cementitious compound (calcium silicate hydrate) that improves concrete strength and may improve aggregate-paste bonding. This reaction reduces the pH of the pore fluid by reducing the alkali content; in spite of the need for a high pH to prevent the depassivation protection of the embedded reinforcing steel, silica fume is still an effective corrosion inhibitor in concrete. (Wolsiefer, 1993.)

The greatest protection with silica fume results from the concrete pores being filled in for a better interparticle arrangement that decreases permeability. This hinders the water, oxygen, and chloride ingress that can cause corrosion of reinforcing steel. The physical structure of the hardened cement paste with silica fume is a dense and low permeability cement matrix that results from a refinement and segmentation of the capillary pores. The decreased permeability negates any increased corrosion susceptibility from the elevated $Cl^-/OH^-$ ratio of the pore solution, which is a result of the reduction in pH during hydration. The

use of silica fume also increases the electrical resistivity of concrete, and this can reduce ionic conduction as a result of the lower ionic content of the capillary pore water. (Rasheeduzzafar et al., 1992; Khedr & Idriss, 1995.)

**Experimental Results:**

A total of nineteen papers and reports were found that included silica fume as a corrosion inhibitor. The tests were typically performed on small reinforced concrete slabs and beams with two layers of reinforcing steel, and on concrete cylinders with embedded reinforcing steel. The concrete specimens were typically subjected to continuous or cyclic ponding with sodium chloride, or to partial immersion in sodium chloride. A number of non-destructive and destructive electrochemical and physical tests, as well as visual surveys, were typically performed on the specimens over time to characterize their behavior. The silica fume testing programs were performed on concretes with water-to-cement (w/c) ratios ranging from 0.22 to 0.70; the silica fume dosages ranged from 2% to 15% addition by weight of cement, or 4% to 30% cement replacement. There were also a few tests of mortars containing silica fume. Finally, a few studies also reported on field experience with concretes containing silica fume. Studies of silica fume used as a corrosion inhibitor in conjunction with chemical or other mineral admixtures will be summarized in a later section.

Overall, the tests reported in the literature indicated that silica fume, used as an admixture or as a cement replacement, was able to increase a concrete's resistance to chloride-induced corrosion. This was typically achieved because silica fume concrete had a dense pore structure with a low diffusion coefficient (low permeability), which substantially reduced the rate of ingress of chlorides into the concrete, thereby increasing the time it took for chlorides to reach corrosion threshold concentrations at the level of the embedded reinforcing steel. Proper curing of silica fume concrete was also essential to prevent shrinkage cracking. (Berke et al., 1988; Gautefall & Havdahl, 1989; Anqi et al., 1991; Philipose et al., 1991; Berke & Hicks, 1992; Ozyildirim, 1993; Pigeon et al., 1993; Al-Amoudi et al., 1994; McGrath & Hooton, 1997.)

Silica fume concrete permeability was typically measured either directly by determining diffusion coefficients based on chloride concentrations versus depth over time from long-term ponding or immersion tests, or indirectly by using a rapid chloride permeability test that determined the electrical charge passing through a specimen in a

specified short period of time (Berke et al., 1988). Additions of silica fume were always able to reduce the chloride permeability of concrete, particularly for concrete at early ages. The reduction in permeability increased with the amount of silica fume used, with reduction in w/c, and with increased curing time. (Berke et al., 1988; Berke, 1989; Anqi et al., 1991; Philipose et al., 1991; Pigeon et al., 1993; Wolsiefer, 1993; Gjorv, 1995). The reductions in permeability were most dramatic as silica fume content increased from zero to about 7% to 11% by weight of cement; there were some additional reductions in permeability as silica fume content was further increased (Berke et al., 1988; Anqi et al., 1991; Wolsiefer, 1993; Gjorv, 1995; McGrath & Hooton, 1997). For tests on reinforced concrete cubes, beams and cylinders subjected to aggressive chloride environments, silica fume was able to reduce the diffusion coefficient of the concrete by five to fifteen times for 9% to 15% cement replacement (Anqi et al., 1991; Gjorv, 1995; Incorvia, 1996).

The reductions in permeability reported above resulted in chloride concentrations at the level of the reinforcing steel in test specimens with silica fume that were always substantially less than those in control specimens (Figure 2.4) (Gautefall & Haudahl, 1989; Sherman et al., 1996). In long-term chloride ponding tests on concrete beams, slabs, and cylinders, silica fume specimens had 90% to 98% lower chloride concentrations at the level of the reinforcing steel than did companion control specimens, and the chloride concentrations of the silica fume specimens were below accepted threshold values (Anqi et al., 1991; Ozyildirim, 1993; Incorvia, 1996).

As detailed above, silica fume concrete has been found to be much less permeable and therefore much more resistant to the ingress of chloride ions than conventional concrete. Also, silica fume in dosages up to 30% cement replacement did not reduce the concrete pH below 11.5, the threshold level to maintain passivity of the embedded reinforcing steel. (Gjorv, 1995.) As a result, corrosion of reinforcing steel embedded in concrete and mortar beams and cylinders subjected to aggressive chloride environments was inhibited by the use of silica fume in the concrete mix (Figure 2.5) (Berke, 1989; Deja et al., 1991; Gjorv, 1995). In one test series, the time to initiation of reinforcing steel corrosion was increased by five times simply by using concrete with 10% silica fume replacement by weight of cement (Al-Amoudi et al., 1994). This was in part due to the high resistivity of silica fume concrete, which was typically able to minimize the microcell corrosion current along the reinforcing

steel and the macrocell corrosion between layers of reinforcement (Berke et al., 1988; Berke, 1989; Wolsiefer, 1993; Gjorv, 1995). For tests on reinforced concrete beams, silica fume at 4% to 15% addition by weight of cement increased electrical resistivity by 2 to 9 times (Berke, 1989; Anqi et al., 1991). However, it has been noted that resistivity alone is not always a good measure of corrosion activity (Berke et al., 1991).

In cases when some corrosion activity was measured during chloride ponding and immersion tests of reinforced concrete beams, prisms, and cylinders, silica fume concretes still far outperformed control concretes. This was the case for a variety of different measures of corrosion activity, including polarization resistance, macrocell corrosion, and half-cell potential. (Berke, 1989; Berke et al., 1991; Rasheeduzzafar et al., 1992; Al-Amoudi et al., 1994; Khedr & Idriss, 1995.) For long-term tests on reinforced concrete prisms immersed in sodium chloride solution, concretes with 10% and 20% cement replacement with silica fume performed, respectively, 3 and 4 times better than the control in corrosion resistance with respect to half-cell values (Rasheeduzzafar et al., 1992). However, it was found that silica fume at very low dosages (less than about 4% addition by weight of cement) in conjunction with w/c above 0.43, and silica fume at moderate dosages (less than about 7% addition by weight of cement) in conjunction with high w/c (0.50 or above) were not effective in reducing the rate of corrosion in reinforced concrete cylinders immersed in a chloride solution. (Berke et al., 1991.)

High silica fume dosages were not necessary for maximum corrosion protection. It was found that concrete mixes with 10% and 20% silica fume cement replacement (with w/c between 0.44 and 0.50) offered similar levels of corrosion protection. (Rasheeduzzafar et al., 1992; Khedr & Idriss, 1995.) A maximum optimal silica fume dosage of 10% to 15% cement replacement has been indicated for moderate w/c concrete, which has offered several times better corrosion protection than concrete mixes without silica fume. Some tests indicated that using such silica fume concretes was more effective than simply lowering w/c of conventional concrete, to improve concrete durability. (Anqi et al., 1991; Khedr & Idriss, 1995.) Silica fume concretes with w/c of about 0.40 were even able to offer similar corrosion resistance to heat-cured conventional concretes with w/c of about 0.35. In that study, silica fume concrete with 7.5% silica fume cement replacement and a low w/c (0.32) outperformed all other conventional and silica fume concretes tested. (Sherman, et al., 1996.)

For very low w/c (0.25) high-performance concretes, silica fume addition resulted in a material that was also extremely resistant to internal damage due to high temperature drying (Pigeon et al., 1993). Concrete compressive strength was typically found to increase with increasing silica fume dosage and with decreasing w/c (Berke et al., 1988; Anqi et al., 1991; Khedr & Idriss, 1995).

In field applications over a period of more than twenty years, well-mixed silica fume concretes with low w/c (less than 0.40) have performed very well, even in hostile environments. Proper curing was essential to prevent initial cracking in these applications. (Gjorv, 1995.) Such cracking negates the benefits of the silica fume additions.

Based on the studies summarized above, the recommended optimal dosages for silica fume in structural concrete are in the range of 10% to 15% cement replacement.

### 2.3.2. Fly Ash

**Product Description:**

Fly ash is a finely divided residue that is a byproduct of the combustion of pulverized coal in electric power plants. Coal impurities, such as clay, feldspar, quartz, and shale, fuse in suspension and are carried away in the exhaust gas. The fused particles solidify into solid or hollow spheres, known as fly ash. The fly ash is then collected from the exhaust gas by electrostatic precipitators or bag filters. Fly ash is primarily silicate glass containing silica, alumina, iron, and calcium. The particle sizes of fly ash range from less than 1 μm to 100 μm and are typically less than 20 μm. Class F fly ash is generally a low-calcium (less than 10% CaO) material, with carbon contents typically less than 5%, but sometimes ranging as high as 10%. Class C fly ash is a high-calcium (10% to 30% CaO) material, with carbon contents usually less than 2%. (Kosmatka & Panarese, 1988.)

**Mechanism of Protection:**

Fly ash replacement of cement provides greater hydration and less permeability. Fly ash replacement causes significant pore refinement, reduced permeability to water and chloride ions, and increased electrical resistivity. The corrosion resistance is due to a reduction in the pore sizes improving the physical structure of the cement matrix. The pozzolanic action between fly ash and the calcium hydroxide ($Ca(OH)_2$) liberated during hydration of concrete densifies the paste structure. $Ca(OH)_2$ is transformed by the silica to C-

S-H, filling the voids, and the aluminate hydrates bind chloride, forming chloroaluminates. The tighter pore structure overshadows the potentially negative effect of the decrease in pH of the pore solution from adding the fly ash, because fly ash can bind the free chlorides, thereby inhibiting corrosion. (Kouloumbi & Batis, 1992; Hussain & Rusheeduzzafar, 1994.)

**Experimental Results:**

A total of seventeen papers and reports were found that included fly ash as a corrosion inhibitor. The tests were typically performed on small reinforced concrete slabs and beams with two layers of reinforcing steel, and on concrete cylinders with embedded reinforcing steel. The concrete specimens, some with admixed chlorides, were typically subjected to continuous or cyclic ponding with sodium chloride, or to partial immersion in sodium chloride. A number of non-destructive and destructive electrochemical and physical tests, as well as visual surveys, were typically performed on the specimens over time to characterize their behavior. The fly ash testing programs were performed on concretes with water-to-cement (w/c) ratios ranging from 0.28 to 1.10; the fly ash dosages ranged from 11% to 71% addition by weight of cement, 10% to 71% cement replacement, or 10% to 30% sand replacement. There were also a few tests of mortars containing fly ash. Studies of fly ash used as a corrosion inhibitor in conjunction with chemical or other mineral admixtures will be summarized in a later section.

The tests reported in the literature indicated that fly ash, used as an admixture or as a cement or sand replacement, was able to increase a concrete's resistance to chloride-induced corrosion. This was typically achieved because fly ash concrete was less permeable than conventional concrete to the ingress of chlorides (due to a more refined pore structure), and also because fly ash was able to bind much of the chloride present in concrete, thereby reducing the total amount of free chloride available to initiate reinforcing steel corrosion without reducing the concrete pH below 12.5. (Al-Amoudi et al., 1989; Kouloumbi & Batis, 1992; Al-Saadoun et al., 1993; Hussain & Rasheeduzzafar, 1994.)

Fly ash concrete permeability was typically measured either directly by determining diffusion coefficients based on chloride concentrations versus depth over time from long-term ponding or immersion tests, or indirectly by using a rapid permeability test that determined the electrical charge passing through a specimen in a specified short period of time (Berke et al., 1991). Additions of Class C or Class F fly ash were always able to

substantially reduce the chloride permeability of concrete, even at relatively high w/c (up to 0.60). The reduction in permeability continued with increases in fly ash dosage up to 60% cement replacement, beyond which permeability increased; however, there was little difference between fly ash effectiveness at 40% and 60% dosages. (Al-Amoudi et al., 1989; Gautefall & Havdahl, 1989; Ellis et al., 1991; Philipose et al., 1991; Kouloumbi & Batis, 1992; Zhang et al., 1992; McGrath & Hooton, 1997; Naik et al., 1997.) Diffusion coefficients typically dropped by five to ten times for fly ash cement replacement in the 20% to 40% range (Al-Saadoun et al., 1993; Hussain & Rasheeduzzafar, 1994; Schiessl & Wiens, 1997).

The primary source of the reduction in permeability in fly ash concrete was the refined pore structure that resulted in a significant reduction in median pore size even though the total porosity was often not significantly affected. These improvements in pore structure were typically not immediate, but rather they occurred over time with the pozzolanic reaction; adequate curing was essential in the development of the refined pore structure. (Al-Amoudi et al., 1989; Kouloumbi & Batis, 1992; Al-Saadoun et al., 1993; Hussain & Rasheeduzzafar, 1994.) Lignite fly ash provided greater reductions in permeability than bituminous and sub-bituminous fly ashes (Al-Saadoun et al., 1993; Hussain & Rasheeduzzafar, 1994).

As noted above, fly ash concrete typically had somewhat lower permeability than the control concrete, and as a result, chloride concentrations measured in fly ash concrete were typically lower than in the controls. Also, there were fewer free chlorides available in the pores of the fly ash to possibly initiate reinforcing steel corrosion, due to the ability of fly ash to bind chlorides. (Kouloumbi & Batis, 1992; Zhang et al., 1992; Al-Saudoun et al., 1993; Hussain & Rasheeduzzafar, 1994; Kouloumbi et al., 1994; Naik et al., 1997.) However, the concentration of free chloride ions in pore solution alone was not a sufficient indicator for chloride-induced corrosion (Kayyali & Haque, 1995). That study also showed that the use of superplasticizers in fly ash concrete could lead to a release of free chloride into the pore solution, thereby increasing the likelihood of reinforcing steel corrosion.

In studies where corrosion measurements were made, fly ash concrete typically outperformed control concretes. Fly ash concrete resistivity was more than two times greater than that in the controls, and it had longer times to corrosion initiation and lower corrosion

rates than the controls as well (Figures 2.6 and 2.7). (Maslehuddin et al., 1989; Berke et al., 1991; Al-Saadoun et al., 1993; Al-Amoudi et al., 1994; Hussain & Rasheeduzzafar, 1994; Schiessl & Wiens, 1997.) In long-term tests of reinforced concrete cylinders immersed in sodium chloride solution, time to initiation of corrosion of steel in 20% cement replacement fly ash concrete was 50% longer than in the control (Al-Amoudi et al., 1989). Also, in long-term tests of reinforced concrete beams, prisms, and cylinders immersed in sodium chloride solution, corrosion rates of reinforcing steel in 20% cement or sand replacement fly ash concrete were up to ten times less than those in plain concrete (Al-Amoudi et al., 1989; Maslehuddin et al., 1989). Even greater reductions in corrosion rates (up to 19 times less than the control) were obtained when 30% sand replacement fly ash concrete was used (Figure 2.7) (Maslehuddin et al., 1989).

Although fly ash dosages as low as 10% were found to be beneficial in reducing corrosion activity (Lee & Lee, 1997), one study indicated that for concrete with moderately high w/c values, fly ash dosages of less than 15% were not effective in preventing corrosion (Berke et al., 1991).

The improved physical structure of fly ash concrete has also typically led to increased compressive strengths over time, although early compressive strengths were sometimes less than those in the control concrete (Maslehuddin et al., 1989; Ellis et al., 1991; Zhang et al. 1992; Lee & Lee, 1997). It has been reported that concrete with fly ash dosages greater than 25% addition by weight of cement could be susceptible to carbonation (reduction in pH) at crack locations (Berke et al., 1991).

Overall, the most commonly recommended dosage of fly ash to both extend the time to corrosion initiation and reduce corrosion rates of reinforcing steel is 30% cement replacement (Al-Saadoun et al., 1993; Hussain & Rasheeduzzafar, 1994; Kouloumbi et al., 1994).

### 2.3.3. Ground Granulated Blast Furnace Slag

**Product Description:**

Ground granulated blast furnace slag is made from iron blast-furnace slag. Slag is a nonmetallic product containing silicates and aluminosilicates of calcium and other bases produced in a molten state from iron ore in a blast furnace. The molten slag is rapidly water-

cooled from 2730°F, to form a glassy, sand-like material. This material is then ground to less than 45 μm; the resulting product has a rough, angular surface. (Kosmatka & Panarese, 1988.)

**Mechanism of Protection:**

The addition of slag refines and reduces the pore structure of concrete, therefore reducing the permeability. Like fly ash and cements with high $C_3A$ contents, slag also has the ability to bind chloride ions. Finally, slag also provides increased corrosion resistance due to a passivation of the steel. (Deja et al., 1991.)

**Experimental Results:**

A total of twelve papers and reports were found that included granulated blast furnace slag as a corrosion inhibitor. The tests were typically performed on small reinforced concrete slabs and beams with two layers of reinforcing steel, and on concrete cylinders with embedded reinforcing steel. The concrete specimens were typically subjected to continuous or cyclic ponding with sodium chloride, or to partial immersion in sodium chloride. A number of non-destructive and destructive electrochemical and physical tests, as well as visual surveys, were typically performed on the specimens over time to characterize their behavior. The granulated blast furnace slag testing programs were performed on concretes with water-to-cement (w/c) ratios ranging from 0.30 to 0.89, and the granulated blast furnace slag dosages ranged from 40% to 50% addition by weight of cement, or 20% to 100% cement replacement. There were also a few tests of mortars containing granulated blast furnace slag. Studies of granulated blast furnace slag used as a corrosion inhibitor in conjunction with other mineral admixtures will be summarized in a later section.

In general, it was found that greater durability should be expected in concrete with slag as an admixture. Slag improved the long-term corrosion resistance of concrete by lowering the corrosion rates due to decreased permeability. (Kouloumbi et al., 1994; Montani, 1996.) Permeability tests indicated that as the slag content increased, the chloride permeability decreased (Figure 2.8). The permeability of slag concrete was less affected by increases in w/c than ordinary Portland cement concrete. (Rose, 1987.)

The addition of slag decreased the rate of ingress of chloride ions, which is a diffusion controlled process; a decrease in w/c improved the resistance further (Philipose et al., 1991; Schiessl & Wiens, 1997). Slag also significantly reduced oxygen diffusion when

compared to conventional concrete (Gjorv, 1995). In tests on concrete beams and cylinders immersed in chloride solution, chloride ion concentration below the ½ in. depth was greatly reduced as the percentage of slag was increased (Figure 2.8). The chloride ion concentration at the 1½ in. depth increased in all concrete mixes with an increased time of exposure, but the ordinary Portland cement concretes had a greater rate of increase than the slag concretes. (Rose, 1987.) After 28 days curing, steam-cured slag concretes had very low chloride concentrations, and those moist-cured had low chloride concentrations (Rose, 1987; Ozyildirim, 1993). In a long-term chloride ponding test of slabs and cylinders, the chloride content of slag concrete at 1¾ in. was below the threshold level, for pavements and decks, of 1.3 lb/yd$^3$; the chloride content was also lower than (or at) the threshold at the 1 in. depth (Ozyildirim, 1993).

Corrosion potential also decreased as the slag content increased. No corrosion was found in the 40% cement replacement slag concrete, and the chloride level of the control was about 8 times greater than that of the 40% cement replacement slag concrete at all depths. (Rose, 1987.) Corrosion currents immediately after curing were found to be independent of the amount of slag (from 20% to 75% cement replacement) and were up to 10 times the current for pure Portland cement mortar. This difference disappeared with time. Therefore, laboratory tests performed on different ages of specimens could give contradictory results. (Valantini et al., 1990.)

Carbonation (reduction in pH due to carbon dioxide exposure) progressed faster in slag specimens. With a slag dosage of 70% cement replacement, carbonation of concrete beams, exposed outdoors in an ultra hot climate, progressed beyond the depth of steel at 120 months. In this case, steel reinforcement in contaminated slag concrete experienced greater corrosion loss than concrete made with normal Portland cement, in either carbonated or uncarbonated concrete, regardless of curing, cover to reinforcement, or w/c. (Olsen & Summers, 1997.)

Slag contents had to be limited to about 35% cement replacement if early strength development similar to the control was needed (Montani, 1996). The typical optimum dosage is 40% cement replacement with slag.

## 2.4. COMBINATIONS AND DIRECT COMPARISONS

### 2.4.1. Combinations of Chemical and/or Mineral Admixtures

A total of twelve papers and reports were found that included various double combinations of calcium nitrite, amines and esters, silica fume, fly ash, and/or granulated blast furnace slag as corrosion inhibitors. The tests were typically performed on small reinforced concrete slabs and beams with two layers of reinforcing steel, and on concrete cylinders with embedded reinforcing steel. The concrete specimens were typically subjected to continuous or cyclic ponding with sodium chloride, or to partial immersion in sodium chloride. A number of non-destructive and destructive electrochemical and physical tests, as well as visual surveys, were typically performed on the specimens over time to characterize their behavior. There were also a few tests of mortars. The testing programs were as follows:

- The concretes containing both calcium nitrite and silica fume had water-to-cement ratios ranging from 0.38 to 0.48; the calcium nitrite dosages ranged from 2 gallons to 4 gallons of 30% calcium nitrite solution per cubic yard of concrete, and the silica fume dosages ranged from 4% to 15% addition by weight of cement, or 6.5% to 15% cement replacement.

- The concretes containing both calcium nitrite and fly ash had water-to-cement ratios ranging from 0.45 to 0.60; the calcium nitrite dosages were 3% addition by weight of cement, and the fly ash dosages ranged from 20% to 30% cement replacement, or 10% sand replacement.

- The concretes containing both silica fume and fly ash had water-to-cement ratios ranging from 0.29 to 1.30; the silica fume dosages ranged from 2% to 15% addition by weight of cement, or 5% to 8% cement replacement, and the fly ash dosages ranged from 10% to 35% addition by weight of cement, or 30% to 40% cement replacement.

- The concretes containing both silica fume and granulated blast furnace slag had water-to-cement ratios ranging from 0.30 to 0.45; the silica fume dosages ranged from 3% to 5% addition by weight of cement, or 8% cement replacement, and the granulated blast furnace slag dosages ranged from 45% to 47% addition by weight of cement, or 25% to 40% cement replacement.

- The concrete containing both fly ash and granulated blast furnace slag had a water-to-cement ratio of 0.50; the fly ash dosage was 20% cement replacement, and the granulated blast furnace slag dosage was 46% cement replacement.

There were not any tests on individual concrete mixes containing three or more chemical and/or mineral corrosion inhibiting admixtures. Finally, a few studies reported on field experience with concrete containing Rheocrete and fly ash or silica fume and fly ash.

Calcium nitrite was found to be compatible with concrete containing silica fume to provide reduced permeability, and the calcium nitrite was able to provide additional protection and durability in the presence of chlorides if and when they did ingress (Figure 2.9) (Berke & Rosenberg, 1989; Berke & Hicks, 1992; Berke & Weil, 1992; McDonald, 1995). Overall, calcium nitrite and silica fume together improved the durability of concrete in corrosive environments, and they can be used to maximize long-term corrosion protection, minimize life cycle costs, and maximize structural life, while enhancing compressive strength at the same time. (Berke et al., 1988; Berke, 1989; Berke & Hicks, 1992.) Diffusion results from concrete beams and cylinders with w/c of 0.48 subjected to sodium chloride exposure indicated that silica fume reduced chloride ingress, and calcium nitrite further enhanced the reduction of chloride ingress (Berke, 1989). Silica fume significantly increased concrete resistivity, while calcium nitrite slightly reduced resistivity. The addition of 2 gal/yd$^3$ of calcium nitrite, to 10% addition by weight of cement silica fume concrete, would provide a reservoir of calcium nitrite that would remain at the steel providing added passivation protection against a high chloride content, estimated to be the equivalent protection of 5-1/2 gal/yd$^3$ of calcium nitrite. (Berke et al., 1988.) Optimum combined dosages are calcium nitrite at 2 gal/yd$^3$ to 4 gal/yd$^3$ and silica fume at 7.5% to 10% cement replacement. (Berke et al., 1988; Berke, 1989; Berke & Hicks, 1992).

Calcium nitrite was also able to improve the corrosion resistance of concrete with fly ash (Figure 2.10) (Berke & Rosenberg, 1989).

Silica fume further reduced the permeability (as measured by chloride diffusion coefficient) in concrete when used in combination with fly ash (Ellis et al., 1991; Gjorv, 1995; McGrath & Hooton, 1997). When used in combination, the silica fume was more efficient than the fly ash in reducing the ingress of chlorides (Figure 2.11), though a low fly ash dosage was used (Gautefall & Havdahl, 1989; Berke et al. 1991). The silica fume also contributed most to increasing concrete resistivity when in combination with fly ash (Berke et al., 1991; Gjorv, 1995). Addition of fly ash to silica fume concrete was also found to improve concrete compressive strength (Ellis et al., 1991). Overall, concrete with

combinations of fly ash and silica fume offered increased long-term corrosion protection in concrete, particularly for low w/c concrete. Mixes with 15%/15%, 7.5%/30%, 6.25%/12.5%, and 12.5%/25% combinations of silica fume/fly ash additions by weight of cement were effective in reducing corrosion rates. (Figure 2.12) (Berke et al., 1991.)

Silica fume also further reduced the permeability (as measured by chloride diffusion coefficient) in concrete when used in combination with granulated blast furnace slag (McGrath & Hooton, 1997). Concrete with combinations of slag and silica fume had higher strengths and lower permeability than those containing fly ash and silica fume (Ozyildirim, 1993). A slag and silica fume system would have an expected service life of ten times that of an ordinary Portland cement system. (Philipose et al., 1991).

When slag and fly ash were combined there was a reduction of the concrete diffusion coefficients (Schiessl & Wiens, 1997).

In a two-year field exposure program using concrete (low w/c of 0.34) with Rheocrete (1 gallon of amines and esters solution per cubic yard of concrete) and fly ash (22% addition by weight of cement), half-cell potentials were high near ground level and decreased towards the top of marine piles. The readings did not indicate corrosion, which was confirmed by exposing a section of spiral steel, by coring, that was found not to be corroding. Chloride ion content data indicated that the pile caps (without Rheocrete) had higher chloride levels at 1½ in. to 3 in. depths compared to the pile samples, even though the pile caps had less exposure to saltwater splash. (Krauss & Nmai, 1996.)

### 2.4.2. Direct Comparisons of Chemical and/or Mineral Admixtures

A total of eleven papers and reports were found that included direct comparisons of two or more of calcium nitrite, amines and esters, silica fume, fly ash, and/or granulated blast furnace slag (each used individually) as corrosion inhibitors in structural concrete. The tests were typically performed on small reinforced concrete slabs and beams (both cracked and non-cracked) with two layers of reinforcing steel, and on concrete cylinders with embedded reinforcing steel. The concrete specimens were typically subjected to continuous or cyclic ponding with sodium chloride, or to partial immersion in sodium chloride. A number of non-destructive and destructive electrochemical and physical tests, as well as visual surveys, were

typically performed on the specimens over time to characterize their behavior. Testing programs were as follows:

- Calcium nitrite concretes had water-to-cement ratios ranging from 0.32 to 0.50, and the dosages ranged from 2 gallons to 6 gallons of 30% calcium nitrite solution per cubic yard of concrete.
- Amines and esters concretes had water-to-cement ratios ranging from 0.40 to 0.50, and the dosage was 1 gallon of solution per cubic yard of concrete.
- Silica fume concretes had water-to-cement ratios ranging from 0.30 to 0.90, and the dosages were 2% to 15% addition by weight of cement, or 5% to 15% cement replacement.
- Fly ash concretes had water-to-cement ratios ranging from 0.22 to 0.50, and the dosages were 23% to 71% addition by weight of cement, or 10% to 71% cement replacement.
- Granulated blast furnace slag concretes had water-to-cement ratios ranging from 0.30 to 0.50, and the dosages were 24% to 60% cement replacement.

In five reports, direct comparisons were made of the performance of amines and esters and calcium nitrite, in cracked and non-cracked beams. Calcium nitrite concrete, even at a high admixture dosage and a relatively low water-to-cement (w/c) ratio, still had chloride concentrations comparable to untreated concrete, while the chloride concentrations in the amines and esters concrete were typically much lower (Figure 2.13). (Nmai & Krauss, 1994; Nmai, 1999) For example, chloride ion concentrations, at the top of rebar (1½ in. depth) on either side of a crack, were measured to be 12.0 lb/yd$^3$ for untreated concrete, 13.0 and 14.7 lb/yd$^3$ for concrete treated with calcium nitrite at 2 and 4 gal/yd$^3$, and 5.0 lb/yd$^3$ for amine and ester treated concrete (Nmai et al., 1992). However, in non-cracked concrete with a low w/c of 0.40, calcium nitrite had lower corrosion current and longer time to corrosion than amines and esters; both were lower than a control (Berke et al., 1993). In non-cracked concrete with a high w/c of 0.50, amines and esters had lower or comparable corrosion current and a longer time to corrosion than concrete with calcium nitrite at a high dosage; both concretes outperformed the control (Figure 2.14).

In cracked concrete with a w/c of 0.50 the amines and esters had a lower corrosion current than calcium nitrite. Calcium nitrite (at high dosages) and amines and esters

performed better than the control concrete. (Nmai & Krauss, 1994.) Specifically, in the cracked specimens, corrosion was initiated in untreated concrete at 6 days, at 17 and 39 days for concrete treated with 2 and 4 gal/yd$^3$ of calcium nitrite, and at 118 days for concrete treated with 1 gal/yd$^3$ of amines and esters (Nmai et al., 1992). In another study of non-cracked concrete specimens with a w/c of 0.45, calcium nitrite at 4 gal/yd$^3$ entered active corrosion at about 65 weeks, as opposed to 40 weeks for the control, and 33 weeks for Rheocrete at 1 gal/yd$^3$ and Armatec at 0.5 gal/yd$^3$ (Pyc et al., 1999).

It was reported by some researchers that the overall performance of the amines and esters inhibitor concrete at a 1 gal/yd$^3$ admixture dosage was comparable to or better than the calcium nitrite concrete at a 6 gal/yd$^3$ admixture dosage (Nmai & Krauss, 1994). Others found that amines and esters provided minimal or no protection against corrosion of reinforcing steel or chloride ingress, with calcium nitrite performing the best, and the amines and esters having similar or even higher corrosion rates and corrosion damage than the control (Figure 2.15) (Berke et al., 1993; Pyc et al., 1999).

In a direct comparison of the performance of calcium nitrite and silica fume, concrete treated with 2 gal/yd$^3$ of calcium nitrite would be expected to protect against 6 lb/yd$^3$ of chlorides, and silica fume at 10% addition by weight of cement would also be expected to protect against 6 lb/yd$^3$ of chlorides (Berke et al., 1988).

In one direct comparison of the performance of concretes with fly ash at low dosage (10% cement replacement) and silica fume at moderate dosage (5% to 15% cement replacement), the chloride permeability of the silica fume concrete was lower than the fly ash concrete, and both outperformed ordinary Portland cement concrete (Gautefall & Havdahl, 1989). In another study, chloride permeability of fly ash concrete at moderate to high dosages (40% to 60% cement replacement) was comparable to that of silica fume concrete at moderate dosages (5% to 15% cement replacement) (Naik et al., 1997). In still another study, Class F fly ash concrete at high dosages (47% and 71% addition by weight of cement) had lower permeability, and higher strength, than silica fume concrete at a moderate dosage (10% addition by weight of cement). These Class F fly ash concretes at high dosages also had lower chloride permeabilities than Class C fly ash concretes and slag concrete at a moderate dosage (50% addition by weight of cement). (Ellis et al., 1991.)

In one chloride analysis testing program, on cores from concrete and mortar slabs ponded with sodium chloride solution, the following diffusion ranking was determined: diffusion of the control was greater than slag concrete, which was equal to fly ash concrete, which was greater than silica fume concrete, which was greater than slag/silica fume concrete, which was equal to fly ash/silica fume concrete. This research ranking differed from that reported elsewhere, which found that fly ash and slag concretes (with moderate to high dosages) have similar or lower diffusion values than silica fume concrete in long duration tests. (McGrath and Hooton, 1997.)

Fly ash concrete at moderate to high dosages (40% and 60% cement replacement) had electrolytic resistance greater than slag concrete at moderate to high dosages (46% and 74% cement replacement); fly ash at a low dosage (20% cement replacement) performed the same as the slag concrete (Schiessl & Wiens, 1997). Silica fume concrete at a moderate dosage (10% cement replacement) had lower corrosion potentials than fly ash concrete at a low dosage (20% cement replacement) and slag concrete at a high dosage (60% cement replacement); the fly ash concrete performed better than the slag concrete, and all three concretes performed better than ordinary Portland cement concrete (Figure 2.16) (Al-Amoudi et al., 1994). From the above comparisons, it appears that silica fume can provide the best overall corrosion protection at moderate dosages, in comparison with fly ash and slag.

## 2.5. OPTIMUM DOSAGES OF INHIBITORS PER THE LITERATURE REVIEW

Following is a summary of the optimum dosages of chemical and mineral durability enhancing admixtures, as determined from the literature review. Note that some combinations do not indicate a range, but a specific value. This is an indication of limited testing of dosages rather than an optimized dosage recommendation.

1. Calcium nitrite: 3 gal/yd$^3$ to 5 gal/yd$^3$, with a w/c ratio less than 0.50.
2. Amines and esters:
   - Rheocrete 222: 1 gal/yd$^3$, with a w/c of 0.50.
   - Armatec 2000: 0.5 gal/yd$^3$, with a w/c of 0.50.
3. Silica fume: 10% to 15% cement replacement, with a w/c less than 0.50.
4. Fly ash: 25% to 30% cement replacement, with a w/c less than 0.50.
5. Slag: 40% to 50% cement replacement, with a w/c less than 0.50.

6. Calcium nitrite and silica fume: 2 gal/yd$^3$ to 4 gal/yd$^3$ and 7.5% to 10% cement replacement, with a w/c less than 0.50.
7. Calcium nitrite and fly ash: 2 gal/yd$^3$ to 4 gal/yd$^3$ and 20% to 30% cement replacement, with a w/c less than 0.50.
8. Silica fume and fly ash: 7.5% to 15% cement replacement and 15% to 30% cement replacement with a w/c less than 0.50.
9. Silica fume and slag: 5% to 7.5% cement replacement and 25% to 45% cement replacement, with a w/c less than 0.50.
10. Fly ash and slag: 20% cement replacement and 45% cement replacement, with a w/c less than 0.50.
11. Rheocrete 222 and fly ash: 1 gal/yd$^3$ and 20% addition by weight of cement, with a w/c less than 0.50.
12. DSS: 1/2% to 1% addition by weight of cement.

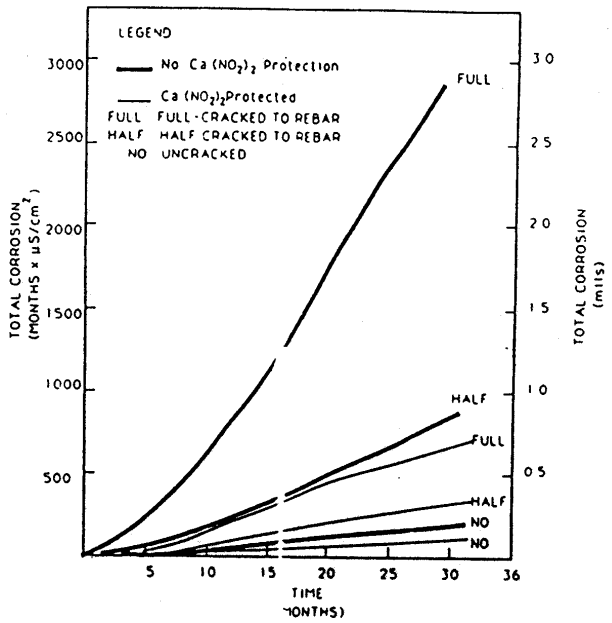


**Figure 2.1: Total Corrosion Vs. Time for Concrete with Calcium Nitrite (Berke & Weil, 1992)** *Reprinted, with permission*

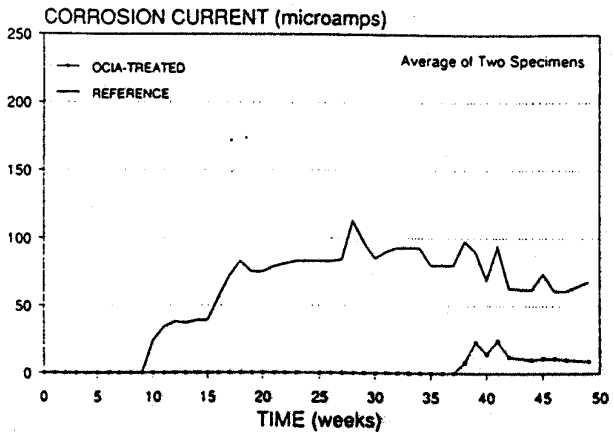


**Figure 2.2: Macrocell Corrosion Current Vs. Time using OCIA (non-cracked, w/c = 0.40, 1 gal/yd$^3$) (Nmai et al., 1992)**

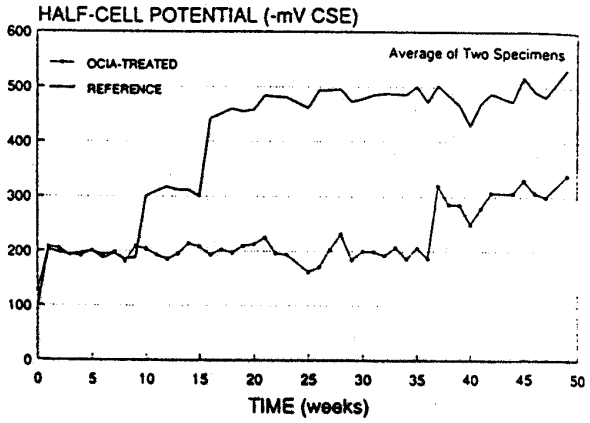


**Figure 2.3: Half-Cell Potential Vs. Time using OCIA (non-cracked, w/c = 0.40, 1 gal/yd$^3$) (Nmai et al., 1992)**

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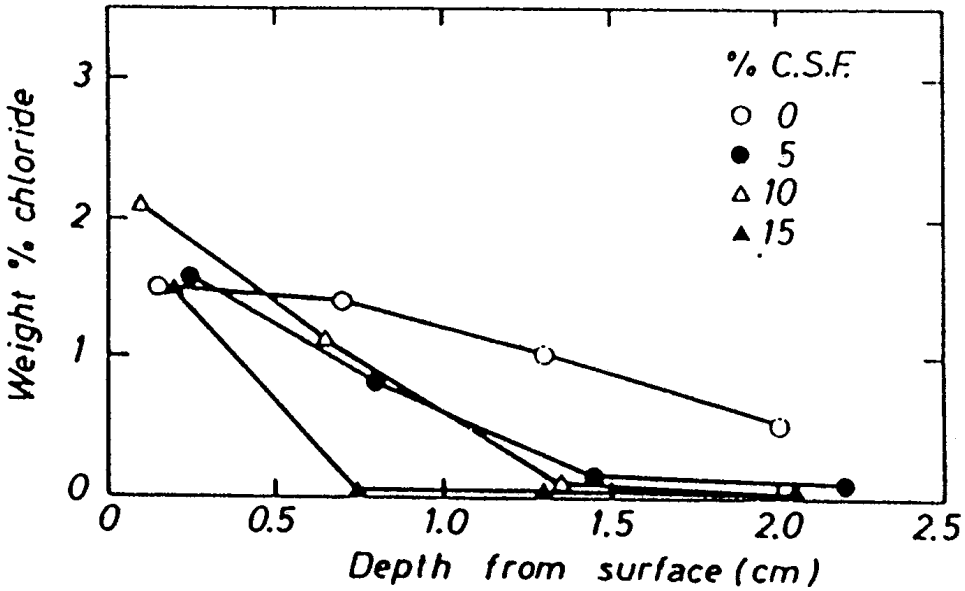


**Figure 2.4: Chloride Concentration Vs. Depth using Silica Fume Cement Replacement (w/c = 0.50) (Gautefall & Havdahl, 1989)**

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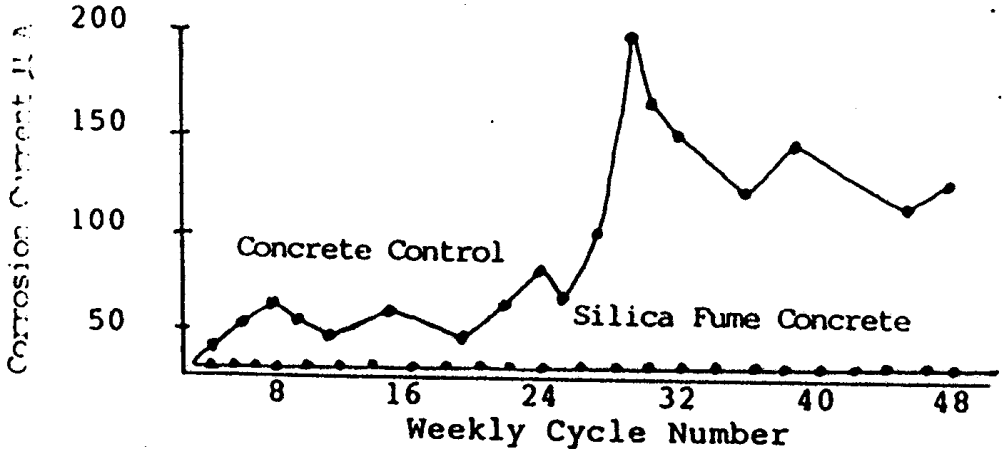


**Figure 2.5: Macrocell Corrosion Vs. Time using Silica Fume at 20% Addition by Weight of Cement (Wolsiefer, 1993)**

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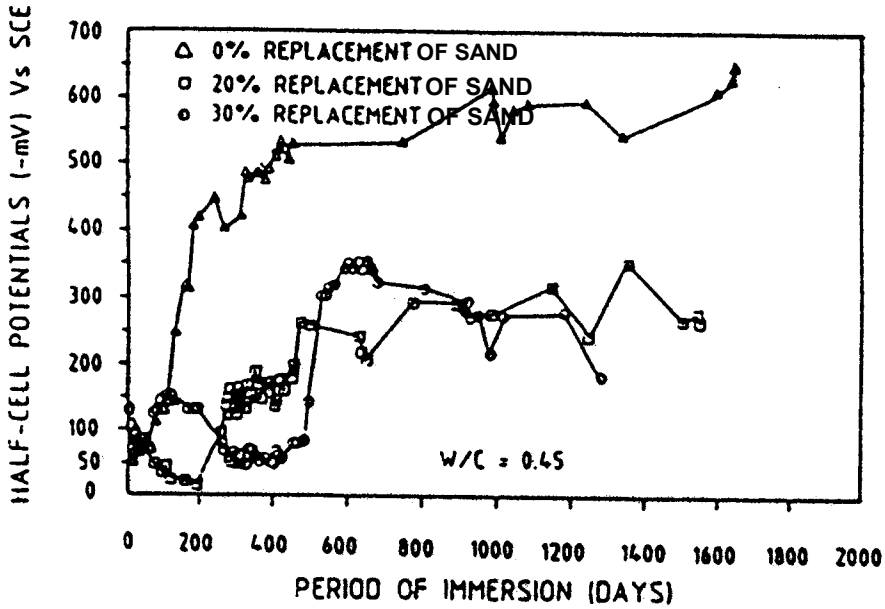


**Figure 2.6: Half-Cell Potentials Vs. Time using Fly Ash Concrete (Maslehuddin et al., 1989)**

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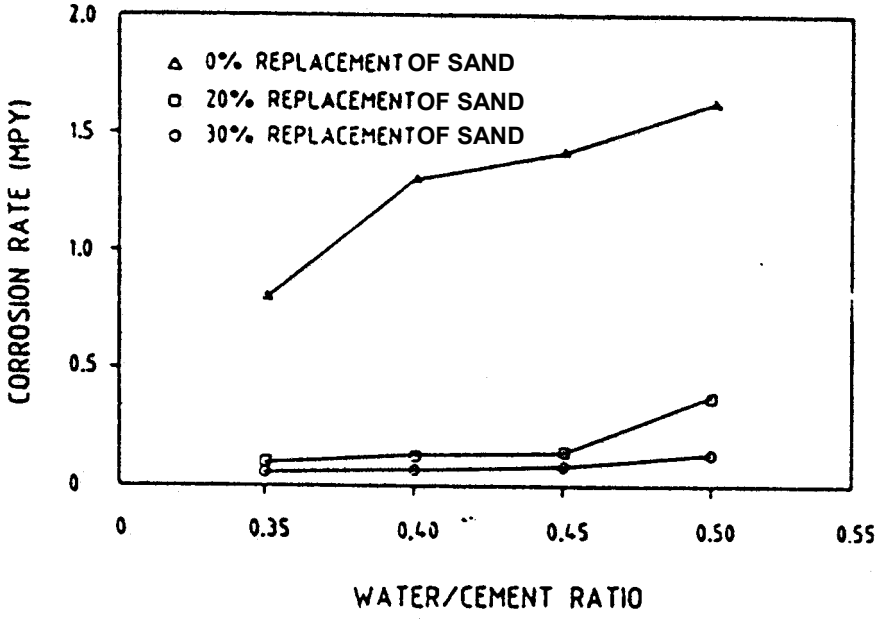


**Figure 2.7: Corrosion Rates Vs. w/c for Fly Ash Concrete (Maslehuddin et al., 1989)**

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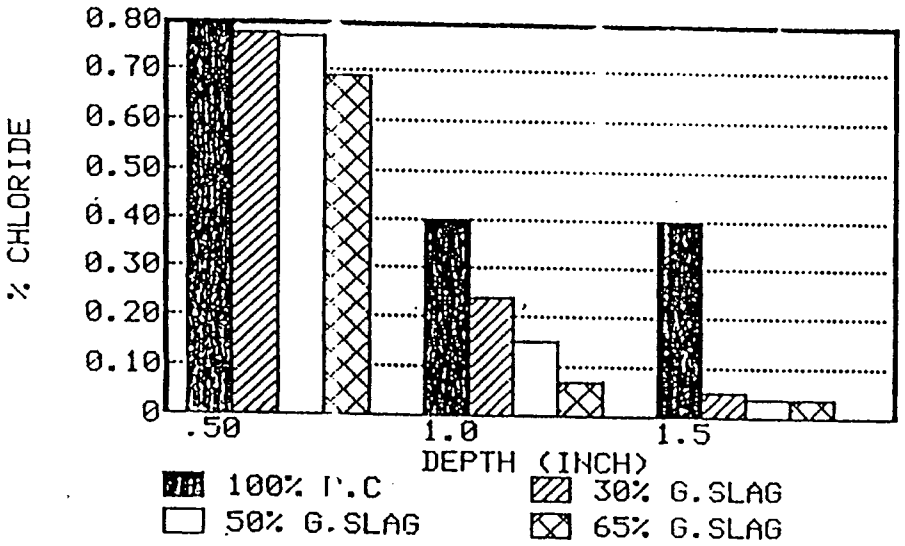


**Figure 2.8: Chloride Content Vs. Depth Below Surface of Slag Concrete at 365 Days (w/c = 0.50) (Rose, 1987)**

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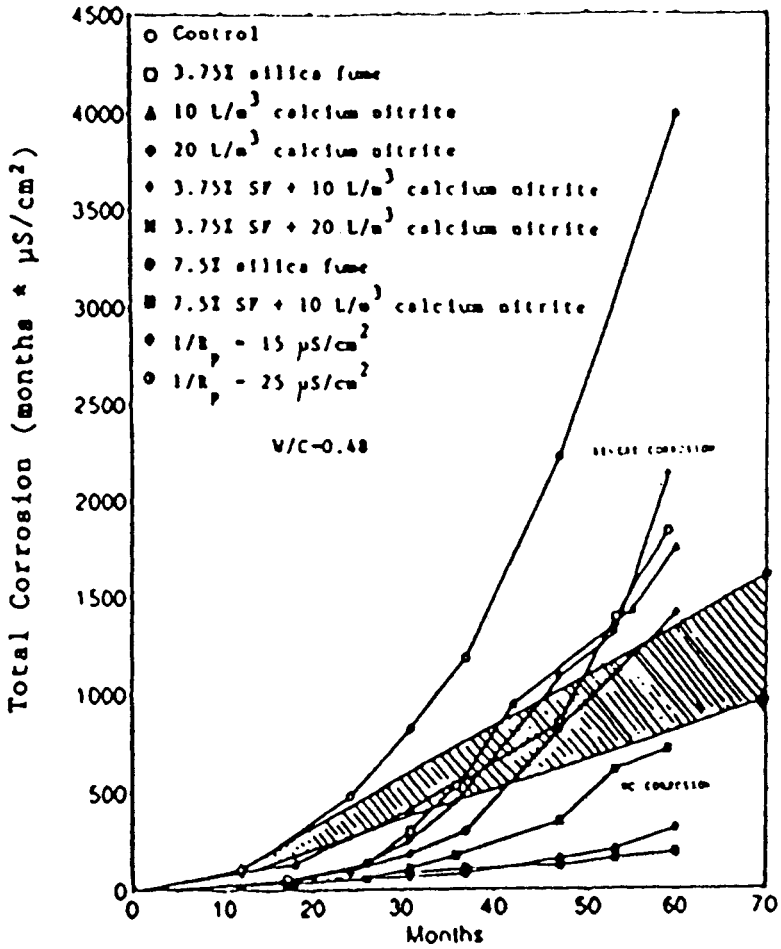


**Figure 2.9: Total Corrosion as a Function of Calcium Nitrite and Silica Fume Content (Berke and Weil, 1992)** *Reprinted, with permission*

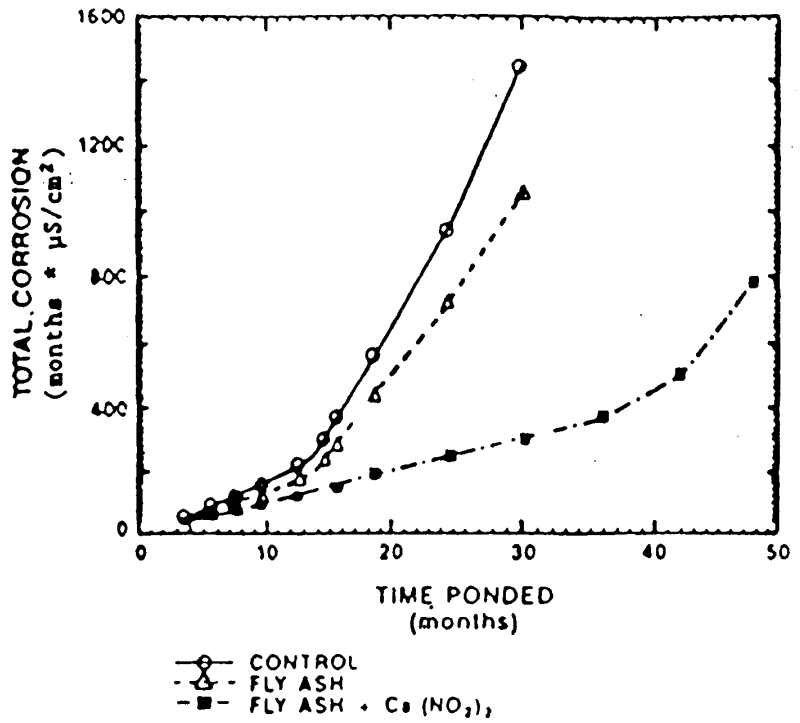


**Figure 2.10: Corrosion Rate as a Function of Calcium Nitrite and Fly Ash (Berke and Weil, 1992)** *Reprinted, with permission*

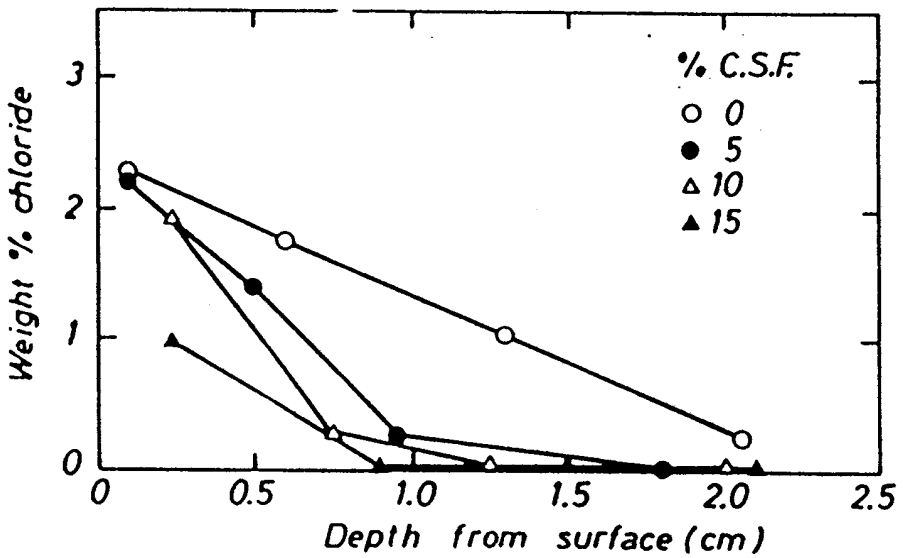


**Figure 2.11: Chloride Profile of Silica Fume with 10% Fly Ash Blended Cement (w/c = 0.50) (Gautefall & Havdahl, 1989)**

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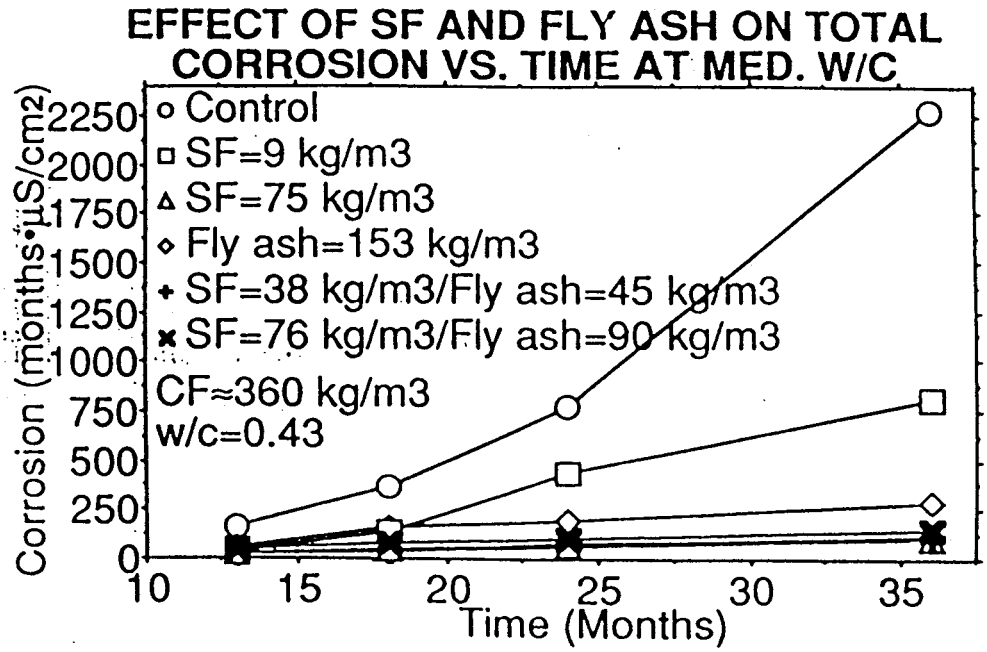


**Figure 2.12: Total Corrosion Vs. Time as a Function of Pozzolans (Berke et al., 1991)**

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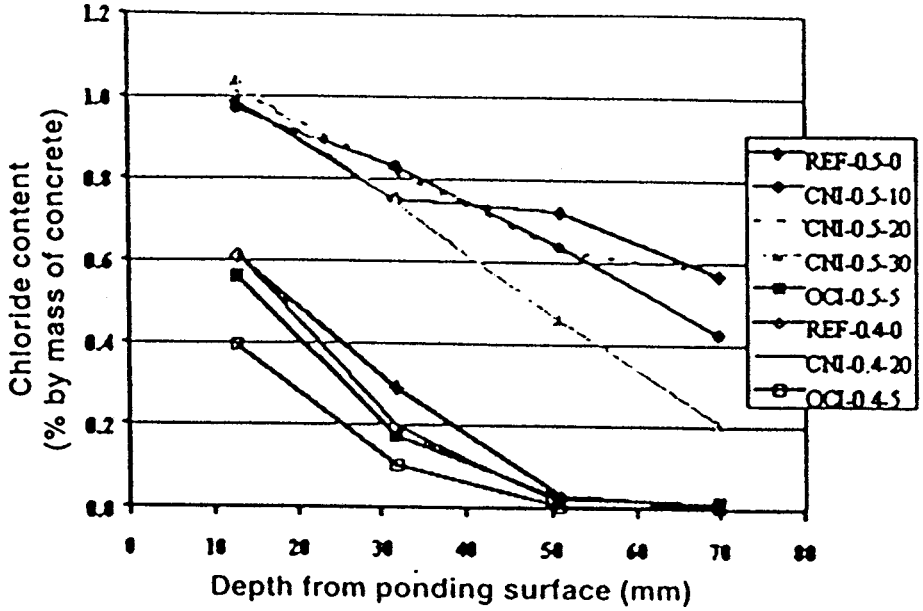


**Figure 2.13: Chloride Profile with Calcium Nitrite and OCIA at 1000 Days (Nmai, 1999)** *Reprinted, with permission, copyright ACI International*

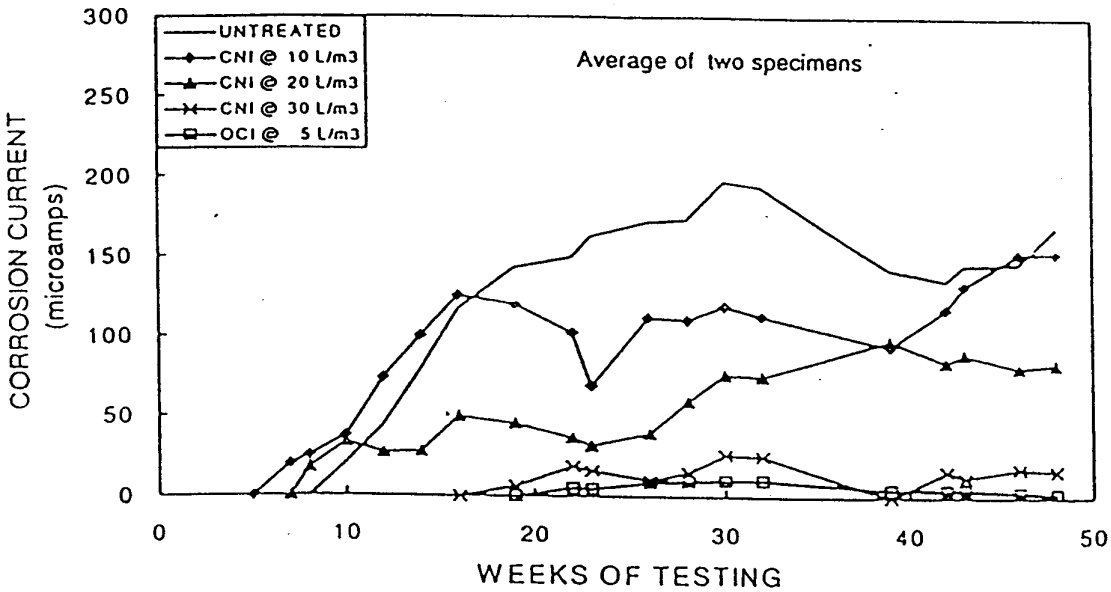


**Figure 2.14: Macrocell Corrosion Current (Non-Cracked) with Calcium Nitrite and OCIA (w/c = 0.50) (Nmai and Krauss, 1994)**

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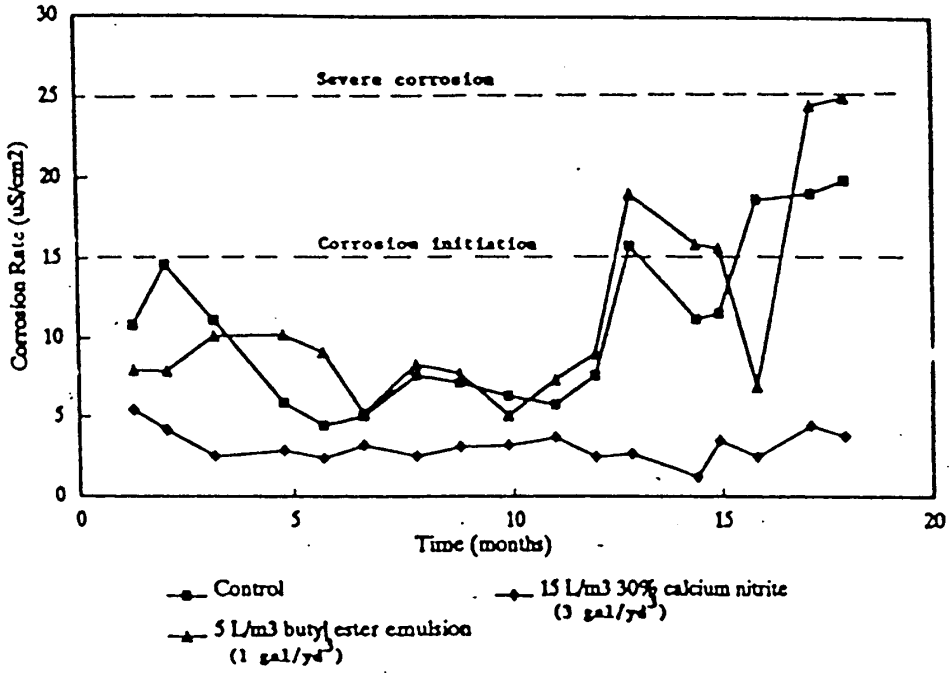


**Figure 2.15: Corrosion Rates for Calcium Nitrite and Butyl Ester (w/c = 0.40) (Berke et al., 1993)** *Reprinted, with permission, copyright NACE International*

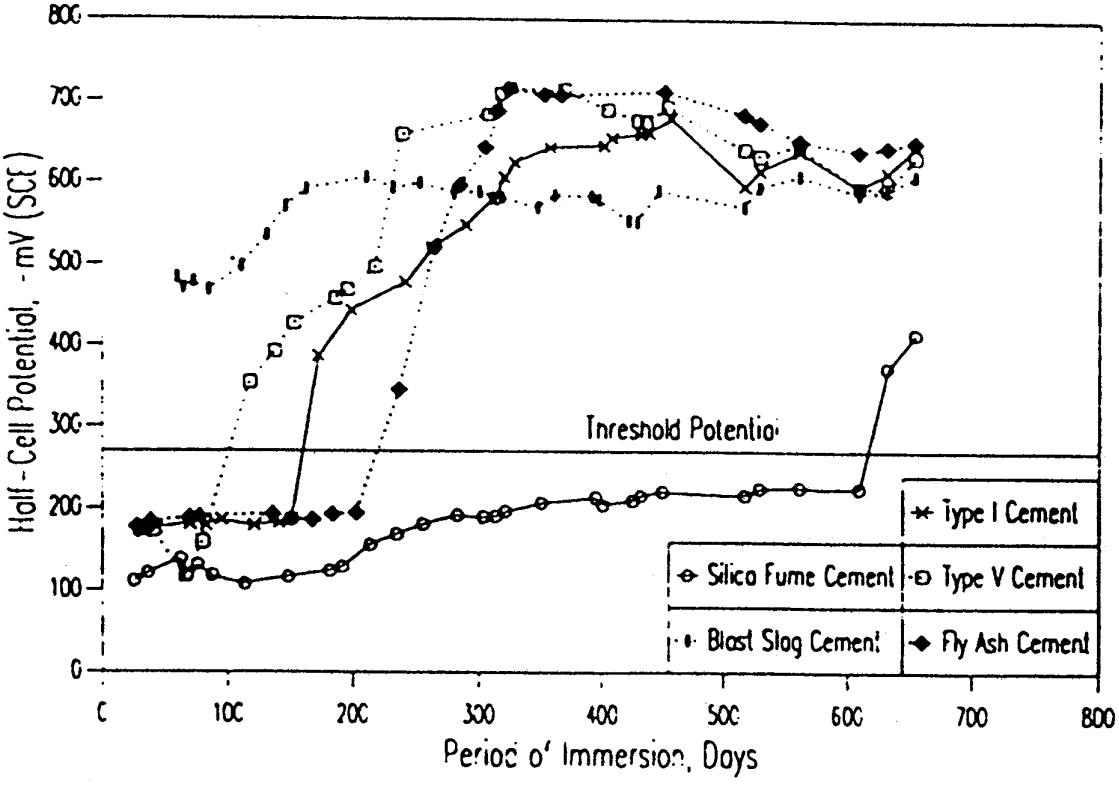


**Figure 2.16: Half-Cell Potentials for Silica Fume (10% Cement Replacement), Fly Ash (20% Cement Replacement) and Slag (60% Cement Replacement) Concrete (w/c = 0.50) (Al-Amoudi et al., 1994)**

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## 3. SURVEY OF NEW ENGLAND STATES CORROSION INHIBITOR USE

A survey was conducted of the New England state DOTs in 1999, to determine their use of chemical corrosion inhibitors and mineral durability enhancing admixtures in structural concrete. Table 3.1 below shows which of these corrosion-inhibiting admixtures have been used; Table 3.2 indicates the typical applications when chemical corrosion inhibitor admixtures have been used. Most New England states have typically almost always used epoxy coated reinforcing steel in conjunction with the use of corrosion inhibitors. All of the states, except Vermont, have used calcium nitrite (DCI) as an inhibitor. Connecticut and Rhode Island have also recently used amines and esters (Rheocrete) as an inhibitor. All of the states have also used mixes containing silica fume, mixes containing fly ash, and mixes containing granulated blast furnace slag. Only a few states have used combinations of chemical and mineral admixtures, or multiple mineral admixtures, as indicated in Table 3.1.

The New England DOTs have used the following water-to-cement ratios and admixture dosages in structural concrete mixes. Water-to-cement ratios (low w/c are for precast concrete) and dosages are typically in the optimum ranges reported from the literature review. The reduction of mix water as calcium nitrite solution is added is not consistent among the states. Some states reduce the mix water on a one to one ratio, while others reduce the mix water by amounts proportional to assumed or actual water content of the solution. For this study the actual water content by weight of the solution was determined, and the mixing water was reduced by that amount. Cementitious materials were typically reported as addition, rather than replacement of cement.

- The calcium nitrite (DCI) concretes had water-to-cement ratios ranging from 0.30 to 0.46; the calcium nitrite dosages ranged from 2 to 4 gallons of 30% calcium nitrite solution per cubic yard of concrete.

- The amines and esters (Rheocrete) concretes had water-to-cement ratios ranging from 0.30 to 0.46; the Rheocrete dosage was 1 gallon per cubic yard of concrete.

- The silica fume concretes had water-to-cement ratios ranging from 0.30 to 0.46; the silica fume dosages ranged from 4% to 8% addition by weight of cement (the low silica fume dosage was from a blended cement).

- The fly ash concretes had water-to-cement ratios ranging from 0.30 to 0.46; the fly ash dosages ranged from 15% to 25% addition by weight of cement.

- The granulated blast furnace slag concretes had water-to-cement ratios ranging from 0.30 to 0.46; the granulated blast furnace slag dosages ranged from 25% to 50% addition by weight of cement.

- The calcium nitrite (DCI) and silica fume concretes had water-to-cement ratios ranging from 0.30 to 0.46; the calcium nitrite dosage was 4 gallons of 30% calcium nitrite solution per cubic yard of concrete, and the silica fume dosage was 8% addition by weight of cement.

- The calcium nitrite (DCI) and fly ash concretes had water-to-cement ratios ranging from 0.30 to 0.46; the calcium nitrite dosages ranged from 2 to 6 gallons of 30% calcium nitrite solution per cubic yard of concrete, and the fly ash dosages ranged from 15% to 33% addition by weight of cement.

- The calcium nitrite (DCI) and granulated blast furnace slag concretes had water-to-cement ratios ranging from 0.30 to 0.46; the calcium nitrite dosages ranged from 2 to 4 gallons of 30% calcium nitrite solution per cubic yard of concrete, and the granulated blast furnace slag dosages ranged from 25% to 100% addition by weight of cement.

- The silica fume and fly ash concretes had water-to-cement ratios ranging from 0.30 to 0.46; the silica fume dosage was 8% addition by weight of cement, and the fly ash dosage was 20% addition by weight of cement.

- A silica fume and granulated blast furnace slag concrete mix has been used in New Hampshire, but water-to-cement ratios and admixture dosages were not provided.

- The fly ash, silica fume, and calcium nitrite concretes had water-to-cement ratios ranging from 0.30 to 0.46; the calcium nitrite dosage was 4 gallons of 30% calcium nitrite solution per cubic yard of concrete, the silica fume dosage was 8% addition by weight of cement, and the fly ash dosage was 25% addition by weight of cement.

**Table 3.1: Chemical and Mineral Corrosion Inhibiting Admixtures Used by New England State DOTs**

| | DCI | Rheo -crete | SF | FA | Slag | DCI/ SF | DCI/ FA | DCI/ Slag | SF/ FA | SF/ Slag | FA/ SF/ DCI | Max w/c |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| CT | X | X | X | X | X | | | | | | | 0.44 |
| ME | X | | X | X | X | | X | | | | | 0.42 |
| MA | X | | X | X | X | | X | X | | | | NA |
| NH | X | | X | X | X | X | X | X | X | X | X | 0.46 |
| RI | X | X | X | X | X | | | | | | | 0.40 |
| VT | | | X | X | X | | | | X | | | 0.40 |

**Table 3.2: Structures Using Chemical Corrosion Inhibiting Admixtures by New England State DOTs**

| | Precast Prestressed Piles | Pier Caps | Precast Prestressed Beams | Abut-ments | Deck | Para-pets | Back Walls | Bridge Sidewalks |
|---|---|---|---|---|---|---|---|---|
| CT | | X | X | X | X | X | | |
| ME | X | X | X | | X | | | |
| MA | X | | X | | X | | | |
| NH | X | X | X | | X | | | |
| RI | X | X | X | X | X | X | X | X |
| VT | | | | | | | | |

## 4. TYPICAL TEST METHODS USED

Following are descriptions of the predominant test methods used in the studies cited in the literature review. Several of these have been used successfully in many WJE projects, and some will be used for this NETC 97-2 project's research.

### 4.1. MACROCELL CORROSION CURRENT (adaptation of ASTM G109)

Macrocell corrosion current is generated between two layers of reinforcing steel in concrete slabs, by corrosion (Figure 4.1). It is a measure of the weight of reinforcing steel consumed (or extent of corrosion) by the corrosion process. The test measures the coupled current of a macrocell formed by reinforcing steel exposed to a corrosive, chloride rich, top layer in the concrete slab, and reinforcing steel at the bottom of the slab exposed to low-chloride concrete. The top steel acts as the anode, losing electrons, and the bottom steel is the cathode. A resistor connects the top and bottom layers of steel, and the voltage is measured across the resistor. The slabs tested can be either pre-cracked or non-cracked, and they are typically exposed to cyclic ponding with a sodium chloride solution. WJE has found that there is good correlation between macrocell corrosion currents measured in the slab and the extent of corrosion found on the anodic reinforcing steel after removal from the slab. Therefore, this is a low-cost, simple, and reliable test method that has provided meaningful results in several studies. This method, used with the specimens described in the research plan, most closely simulates actual field conditions. (ASTM G109, 1994; WJE, 1995; Thompson et al., 1996; WJE, 1998.)

### 4.2. MACROCELL ELECTRICAL RESISTANCE

In the electrical resistance test, the electrical resistance of the concrete and reinforcing steel between the reinforcing bar layers is measured in ohms. Concrete electrical resistance usually increases as Portland cement hydrates. Concrete exposed to a chloride solution environment will have electrical resistance that decreases or remains low. A special AC apparatus is used to test electrical resistivity of concrete slabs, with top and bottom reinforcing steel, exposed to a chloride solution environment (Figure 4.1). (WJE, 1995; WJE, 1998.)

## 4.3. HALF-CELL POTENTIAL, ASTM C876

A copper-copper sulfate half-cell survey determines the corrosion activity of reinforcing steel. Potential measurements are made on the top of reinforced concrete slabs in the laboratory and in the field. The test method connects a lead wire between clean metal of an exposed reinforcing steel bar and one terminal of a high-impedance voltmeter. The other terminal of the voltmeter is connected to the copper-copper sulfate half-cell. The half-cell is then placed on the pre-wetted concrete slab above the reinforcing steel. Electrical potential of the embedded steel below is then measured (Figure 4.2). Potentials more negative than a critical value indicate a high probability of corrosion. This "critical value" has been cited as a number of different values, most commonly -0.240 mV, and -0.350 mV. Potentials less negative than -0.20 mV indicate a low probability of corrosion. (Pfeiffer, 1989; WJE, 1991; ASTM C876, 1994; WJE, 1995; Thompson et al., 1996; McDonald et al, 1998.)

## 4.4. LINEAR POLARIZATION RESISTANCE (LPR), ASTM G59

Linear Polarization Resistance is based on determination of polarization resistance of a specimen exposed to a corrosive environment. The polarization resistance is inversely proportional to the corrosion rate. The advantage of LPR is the ability to record instantaneous corrosion rates. This on-line monitoring process permits qualitative comparisons of corrosion rates of different specimens and an accurate determination of very small corrosion rates. The dimension of measurement is $R_p$ (ohm $cm^2$). The test involves applying a small DC polarization at specified rates and measuring the resulting current. Typical specimens used are concrete cylinders with embedded/protruding reinforcing steel, subjected to ponding in a sodium chloride solution. Guidelines have been established for LPR measurements into categories of no corrosion and severe corrosion, with an intermediate range where the results are inconclusive. The ASTM standard and some researchers differ as to the exact values of these boundaries. This testing procedure is very costly and complicated. (ASTM G59, 1994; Thompson et al., 1996.)

## 4.5. ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY (EIS)

An alternative method to Linear Polarization Resistance is Electrochemical Impedance Spectroscopy. EIS uses AC to measure characteristics of a corroding metal

surface and the surrounding concrete. EIS determines the performance characteristics of the corroding metal and coating system. However, this technique is labor-intensive and requires special training to interpret the results. The test uses a computer controlled potentiostat and analyzer that measures the response of the system to low-magnitude AC potential applied to reinforcing bars in a concrete prism. As the frequency of the applied AC potential is varied, different characteristic responses of an AC system (impedance, capacitance, inductance, diffusion, and transmission related effects) are noted. (WJE, 1998; Thompson et al., 1996.)

### 4.6. CYCLIC POTENTIODYNAMIC POLARIZATION (CPP), ASTM G5 and G61

Cyclic Potentiodynamic Polarization gives corrosion behavior of steel, in terms of pitting tendency. CPP can establish the effect of chemical corrosion inhibitors on anodic and cathodic reactions. In this test, the potential of a reinforcing steel bar, in a concrete prism or concrete pore solution, is scanned to a value that exceeds the pitting potential, reversed, and returned to some predetermined value. (Thompson et al. 1996.)

### 4.7. RAPID CHLORIDE PERMEABILITY (RCP), ASTM C1202, AASHTO T277

The Rapid Chloride Permeability test determines the electrical conductance of concrete to provide a rapid indication of its resistance to the penetration of chloride ions. RCP monitors the amount of electrical current passed through a concrete cylindrical slice during a 6-hour period. A potential difference of 60 volts DC is maintained across the ends of the specimen, one of which is immersed in sodium chloride solution and the other in a sodium hydroxide solution (Figure 4.3). It was originally believed that the total charge passed, in coulombs, was related to the resistance of a specimen to chloride ion penetration. RCP is only applicable to types of concrete for which such a relationship has been established by long-term chloride ponding procedures (AASHTO T259, 90 day ponding test). The correlation between charge passed and permeability can be dubious (Figure 4.4), especially in cases where mineral admixtures such as silica fume have been used. In such tests, RCP can overestimate the magnitude of improvement with admixtures and underestimate the effectiveness of low water-to-cement ratio (approx. 0.30) ordinary concrete, when compared to actual chloride data. The charge passed is more of a function of the movement of hydroxyl ions than the movement of chloride ions. The RCP test does have

a good correlation with electrical resistivity. (Rose, 1987; ASTM C1202, 1994; Pfeifer et al., 1994; Wee et al., 1999.)

## 4.8. VISUAL INSPECTIONS AND AUTOPSIES

Detailed visual inspections of the test specimens are conducted periodically (during drying cycles). Autopsies are conducted on the specimens at the end of a study (dependent on corrosion currents, linear polarization, and AC impedance measurements). The reinforcing steel is recovered from the specimens and a qualitative assessment of the amount of corrosion is made. The amount of corrosion is typically documented and photographed during autopsies. (WJE, 1995.)

## 4.9. CHLORIDE INGRESS ANALYSIS, ASTM C114, AASHTO T259

At the conclusion or during the testing, a single core can be removed from reinforced concrete slabs to enable the chloride contents at the level of the reinforcing steel to be determined. The cores are sliced, the slices pulverized, and then a chemical procedure is performed to determine chloride contents. As an alternative to cored samples, holes can be drilled to depth in the concrete, and the displaced material recovered. Chloride concentration profiles can then be determined, which may be directly used to estimate the diffusion coefficient. (WJE, 1995.) Chloride contents can be analyzed as water-soluble or acid-soluble, with the latter generally being preferred in corrosion studies.

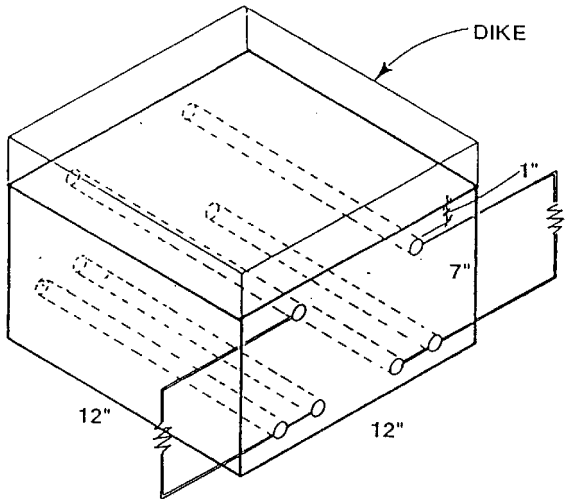


**Figure 4.1: Non-Cracked Reinforced Concrete Slab Specimen (WJE, 1995)**

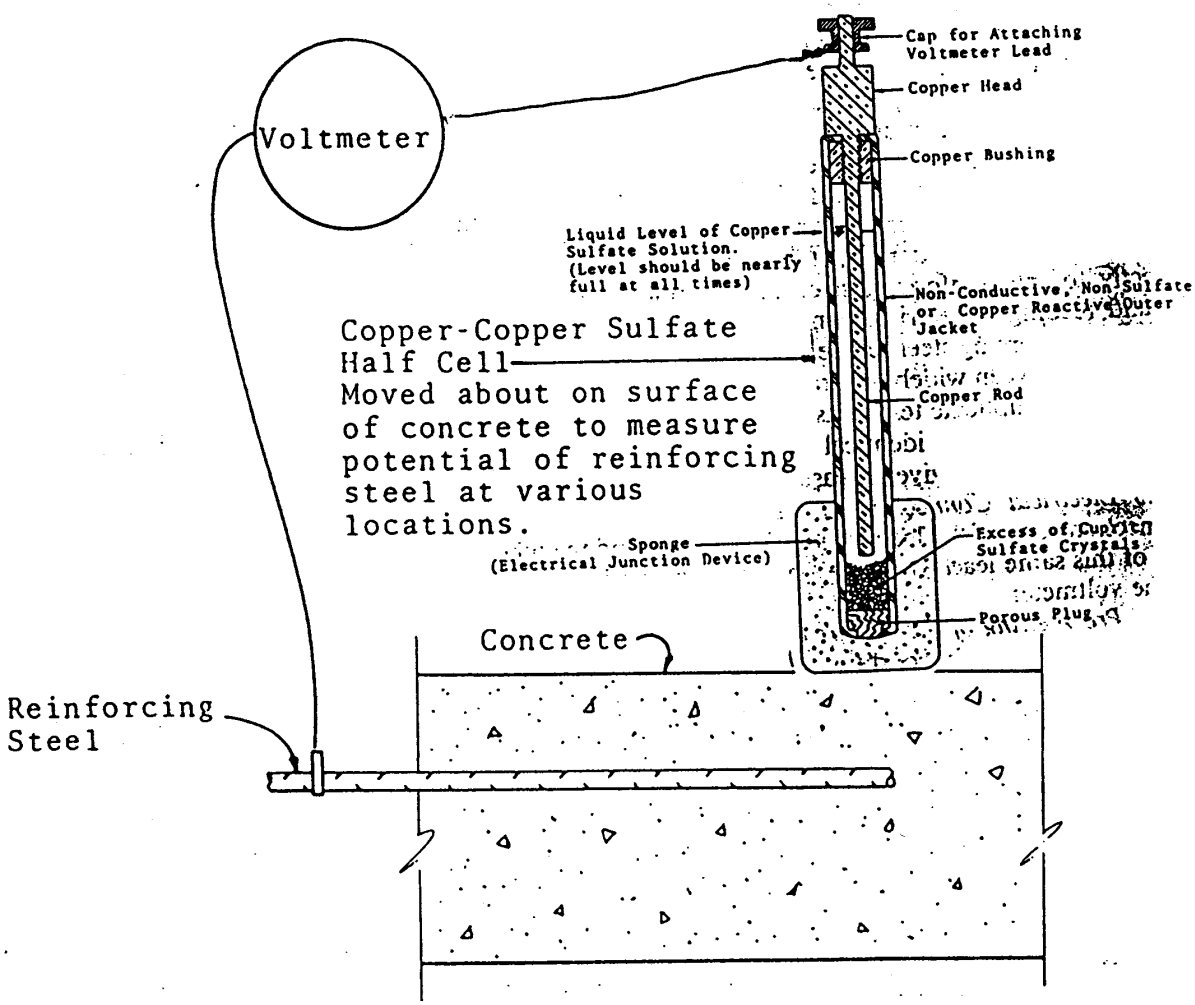


**Figure 4.2: Copper-Copper Sulfate Half-Cell Circuitry (ASTM C876, 1994)**

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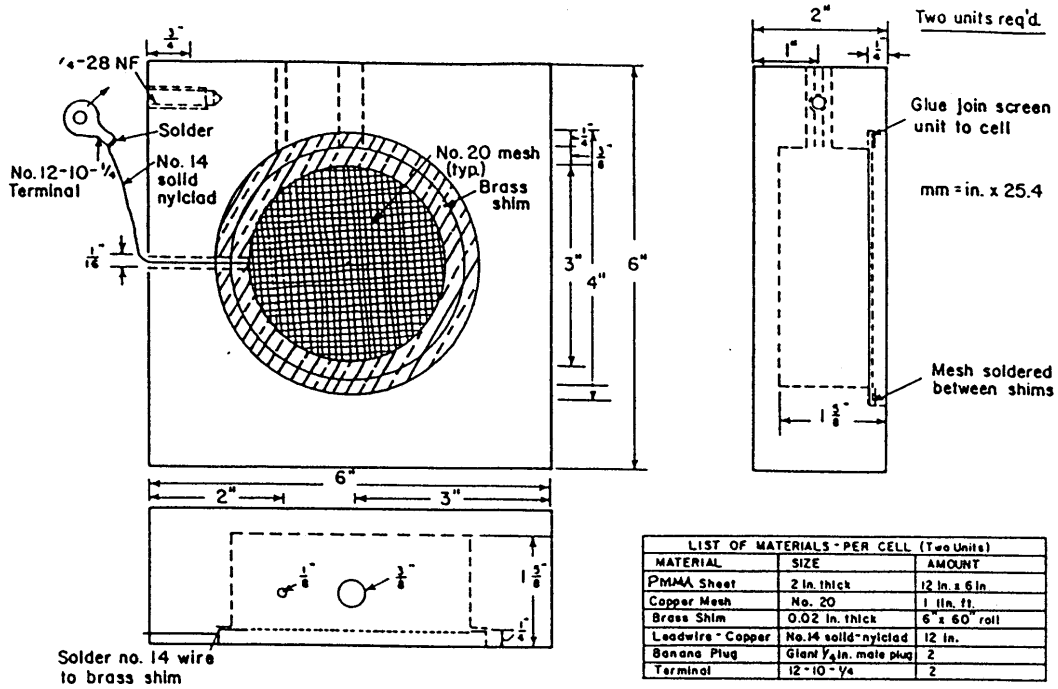


| LIST OF MATERIALS - PER CELL (Two Units) | | |
|---|---|---|
| MATERIAL | SIZE | AMOUNT |
| PMMA Sheet | 2 in. thick | 12 in. x 6 in |
| Copper Mesh | No. 20 | 1 lin. ft. |
| Brass Shim | 0.02 in. thick | 6" x 60" roll |
| Leadwire - Copper | No. 14 solid-nylclad | 12 in. |
| Banana Plug | Giant ¼ in. male plug | 2 |
| Terminal | 12 - 10 - ¼ | 2 |

**Figure 4.3: Rapid Chloride Permeability Test Schematic (Rose 1987; ASTM C1202, 1994)**

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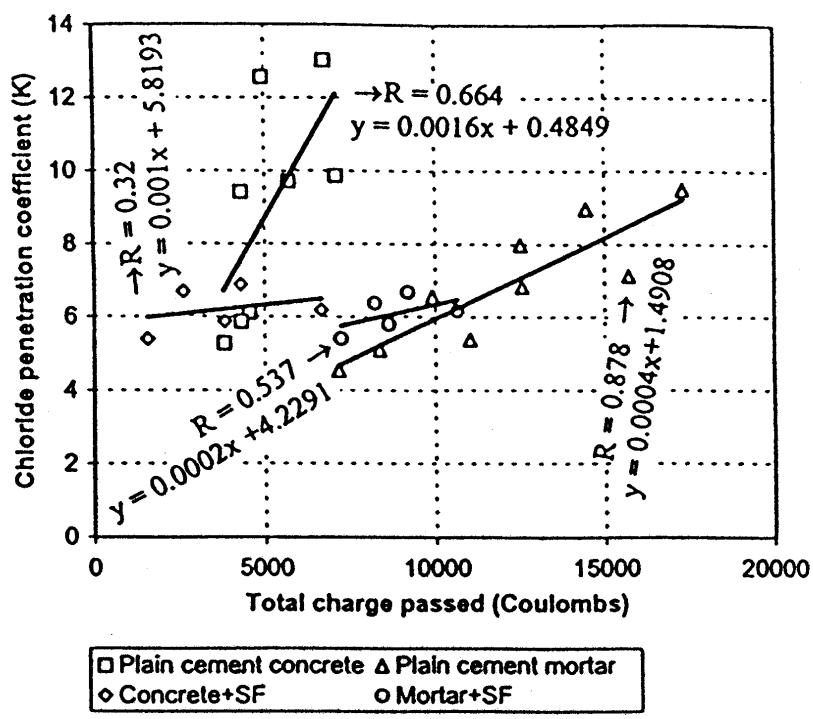


**Figure 4.4: Permeability Vs. Total Charge Passed of Silica Fume Concrete (Wee et al., 1999)** *Reprinted, with permission, copyright Elsevier Science*

# 5. EXPERIMENTAL PROGRAM

After careful analysis of the literature review and survey of New England state DOTs, a research plan was developed by the Project Team for New England Transportation Consortium NETC 97-2. The testing protocols follow those used successfully in several studies for Federal Highway Administration (FHWA), NCHRP, and other organizations, which were developed by Wiss, Janney, Elstner Associates (WJE).

It should be noted that test protocol was originally to be based on NCHRP 10-45 (Thompson et al, 1996). The NCHRP 10-45 study attempted to use relatively short-term laboratory tests on small specimens to develop a life prediction model for the durability of reinforced concrete structures in corrosive environments. Specifically, NCHRP 10-45 sought to: 1) develop procedures to evaluate and qualify corrosion inhibiting admixtures, and 2) recommend performance criteria for acceptance of corrosion inhibiting admixtures. Many of the test specimens used in NCHRP 10-45 had not previously been tested. (Thompson et al., 1996). Results of NCHRP 10-45 have not been published. Given the status of NCHRP 10-45, the Project Team for NETC 97-2 instead used the reliable test methods and specimen types that have proven effective in the past. A summary of the experimental research plan is presented below.

## 5.1 CONCRETE SPECIMENS

The specimens were cast in replicates of three, one pre-cracked and two non-cracked, for each of 14 mix designs, as shown in Table 5.1. Mixes included a control, single admixtures, and combinations of double or triple combinations of admixtures. Two mixes also replicated admixture combinations, but with a higher w/c ratio.

### 5.1.1 Specimen Details

The test specimens were chosen to approximate a bridge deck with two layers of reinforcing steel (See Fig. 5.1). The top surface of each specimen is exposed to chlorides, the sides are sealed, and the bottom is exposed to air. The experimental tests use pre-cracked and non-cracked concrete slabs 7 in. x 12 in. x 12 in. Each specimen has top and bottom 5/8 in. diameter (#5) “black” (uncoated) reinforcing steel bars with 1 in. clear cover top and bottom. There is 3-3/4 in. of clear concrete between the layers of reinforcing steel. There are two top

bars spaced 3 in. on center from the sides of the specimen, and there are two sets of two bottom reinforcing steel bars placed 2 in. and 4 in. on center from the sides; each bottom bar set corresponds with one of the top bars. The clear cover in specimens is less than the clear cover that would be used in construction in order to accelerate the testing.

There are lead wires electrically connecting the top and bottom reinforcing steel layers. The reinforcing bars were wired with a 10-Ohm resistor between one of the top reinforcing bars and two of the bottom (Figure 5.2). In this set up, the top reinforcing bars are assumed to act as the anode since the NaCl solution is able to penetrate to this area easier, while the bottom reinforcing bars are assumed to be the cathodes. The 10-Ohm resistor was recommended by WJE in FHWA-RD-98-153 (1998), which showed shorter stabilization times of the system when compared to the 100-Ohm resistors, which had been used in the past. The lead wires are used so that the corrosion current can be monitored; in an actual bridge deck the corrosion current would pass through tie steel, bar chairs, or other miscellaneous embedded steel.

The top of each specimen also included a Plexiglas dike around the edges. This dike contains the chloride solution during periods of ponding. The specimens were sealed with an epoxy coating on each of the four sides. This was done to cause the water and the chlorides to propagate from the top of the specimen towards the reinforcing bars. Any leaks or drips that occurred would be isolated and would not be able to attack the reinforcing bars from the sides. This represents the interior part of the bridge deck, as opposed to the side of the deck, which is subjected to water from both the top, and sides. A photo of the specimen is pictured in Figure 5.3.

Replicate specimens of each mix design were provided, type A and B were as shown in the figure, while type C was provided with a pre-crack down to the layer of reinforcing steel. Cracks in the pre-cracked specimens simulate cracks parallel to and directly over the length of reinforcing steel. This models the possibility of narrow cracks in a bridge deck that would allow direct access of chlorides to the reinforcing steel. Cracks were formed using stainless steel metal shims (12 mil thick), cast into the concrete surface during casting and removed after the initial set of the concrete.

### 5.1.2 Materials

The coarse aggregate was 3/4 in. maximum size crushed stone from the Warner Brothers quarry in South Deerfield, Massachusetts. The fine aggregate (sand) was obtained from the Warner Brothers gravel pit in Sunderland, Massachusetts. Both of the aggregates used are approved by the Massachusetts Highway Department, and aggregates from these sources are currently used for highway projects in the western Massachusetts area. The fine aggregate conforms to AASHTO M 6, and the coarse aggregate conforms to AASHTO M 80.

The bulk specific gravity, and absorption capacity was determined using ASTM C 128 and ASTM C 127. The bulk specific gravity of the fine aggregate was 2.7, and the absorption capacity is 1.35%. The bulk specific gravity of the coarse aggregate was 2.9, and the absorption capacity was 1.20%.

Both the coarse and fine aggregates were tested for chloride content using ASTM C 1152, "Acid-soluble Chloride in Mortar and Concrete," at Wiss, Janney, Elstner Associates (WJE), the project consultants based in Northbrook, Illinois. Both aggregates contain less than 0.008% acid-soluble chloride. According to Paul Krauss of WJE, the aggregate is clean of chloride, but it does contain some iron, as well as particles that may be alkali reactive, so unusual half-cell results and / or alkali silica reactions over time could be possible.

The reinforcing steel bars are #5, deformed, uncoated, grade 60 bars (provided by Barker Steel) and conform to AASHTO M 31. They were cut to length, drilled and tapped to receive a 1/4 X 20 bolt. These bolts hold the lead wire in contact with the end of the bars. The bars were wire brushed to remove mill scale and any corrosion products. The bars were then placed in an oven at 240°F to remove moisture and prevent corrosion. The bars were kept in the oven until just before concrete placement. Any visible corrosion product was removed by wire brushing prior to placing the bars in the forms.

Other constituents of the concrete mixture were obtained from the following sources. The mix water used was Amherst town water, the chloride content is 5-10 parts per million (ppm) (which is equivalent to 0.01 to 0.02 lbs/yd$^3$). The AASHTO limit on chloride content of mixing water is 1000 ppm. The Portland cement was manufactured by Blue Circle Cement, Type I/II, and conforms to ASTM C150. Silica fume (Force 10,000 D Microsilica) was manufactured by W. R. Grace and conforms to ASTM C 1116. Type F fly ash (Fort Martin) was manufactured by Mineral Solutions and conforms to ASTM C 618. Ground

granulated blast furnace slag (NewCem) was manufactured by Blue Circle Cement and conforms to ASTM C 595. The calcium nitrite (DCI-S) was manufactured by W. R. Grace and was used as a 33% solution in water. It conforms to ASTM C 494. The DSS was an experimental admixture manufactured by Anhydrides and Chemicals, Inc. (currently manufactured and sold commercially as Hycrete DSS by Anhydrides and Chemicals, Inc. affiliate Broadview Technologies). The air entrainer (Micro-Air) was manufactured by Master Builders, conforms to ASTM C 260. The superplasticizer is a Type F high range water reducer (DARACEM 19), and was manufactured by W. R. Grace. It conforms to ASTM C 494.

### 5.1.3 Water-to-Cementitous (w/c) Ratio

The cementitious material in the water-to-cement (w/c) ratio referred to in the experimental portion of this study is the total cementitious and pozzolanic material including, Portland cement, silica fume, fly ash, and ground granulated blast furnace slag.

A concrete (w/c) ratio of 0.40 was used for 12 of the 14 mixes to model a typical state DOT mix design in New England. Two of the mixes (M13 and M14) have a (w/c) ratio of 0.47, which is within the expected range for normal AASHTO Class A (AE), 0.45 w/c ready-mixed concrete specified for bridge construction. While the lower (w/c) ratio is more representative of actual bridge mix designs, the resulting reduced permeability of the concrete will likely require an extended time frame for getting significant results in this study. The higher (w/c) ratio of 0.47, similar to many other studies, will allow for accelerated testing. However, it may not accurately model admixture behaviors in a typical mix design. By including both (w/c) ratios in this study one will be able to evaluate the validity of typical accelerated tests and provide results for typical (w/c) ratios used in practice. Preliminary information from the research team at CC Technologies regarding the results of NCHRP 10-45 indicates that the 0.40 w/c ratio used was “too good” for the control (Thompson et al., 1996). This low (w/c) ratio resulted in inconclusive results over a two-year testing period, and may likely require testing beyond 24 months.

### 5.1.4 Mix Designs

The concrete was batched using a mix design typical of that used by the New England states DOTs. The NETC technical committee specified maximum cement content of 700 lbs/yd3. An air content of 6% ± 1-1/2%, and a slump of 1 to 5 inches was also recommended. Final mix designs are specified in Table 5.2.

#### 5.1.4.1 Basic Mix Design

The basic mix design, uncorrected for aggregate moisture content is as follows.

| | |
|---|---|
| Total Free Water | 276 lbs/yd$^3$ |
| Fine Aggregate (Oven Dry Basis) | 1280 lbs/yd$^3$ |
| Coarse Aggregate (Oven Dry Basis) | 1800 lbs/yd$^3$ |
| Total Cementitious and Pozzolanic Material | 690 lbs/yd$^3$ |

Added water was then corrected based on aggregate properties for each mix.

#### 5.1.4.2 Corrosion Inhibiting Admixture Batch Quantities

Concrete mixes being tested include an ordinary Portland cement concrete control, which contains no admixtures except air entrainer. Other specimens include various single, double, and triple combinations of admixtures, applied at the following dosages: 1) calcium nitrite (3 gal/yd$^3$), 2) silica fume (6% cement replacement), 3) fly ash (15% cement replacement), 4) slag (25% cement replacement), and 5) DSS (1/2% cement replacement).

Calcium nitrite in combination with the mineral admixtures should provide dual protection, combining the reduced permeability from the mineral admixtures with the passivating mechanism of protection from the calcium nitrite. It was of interest to determine if effects are cumulative, or if there are diminishing returns. The triple combinations were compared to the double combinations to ascertain if further protection is provided

Calcium nitrite was added to mix water as a 33% solution, so for each pound of calcium nitrite solution added, 0.66 pounds of mix water was deducted in order to keep the total free water constant. The DSS was added to mix water as a 20% solution, and for each pound of DSS solution added, 0.80 pounds of mix water was deducted in order to keep the total free water constant. The air entraining admixture and the superplasticizer were added as

needed to maintain the air content and slump within the range specified by AASHTO, and the mix water was deducted on a one to one basis.

Mixes M1, M2, M3, M4, M5, M7, M8, M9, M11, M12, M13, and M14 were cast from January 31, 2000 through March 25, 2000. See Table 5.3 for casting dates and strengths.

Delays in the manufacture and delivery of the DSS caused casting of mixes M6 and M10 to be delayed until May 31, 2000. At this time three other specimens were replaced. Early in the testing protocol, four of the specimens developed cracks at the concrete surface above the top reinforcing bars. These included one of the control specimens (M1A), both of the silica fume specimens (M3A and M3B), and one of the fly ash specimens (M4B). The macrocell and half-cell readings correlating to these specimens were elevated to the level of the "pre-cracked" specimens. Three of the specimens that developed cracks were replaced at the end of the first cycle, at the same time that the DSS specimens were included in the project.

One of the three replaced specimens came from the silica fume mix design (mix 3). Unlike the other mix designs, both of the "non-cracked" silica fume specimens developed cracks within seven weeks of testing. These specimens were cured similarly to all other specimens (see section 5.1.5). Because of this, all three of the silica fume specimens were cracked and behaved similarly. One of these specimens was replaced in order to create a non-cracked comparison with the other admixtures. The second silica fume specimen was left in the project to have a comparison of two specimens one of which was pre-cracked and the other which cracked after curing. One other specimen that was replaced came from the control mix. It was replaced because it had a slight settlement crack along with elevated readings. In addition replacing one of the controls would give a comparison to the other replaced specimens. The third replaced specimen came from the fly ash admixture (mix 4). The crack on this specimen was noticed very early in the project. The other fly ash specimen remained non-cracked in the early stages of testing. The mix design used for the replaced specimens was similar to the original specimens, and shown in Table 5.2. The new mix was also altered according to the aggregate moisture content at the time of casting. Superplasticizer dosages were changed to improve the workability in the re-cast specimens, which reduced cracking.

### 5.1.5 Mixing Procedure and Placement

Specimens were cured under wet burlap and polyethylene film for a period of at least three days; this curing represents realistic construction field conditions. Concrete cylinders for each mix design were cast in triplicate, and the compressive strength was tested at 28 days. Results are included in Table 5.3. Significantly lower strengths were noted for Mix M10 (calcium nitrite and DSS). This is a concern with DSS materials, as the mix with only DSS (M6) also had somewhat reduced strengths. Reduced strength of DSS mixes has been reported by Allyn et al (1998) and Allyn and Frantz (2001). The DSS dosage used in this study was relatively low. Significant increases in strength were noted for specimens that included slag (M5, M9, and M12), as well as both triple combinations (M11 and M12). Slump (workability) was also relatively low for these higher strength mixes.

## 5.2 PREPARATION OF CONCRETE SPECIMENS FOR PONDING

After a minimum of eight weeks total curing time, the sides of the specimens were sealed with two coats of Epoxy Coating to prevent any chlorides from reaching the reinforcing steel from the specimen sides. The specimens were placed on a plinth of wood that allowed free circulation of air to the underside of the specimens (similar to a bridge deck).

After the electrical connections were made, the exposed ends of the reinforcing steel bars were sealed with a high-strength, non-sag epoxy gel adhesive, EPOGEL, manufactured by Sonneborn. This was done to ensure that all chlorides reaching the steel must migrate through the concrete from the top surface of the specimen. A Plexiglas dam three inches high was attached to the tops of the specimens with silicon caulk to contain the salt solution during the ponding.

Three climate control “tents” were constructed and placed over the specimens. The “tents” are made from a wood frame with 1 in. Celotex insulation panels making up the sides and the tops. There is a Gap of 1 in. at the bottom of the “tent” to allow for the circulation of air, which is needed during the drying cycles. An electronic temperature control, in conjunction with two 250-watt heat lamps, maintained the desired minimum temperature (Figures 5.4 and 5.5).

## 5.3 TEST PROCEDURE

The test protocol was based on that developed by Wiss, Janney, Elstner Associates (WJE) and used successfully on past FHWA funded projects.

### 5.3.1 Ponding Cycles

The schedule of ponding was adopted from that reported and used by WJE from 1993 to 1998. This schedule consisted of 24-week cycles. The first 12 weeks of the cycle, consists of the specimens being ponded with 15% NaCl solution (by weight) for 4 days (Monday through Friday). During this time, the temperature is held at a minimum of 70° F. The specimens are then dried for three days (Friday through Monday) at a minimum temperature of 100° F. For the following 12 weeks of the cycle the specimens were continuously ponded for 12 weeks, at which time temperature was held at a minimum of 70° F. Table 5.4 shows the dates for the five 24 week cycles of the project, i.e. from June 26, 2000 through October 14, 2002. Note that results are only included through week 108 due to the end date of the project. However, the specimens with delayed initiation of ponding (M6, M10 and re-cast specimens) included an additional 24 weeks of testing to provide 108 weeks total. This table also shows that two of the mix designs were not ponded at the beginning of the project along with all of the other mix designs, as mentioned previously. These specimens were not ponded until the start of the second cycle. This resulted in a longer time from casting of specimens until the start of the test protocol than the other mixes.

### 5.3.2 Corrosion Activity Monitoring

Four types of evaluation techniques were used to record the amount of corrosion activity in the specimens, visual inspection, macrocell readings, half-cell readings, and destructive evaluations. The specimens were periodically examined visually for any changes in appearance. A more thorough inspection was done at the beginning of each ponding/drying stage of the cycle. This included mapping any rust or precipitate rising up to the top of the specimens and measuring the width of any cracks that developed. Two other types of inspections include readings of macrocell and half-cell voltages.

Using macrocell criteria, the voltage drop between the top and two bottom reinforcing bars was recorded. The macrocell readings measure the activity level of the electron flow from the anodic to cathodic steel through the concrete. This was measured with a Fluke model 8062A digital multimeter. A photograph is presented in Figure 5.6. The macrocell readings were taken every week day during the wet/dry cycle, and every two week days (Monday, Wednesday, and Friday) during the continuous ponding cycle. The macrocell readings were converted into iron loss data, using the following (Virmani et al, 1983; McDonald et al, 1998.):

Metal loss in grams/amp-hour

=atomic weight/[(Faraday's Constant) * (electron charge change)]

$$= \frac{(55.8 grams/mol)(3600 s/hr)}{96489(amp*s)/mol(2 electrons)} = 1.04 \text{ grams/amp-hr}$$

Therefore, 1.04 grams of iron lost per amp hour was used in the conversions. Readings therefore correlate approximately to the amount of iron lost in the reinforcing bars.

Half-cell potential readings were also used to evaluate the corrosion activity at the top reinforcing bars. Half-cell readings measure the voltage between the top of the concrete specimen and the reinforcing bar that is directly below it. The half-cell data is considered to be an indicator of whether or not there is corrosion at the anode, but does not correlate to specific levels of activity. The test set up utilizes a copper-copper sulfate half-cell instrument. The half-cell is connected to the top reinforcing bar with a wire, and is placed on top of a pre-wetted sponge over the reinforcing bar that is to be measured. The half-cell potential meter includes a porous ceramic cap on the bottom, which is in contact with the sponge. This cap and the pre-wetted sponge provide a better connection between the specimen and half-cell. A photograph is shown in Figure 5.7. Half-cell readings were taken on Fridays during the wet/dry cycle and at one to three intervals during the continuous ponding cycle.

Specimens were destructively evaluated for visual assessment of rusting on the surface of the reinforcing bars at the conclusion of testing. In addition, the three replaced specimens were similarly assessed. Chloride ingress testing was performed on the three replaced specimens, however results were inconclusive due to the micro-cracking that occurred in the specimens. Project scope was not able to include replicate specimens with no reinforcing steel as would often be used to obtain reliable chloride ingress data.

Prior to ponding, macrocell readings were all at approximately zero mV, half-cell readings were all below -0.230 mV, and specimens were intact per visual inspection.

**TABLE 5.1: Specimens**

| MIX | MIX COMPONENTS | Specimen | Notes | |
|---|---|---|---|---|
| **M1** | Control<br>w/c=0.40 | M1A | Non-cracked | M1A replaced |
| | | M1A-R | | |
| | | M1B | | |
| | | M1C | Pre-cracked | |
| **M2** | 3 Gal CN/cubic yard<br>w/c=0.40 | M2A | Non-cracked | |
| | | M2B | | |
| | | M2C | Pre-cracked | |
| **M3** | 6% SF<br>w/c=0.40 | M3A | Non-cracked | M3B replaced |
| | | M3B | | |
| | | M3B-R | | |
| | | M3C | Pre-cracked | |
| **M4** | 15% FA<br>w/c=0.40 | M4A | Non-cracked | M4B replaced |
| | | M4B | | |
| | | M4B-R | | |
| | | M4C | Pre-cracked | |
| **M5** | 25% Slag<br>w/c=0.40 | M5A | Non-cracked | |
| | | M5B | | |
| | | M5C | Pre-cracked | |
| **M6** | ½% DSS<br>w/c=0.40 | M6A | Non-cracked | |
| | | M6B | | |
| | | M6C | Pre-cracked | |
| **M7** | 3 Gal CN + 6 % SF<br>w/c=0.40 | M7A | Non-cracked | |
| | | M7B | | |
| | | M7C | Pre-cracked | |
| **M8** | 3 Gal CN + 15% FA<br>w/c=0.40 | M8A | Non-cracked | |
| | | M8B | | |
| | | M8C | Pre-cracked | |
| **M9** | 3 Gal CN + 25% Slag<br>w/c=0.40 | M9A | Non-cracked | |
| | | M9B | | |
| | | M9C | Pre-cracked | |
| **M10** | 3Gal CN + ½% DSS<br>w/c=0.40 | M10A | Non-cracked | |
| | | M10B | | |
| | | M10C | Pre-cracked | |
| **M11** | 3 Gal CN + 6% SF + 15% FA<br>w/c=0.40 | M11A | Non-cracked | |
| | | M11B | | |
| | | M11C | Pre-cracked | |
| **M12** | 3 Gal CN + 6% SF + 25% Slag<br>w/c=0.40 | M12A | Non-cracked | |
| | | M12B | | |
| | | M12C | Pre-cracked | |
| **M13** | 3 Gal CN + 6% SF<br>w/c=0.47 | M13A | Non-cracked | |
| | | M13B | | |
| | | M13C | Pre-cracked | |
| **M14** | 3 Gal CN + 6% SF + 15% FA<br>w/c=0.47 | M14A | Non-cracked | |
| | | M14B | | |
| | | M14C | Pre-cracked | |

**Notes: All w/c ratios are based on total cementitious material**

**Table 5.2: Mix Designs**

| | MIX | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | M1 | M2 | M3 | M4 | M5 | M6 | M7 | M8 | M9 | M10 | M11 | M12 | M13 w/c= 0.47 | M14 w/c= 0.47 | M1R re-cast | M3R re-cast | M4R re-cast |
| | Control | CN | SF | FA | Slag | DSS | CN + SF | CN + FA | CN + Slag | CN + DSS | CN + SF + FA | CN + SF + Slag | CN + SF | CN + SF + FA | Control | SF | FA |
| Total Free Water (lb) | 276 | 255 | 276 | 276 | 276 | 262 | 255 | 255 | 255 | 241 | 255 | 255 | 303 | 303 | 276 | 276 | 276 |
| Fine Aggregate (lb) | 1280 | 1280 | 1280 | 1280 | 1280 | 1280 | 1280 | 1280 | 1280 | 1280 | 1280 | 1280 | 1280 | 1280 | 1280 | 1280 | 1280 |
| Coarse Aggregate (lb) | 1800 | 1800 | 1800 | 1800 | 1800 | 1800 | 1800 | 1800 | 1800 | 1800 | 1800 | 1800 | 1800 | 1800 | 1800 | 1800 | 1800 |
| Cement (lb) | 690 | 690 | 648.6 | 586.5 | 517.5 | 690 | 648.6 | 586.5 | 517.5 | 690 | 545.1 | 476 | 648.6 | 545.1 | 690 | 648.6 | 586.5 |
| Silica Fume (lb) | X | X | 41.4 | X | X | X | 41.4 | X | X | X | 41.4 | 41.4 | 41.4 | 41.4 | X | 41.4 | X |
| Fly Ash (lb) | X | X | X | 103.5 | X | X | X | 103.5 | X | X | 103.5 | X | X | 103.5 | X | X | 103.5 |
| Blast Furnace Slag (lb) | X | X | X | X | 172.5 | X | X | X | 172.5 | X | X | 172.5 | X | X | X | X | X |
| Calcium Nitrite (lb 33% soln.) | X | 32 | X | X | X | X | 32 | 32 | 32 | 32 | 32 | 32 | 32 | 32 | X | X | X |
| DSS (lb) | X | X | X | X | X | 17.2 | X | X | X | 17.2 | X | X | X | X | X | X | X |
| Air Entrainer (oz.) | 6 | 20 | 8 | 8 | 10 | 20 | 20 | 20 | 20 | 20 | 30 | 30 | 20 | 20 | 11 | 8 | 11 |
| Super Plasticizer (oz.) | X | 61 | 55 | 49 | 49 | 82 | 82 | 82 | 82 | 82 | 102 | 102 | X | X | 62 | 69 | 62 |

*Notes: All w/c ratios are 0.40 unless noted, based on total cementitious material
All weights are Dry Weights, aggregate and water weights adjusted per aggregate moisture content prior to each casting.

**Table 5.3: Specimen Summary**

| MIX | Date Cast | Air Content (%) | Slump (in.) | 28-Day Strength (psi) |
|---|---|---|---|---|
| **M1** | 01/31/2000 | 5.0 | 0.75 | 5040 |
| **M1R** | 10/10/2000 | 4.0 | 5.0 | 5496 |
| **M2** | 03/25/2000 | 5.5 | 1.5 | 4735 |
| **M3** | 02/02/2000 | 5.0 | 5.0 | 4950 |
| **M3R** | 10/04/2000 | 4.0 | 3.75 | 5426 |
| **M4** | 02/03/2000 | 4.5 | 2.75 | 5029 |
| **M4R** | 10/10/2000 | 3.5 | 5.5 | 4403 |
| **M5** | 02/05/2000 | 4.5 | 1.25 | 5817 |
| **M6** | 05/31/2000 | 6.5 | 2.0 | 4562 |
| **M7** | 02/12/2000 | 5.0 | 5.0 | 5013 |
| **M8** | 02/26/2000 | 6.0 | 4.5 | 5112 |
| **M9** | 02/26/2000 | 5.0 | 1.5 | 5730 |
| **M10** | 5/31/2000 | 6.5 | 3.0 | 3687 |
| **M11** | 03/04/2000 | 5.0 | 1.5 | 5979 |
| **M12** | 03/04/2000 | 5.0 | 3.0 | 5836 |
| **M13** | 03/14/2000 | 6.0 | 3.0 | 4459 |
| **M14** | 03/14/2000 | 6.0 | 4.0 | 4411 |

**Table 5.4: Project Schedule**

| Time Period | Stage in Project |
|---|---|
| June 26, 2000 – September 18, 2000 | Start of experimental phase of the project, all specimens ponded except for DSS. Wet/dry period |
| September 18, 2000 – December 11, 2000 | Continuous ponding period of first cycle |
| December 11, 2000 – March 5, 2001 | Start of second cycle, DSS specimens are added and specimens from mixes 1, 3, and 4 are replaced. Wet/Dry period |
| March 5, 2001 – May 28, 2001 | Continuous ponding period of second cycle |
| May 28, 2001 – August 20, 2001 | Start of third cycle, wet/dry period. |
| August 20, 2001 – November 12, 2001 | Continuous ponding period of third cycle |
| November 12, 2001 – February 4, 2002 | Start of fourth cycle, wet/dry period. |
| February 4, 2002 – April 29, 2002 | Continuous ponding period of fourth cycle |
| April 29, 2002 – July 22, 2002 | Start of fifth cycle, wet/dry period. |
| July 22, 2002 – October 14, 2002 | Continuous ponding period of fifth cycle |

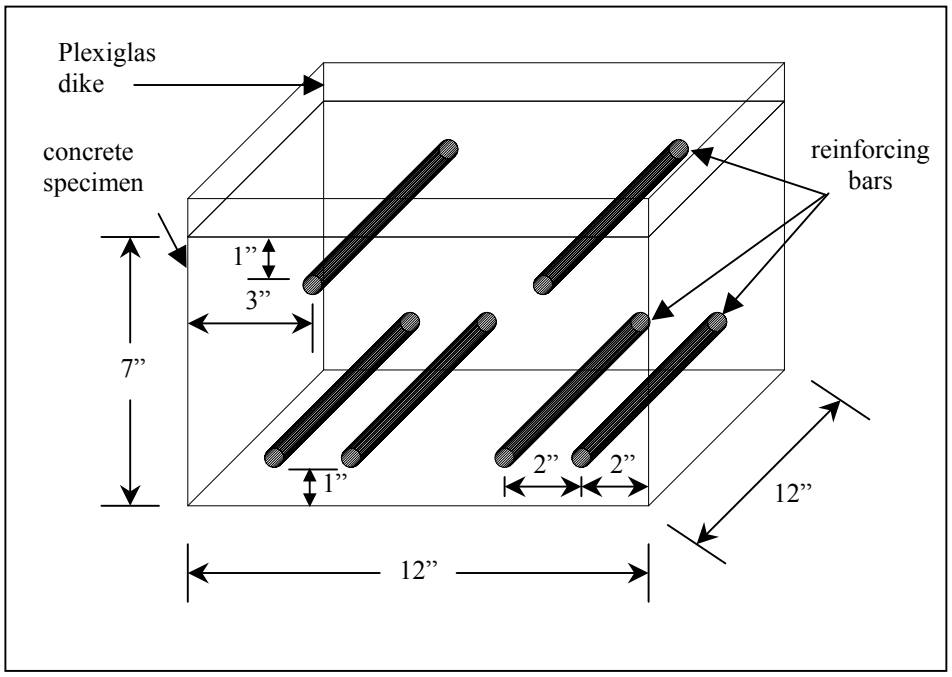


**Figure 5.1: Geometry of Specimens**

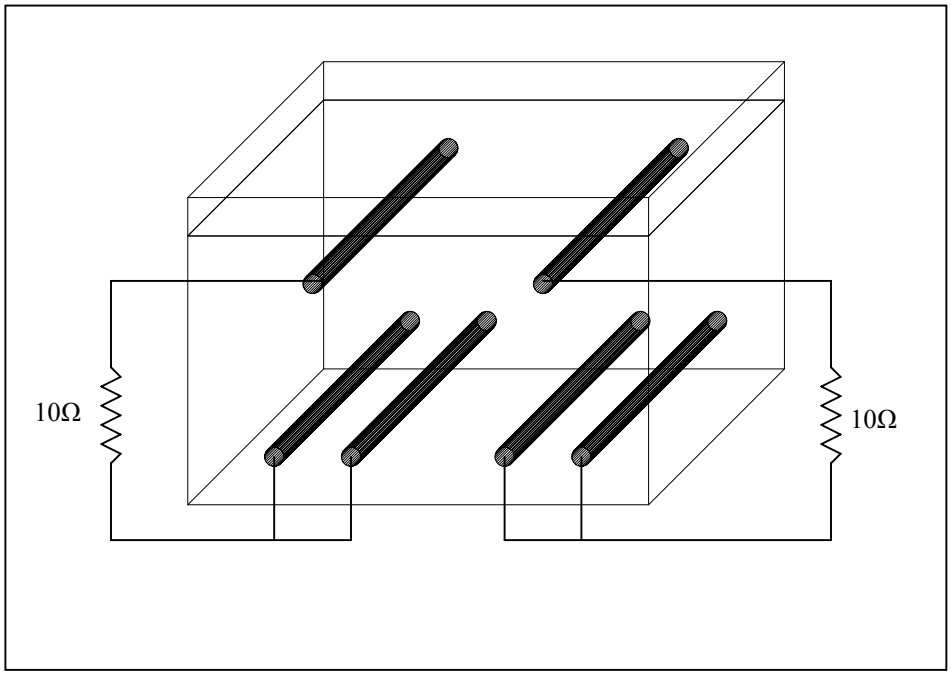


**Figure 5.2: Wiring of Specimens**

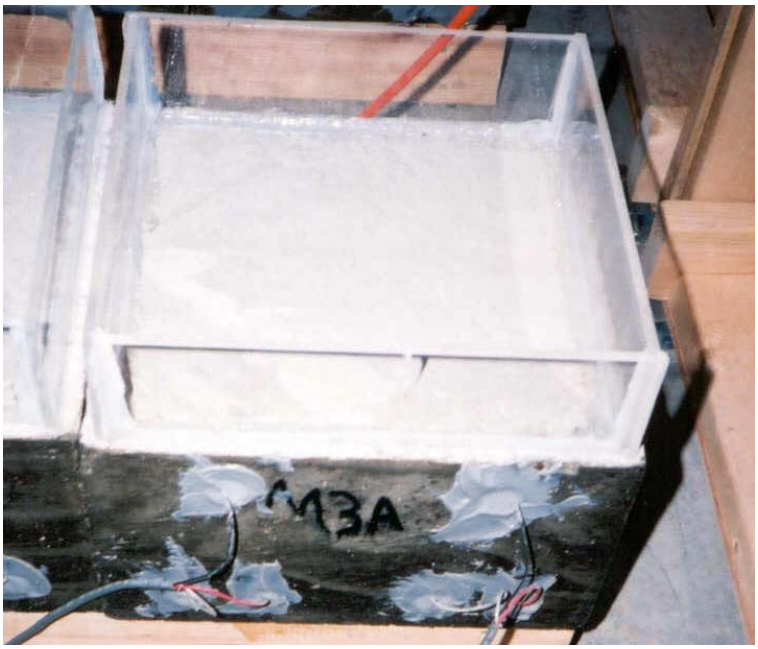


**Figure 5.3: Typical specimen**

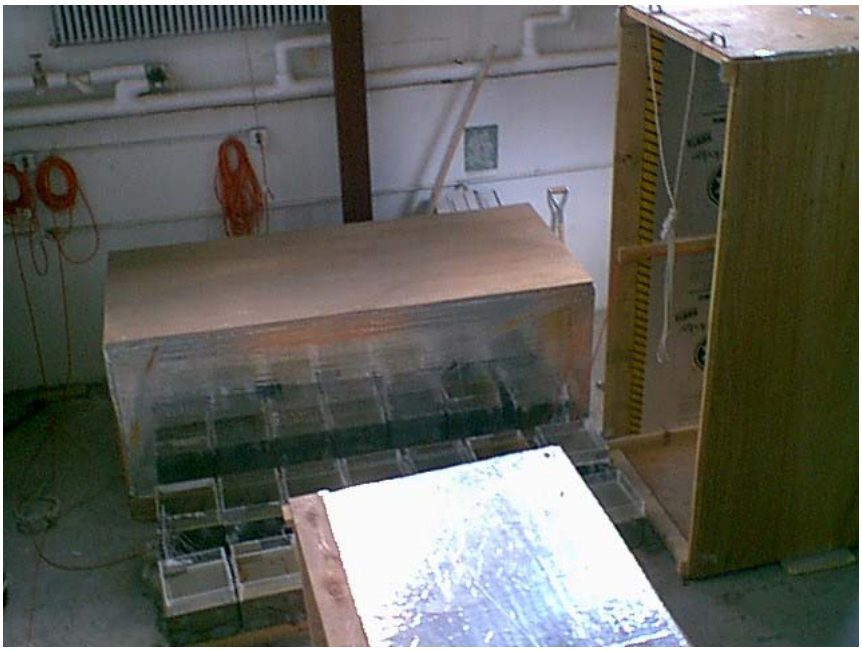

**Figure 5.4: Temperature-Controlled Boxes**

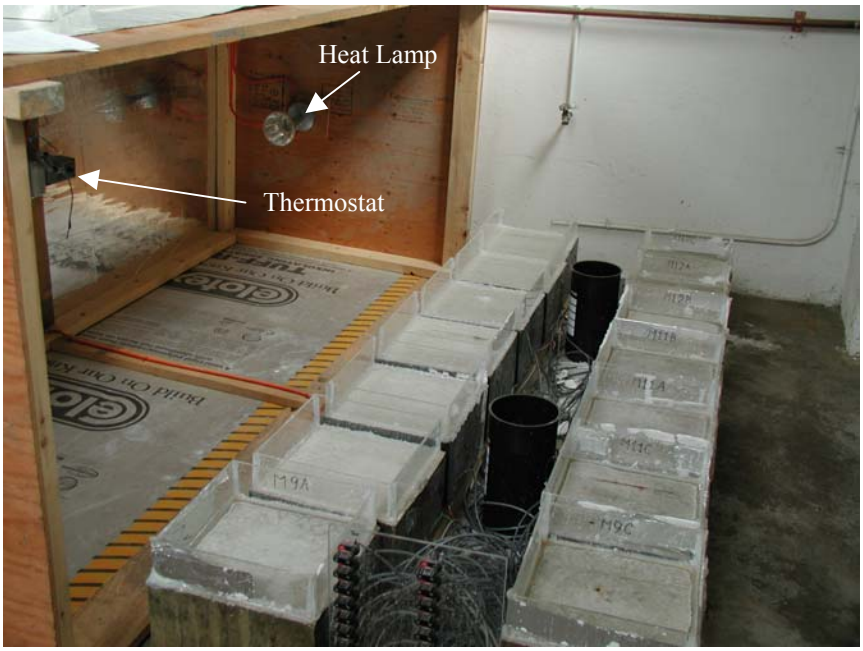


**Figure 5.5: Heat Lamp and Thermostat in the Temperature-Controlled Boxes**

**Figure 5.6: Macrocell Reading**

**Figure 5.7: Half-Cell Reading**

# 6. RESULTS

The data presented encompasses up to 108 weeks of data on 40 specimens and 84 weeks on mixes containing DSS that were autopsied (M6A and M10A). This data includes visual surveys, macrocell readings, half-cell readings, and autopsy information.

## 6.1. MACROCELL CORROSION CURRENT

### 6.1.1 Macrocell Activity

The macrocell data was graphed against time and is presented in Appendix B. In general, pre-cracked specimens showed much larger amounts of activity than their non-cracked counterparts. An exception to this is the original non-cracked silica fume specimens (M3), where shrinkage cracking occurred early in the specimens and subsequent corrosion activity was actually higher than in the pre-cracked counterpart. In addition, the combination of calcium nitrite and silica fume (M7) had initial activity much higher in the pre-cracked specimen, but with time this decreased, while the non-cracked specimens increased in activity with time to eventually reach similar values.

Two features in the macrocell graphs are significant. These are the time it took for the initial activity to occur, which was defined as 0.1 mV, and the time for the readings to elevate significantly. The second point was defined as the time for the readings to reach at least 0.5 mV. The two points signify the time to initial activity and the time to significant corrosion activity. Time to reach these values is tabulated in the first two result columns of Tables 6.1 and 6.2.

It can be seen that many of the control and single admixture specimens showed initial activity almost immediately for the non-cracked specimens. Calcium nitrite (M2) and DSS (M6) did not show any initial activity, nor did the re-cast fly ash specimen (4BR). Time to elevated readings was typically also immediate for those showing any activity. However, it should be noted that the one slag mix (5B1) showed initial activity but readings were never elevated above these, therefore resulting in extreme variations in results depending on which criteria is used to determine “significance”. Non-cracked specimens with double admixtures (M7 to M10) did not perform as well as calcium nitrite alone (M2), with the exception of calcium nitrite with DSS, which combined the two excellent performing single admixtures. Only calcium nitrite plus silica fume (M7) showed

any consistently elevated readings, possibly indicating the potential of micro-cracking when silica fume was used. Triple combinations of calcium nitrite, silica fume, and either fly ash or slag significantly slowed corrosion activity, as did a double combination of calcium nitrite and slag. The performance of M3 and M7 indicates the potential for micro-cracking with silica fume concretes when complete curing does not take place. Curing was similar for all mixes. This potential problem was minimized when additional fly ash or slag was introduced (M11 and M12), and relatively improved when a higher w/c ratio was used (M13). Higher w/c ratio resulted in worse performance when micro-cracking was not a concern (M11 versus M14).

When specimens included a pre-crack (C specimens), all except those including DSS (M6 and M10) showed immediate activity and elevated readings (Table 6.2).

### 6.1.2 Cumulative Macrocell Data

As a measure of corrosion activity, it may be more meaningful to evaluate the cumulative corrosion activity rather than an absolute instantaneous current. This would give information on the total corrosion that has developed over time. This can be used to compare the effectiveness of admixtures in limiting corrosion activity once it initiates as well as the prevention of corrosion initiation. Therefore, the macrocell data was converted into approximate iron lost data.

The conversion was made by dividing the voltage from each reading by the value of the resistor (10 Ohms) and multiplying this by the averaged number of hours at that reading, providing cumulative corrosion current. The corrosion current was then used to calculate the percentage of iron lost from each reinforcing bar using the relationship derived in Section 5.3.2 of 1.04 grams of iron lost per amp hour and an average (measured) initial bar mass of 408 g (0.90 lb). The percentage of iron lost per reinforcing bar was calculated at twelve-week intervals and reported in Figures 6.1 to 6.7. Note that data is only included through 84 weeks for specimens M6A and M10A due to their later casting dates. These two specimens were autopsied at the same time as the other specimens; additional specimens with later casting dates had their ponding cycles extended by 24 weeks as compared to the other specimens.

For non-cracked specimens, minimal cumulative iron lost was consistently found in mixes M2, M6, M9, M10, and M11. Very low values occurred for mixes M8 and M12. When pre-cracking was introduced, DSS specimens (M6C and M10C) showed significantly improved behavior over the control. Of pre-cracked single admixture specimens, fly ash (M4C) and one reading of the slag (M5C) specimens also had reduced iron losses of 1/4 to less than 1/2 of the control. The double combination of M8C provided reductions on the order of the single combination of M4C, while M9C showed significant improvement over M5C. This indicates the benefit of fly ash or slag in preventing corrosion in cracked specimens. Note that this was also seen when comparing M3 and M7 (silica fume without fly ash or slag, which developed micro-cracking) to M11 and M12 (including fly ash or slag) in non-cracked specimens. The addition of fly ash or slag to a silica fume mix (M11 and M12) could therefore act to minimize micro-cracking of incompletely cured concretes, as well as minimize corrosion rates in a cracked member. The two triple combinations (M11C and M12C) performed well, with the addition of fly ash (M11) performing slightly better than the addition of slag (M12). However, neither of these improved significantly on the double admixture of calcium nitrite and slag (M9).

When higher w/c ratio of 0.47 was included in M13 and M14, rather than 0.40 in other specimens, the double combination performed better with the higher w/c ratio in non-cracked specimens (M13A and M13B vs. M7A and M7B), likely due to reduced micro-cracking. The effectiveness of the triple combination improved with the lower w/c (M11A and M11B vs. M14A and M14B). In the pre-cracked specimens, double combinations (M13C vs. M7C) and triple combinations (M14C vs. M11C) performed similarly for both w/c ratios. Ultimately, the triple combinations retarded the rate of corrosion in both cases, showing the effectiveness throughout typical w/c ranges.

For concrete without cracking, results show the best performance from calcium nitrite and DSS, alone or in combination, a double combination of calcium nitrite and slag, and triple combinations of calcium nitrite, silica fume, and either fly ash or slag. When cracking is present, however, calcium nitrite specimens did not show any improvement over the control. For these cracked conditions, DSS, fly ash, a double combination of calcium nitrite and slag, or triple combinations of admixtures showed the least cumulative current. Overall, for all conditions, the results indicate that triple admixture combinations

similar to M11 and M12, a double combination of calcium nitrite and slag, or DSS should be considered. However, DSS needs further study before it can be recommended for field use, to ensure that other material properties are not adversely affected.

## 6.2. HALF-CELL CORROSION CURRENT

The half-cell data was graphed against time and is presented in Appendix C. Readings were taken on Fridays, although some Monday readings were also taken. Monday readings varied by as much as 33% from the Friday readings, indicating the criticality of moisture content when taking half-cell readings, with Friday readings being the more accurate. The half-cell data is considered to be an indicator of whether or not there is corrosion at the anodic reinforcing bars. Many of the studies that were reviewed had different readings that they considered to be the indicator for corrosion. The most common readings included -0.240 mV, -0.350 mV, and -0.450 mV. The time it took for the readings to reach each of these three values was recorded in columns four to six of Tables 6.1 and 6.2. It can be seen that these different criteria can give very different results for some of the specimens. In general, there are slight differences between the criteria of -0.240 mV and -0.350 mV, although mixes 5, 8, 9, 11, and 12 have some readings where these values diverge significantly. In surveying the data in Appendix C it is noted that a visual jump in readings typically exceeds the -0.240 mV value, while other values (-0.350 mV or -0.450 mV) may be too stringent to capture this jump in readings. Perhaps a visual evaluation of the plots is more accurate than defining any particular "critical value" and explains the disagreement as to what this value should be. An exception to the -0.240 mV criteria is M12B1, which never reached this value but had a visual jump in readings at 52 weeks.

## 6.3. VISUAL INSPECTIONS

### 6.3.1 Visible Cracking

The information gathered through the visual surveys included crack propagation in all of the specimens. The surveys were performed near the end of each section of the cycles (approximately every 12 weeks). The maximum widths of the cracks were also measured during these times. This was done using a manual crack gage. Crack widths

usually stabilized at approximately 0.2 mm (0.01 in.), with the exception of the silica fume specimens where the cracks widened continuously. Tables 6.1 and 6.2 show the time to cracking. The values given for the pre-cracked specimens represent information about the extension of the preexisting cracks only.

Non-cracked specimens that did not show any visible cracking at the conclusion of testing were calcium nitrite (M2A and M2B), DSS (M6A and M6B), calcium nitrite/fly ash (M8A and M8B), calcium nitrite/slag (M9A and M9B), and calcium nitrite/DSS (M10A and M10B). Others in which one specimen did not exhibit visible cracking included slag (M5B), calcium nitrite/silica fume/fly ash (M11B), calcium nitrite/silica fume/slag (M12A), calcium nitrite/silica fume with higher w/c ratio (M13B), calcium nitrite/silica fume/fly ash with higher w/c ratio (M14A), and the re-cast fly ash specimen (M4B).

All pre-cracked specimens had crack extensions within the first cycle of ponding, except for specimens including DSS (M6C and M10C), which did not exhibit any extensions, and combinations M11C and M13C, which took in excess of one year of testing to produce crack extensions.

### 6.3.2 Visible Corrosion on Reinforcement

Autopsy results for 26 specimens are shown in Tables 6.3 and 6.4. One non-cracked and the pre-cracked specimen were autopsied for all those tested to 108 weeks. Mixes M6 and M10 only had one non-cracked specimen autopsied. All bottom reinforcement was removed and had no corrosion product with the exception of M14C, which had minimal corrosion, and M14B, which had positive macrocell readings. Corroded surface area is reported. Note that this is surface area only, and is not a representation of volume of corroded material.

Overall, in pre-cracked specimens (Table 6.4), no specimens showed significantly less corroded surface area than the control specimens (M6 and M10 were not autopsied). In the non-cracked specimens (Table 6.3), calcium nitrite (M2), DSS (M6), or combinations of the two (M10) showed no corrosion activity. The triple combination of calcium nitrite/silica fume/slag (M12) also showed no corrosion activity (although it is noted that M12B2 has higher iron losses reported and this specimen was not autopsied). Reduced corrosion activity was also found in the slag (M5), calcium nitrite/fly ash (M8), calcium

nitrite/slag (M9), and calcium nitrite/silica fume/fly ash (M11 and M14). Those with silica fume alone (M3), or silica fume and calcium nitrite only (M7) showed significantly more corrosion than the control.

## 6.4. REPLACED SPECIMENS

Approximate iron lost, visual inspection, and chloride ingress testing were performed for the three replaced specimens. These were removed from the testing program at 24 weeks. The silica fume specimen had the largest number and width of cracks. Destructive evaluations were performed to inspect the reinforcing bars inside. Each top reinforcing bar was inspected further to estimate the amount of corrosion on its surface. These results are presented in Table 6.5. Visually, the control (M1A) showed the least corrosion, silica fume (M3B) had slightly more than the control, and fly ash (M4B) had slightly more than silica fume. Figure 6.8 shows the iron loss data. The percent iron lost is highest for the silica fume (M3B) and lowest for the fly ash specimen (M4B), contradicting the visual inspection data. The disparity between the two sets of data may happen because visual inspection cannot be very precise in its estimate, nor can it take into account the depth of the layer of rust. The bottom reinforcing bars had no visible rust. Macrocell readings were highest for silica fume (M3B) and lowest for fly ash (M4B), while half-cell readings were of similar values for all three specimens.

Three-inch cores were removed from the center section of the replaced specimens and chloride content analysis was performed at WJE. These results are presented in Table 6.6. These show that the silica fume and the fly ash specimens (M3 and M4 respectively) had larger chloride contents right below the surface than the control specimen. This was likely caused by cracks on the surface of specimens, although none were visible in the location of the corings. The silica fume specimen (M3) had the highest concentration through the 1 to 1-1/2 inch level, the depth at which the top reinforcing bars are located. The fly ash specimen (M4) had the lowest concentration at this level, and the results for the control were in between. This can also be attributed to the wide cracks noticed on the silica fume specimens (M3) during the visual inspection, which were noticed at least 4 weeks earlier than the control specimen (M1). The chloride content data correlates with the iron loss data. It appears that chloride ingress results were dominated by the presence of cracks

that allowed penetration of saline solutions. Chloride ingress data only provides meaningful comparisons when specimens are non-cracked or similarly cracked. This is rarely, if ever, the case in reinforced concrete specimens. The results give information on the permeability of the concrete but a crack extending to depth will override the results. Ideally these samples would be taken from duplicate specimens with no reinforcing bars included (as in previous WJE testing), but budget constraints precluded this option.

## 6.5. COMPARISON OF DATA

Tables 6.1 and 6.2 show that the values for initial activity of the macrocell readings usually occur between the time it took the half-cell readings to reach -0.240 mV and -0.350 mV, with -0.450 mV being far too restrictive. The -0.350 mV criteria corresponds more closely to macrocell initial activity in single admixtures, with the -0.240 mV criteria correlating closer to macrocell initial activity in the better performing combinations. Time to elevated macrocell readings generally falls between the -0.350 mV and -0.450 mV criteria. However, -0.350 mV and elevated macrocell readings were not attained in some specimens that corroded, as determined by the autopsies (M8A2, M9B1, and M11A2). For these specimens, initial macrocell activity and –0.240 mV half-cell criteria indicated corrosion activity. Therefore, for determining the "time to initiation of corrosion", initial macrocell activity and a half-cell criteria of –0.240 mV appear to be adequate, although visual inspection for a sudden increase in readings appears to be the best evaluation tool. Half-cell increases typically corresponded directly to a significant increase in macrocell readings.

Time to cracking was not generally a good indicator of corrosion activity, and is subject to individual judgement and error in inspecting specimen surfaces or setting criteria for "cracking".

All criteria, however, provided similar trends in results. Namely, they indicated the relative effectiveness of calcium nitrite (M2), DSS (M6), a double combination of calcium nitrite and DSS (M10), a double combination of calcium nitrite and slag (M9), and triple combinations (M11 and M12) in non-cracked concrete, and the DSS (M6) or a double combination of DSS and calcium nitrite (M10) in cracked concrete. The double

combination of calcium nitrite and slag (M9), and triple combinations (M11 and M12) also performed well in cracked specimens.

Much more distinction between corrosion activity was available when cumulative macrocell current was evaluated, such as the percent iron lost data presented.

## 6.6. RESULTS SUMMARY

The visual inspections, macrocell readings, half-cell readings, and chloride ingress data are important for the purpose of assessing performance and validating data, although the macrocell readings were the most informative. A direct evaluation of relative performance is presented in Tables 6.7 and 6.8 for non-cracked and pre-cracked specimens, respectively. In these tables, data of iron lost (Figures 6.1 to 6.7) was used to determine the relative performance of the mixes to that of the control. Averages of all available data (4 readings for specimens A and B, 2 readings for specimens C) were used. Note that the last 24 weeks of specimens 6 and 10 (A and B) had only 2 readings to average. Due to the vastly different behavior of mix 3A and the recast specimen 3BR, Table 6.7 lists both the average data and that of 3BR only.

For each 12-week cumulative cycle the specimens were rated in relation to the control mixes. A rating of "A" indicates Excellent behavior, with less than 1/20 the corrosion activity of the control. Very Good behavior ("B") indicates corrosion rates between 1/10 and 1/20 that of the control. Good behavior ("C") indicates corrosion rates between 1/10 and 1/3 that of the control. Fair behavior ("D") indicates corrosion rates between 1/3 and 1/2 that of the control. Marginal behavior ("E") indicates corrosion rates between 1/2 and 9/10 that of the control. Poor behavior ("F") indicates corrosion rates exceeding 9/10 of the control.

For non-cracked specimens (Table 6.7), it can be seen that "Excellent" behavior was observed in M2, M6, M9, M10 and M11. "Good" to "Very Good" performance was observed in M8, M12, M13 and M14. "Poor" behavior was only seen in M3 and M7 (due to micro-cracking). Specimens M3R, M4, M5, and M8 improved relative to the control with time.

Pre-cracked specimens are compared to the cracked control (M1C) in Table 6.8. At best, specimens performed in the "Good" to "Very Good" range (M6 and M10). Borderline

“Good” to “Fair” performance was observed in M4, M9, M11, M12, and M14. Corrosion rates in specimens M3, M4, M7, and M8 slowed significantly compared to the control with time. Table 6.9 compares similar pre-cracked data to the non-cracked control data (M1A/B). Only two mixes were consistently improved (“Good”) over the non-cracked control, M6 and M10, both containing DSS. Specimens M4, M9, M11, M12, M14 had somewhat similar values of iron lost to the non-cracked control at the end of testing (much higher at first), although initial corrosion was much higher than the control for M4, M9, and M14. The remaining specimens had much higher corrosion rates. Obviously, DSS far outperforms all other admixtures when cracking is present in the concrete, providing significant corrosion resistance even when chlorides have direct access to the reinforcement. For cracked specimens, triple combinations of admixtures (M11, M12 and M14), double combination of calcium nitrite and slag (M9), and fly ash alone (M4) provide significant improvements over the other single or double combinations of traditional admixtures studied (Note that M12 values ranged from 0.92 to 0.96).

Rating results from Tables 6.7 to 6.9 also agree reasonably well with “Time to Elevated Readings” and “Time to -0.240 mV” reported corrosion activity in Table 6.1. Pre-cracked specimen data from the cumulative macrocell readings was much more informative than that shown in Table 6.2.

A ranking of all specimens based on iron lost is shown in Table 6.10. Results in this table agree with other evaluations reported. A relative magnifier of iron loss referenced to the best performing mix is listed. Note that cracking occurred in specimens with greater than 0.1 percent iron loss (often well before this level of corrosion). This is much lower than the 0.6 percent mentioned in Section 2.1 due to non-uniform corrosion along the bar. Note that autopsies showed corrosion on as little as 10 percent of the surface area for these specimens (Table 6.3).

Overall, mix designs containing DSS (M6 and M10) exhibited the least corrosion, even in cracked concrete. Triple admixture combinations of calcium nitrite, silica fume, and fly ash or slag (M11 and M12) and double combination of calcium nitrite with slag (M9) consistently performed very well. Therefore, the addition of silica fume to calcium nitrite and slag mix designs adds little to performance at added expense. Calcium nitrite with fly ash (M8) also performed well. Adding calcium nitrite to single fly ash or slag

mixes resulted in 70 and 90 percent reductions in cumulative corrosion, respectively, for non-cracked specimens, and an increase of 50 percent and reduction of 55 percent, respectively, for cracked specimens. Adding silica fume to the calcium nitrite and fly ash mix resulted in a 70 and 35 percent reduction in cumulative corrosion in non-cracked and cracked specimens, respectively. Similar results (60 and 55 percent reductions) were found at the higher w/c ratio of 0.47 (M13 and M14). Worse performance was achieved when silica fume was added to the calcium nitrite and slag mix, although performance was still satisfactory. Calcium nitrite as a single admixture (M2AB) showed excellent performance in non-cracked concrete, but very poor performance in the presence of cracking (M2C). Specimens with only silica fume (M3AB), as well as silica fume plus calcium nitrite (M7AB), showed potential for micro-cracking. Even when this was prevented (M3RB), performance was similar to the other pozzolanic admixtures (M4AB and M5AB). General results were similar at the higher w/c ratio of 0.47, although corrosion rates were higher in the non-cracked triple combination specimens as compared to a similar specimen with w/c of 0.40.

Since it is virtually impossible to ensure crack prevention in a structure, only those mixes that performed well in both non-cracked and cracked conditions are recommended. DSS had excellent corrosion prevention properties, and appeared to have mechanisms of protection quite different from the other admixtures included as part of this study. The performance of DSS is especially notable in the pre-cracked conditions, with these specimens far outperforming even the non-cracked control. Its current availability, negative impact on mix strength, and unknown impacts on other concrete properties and interactions with admixtures remain issues that need to be resolved prior to widespread acceptance. DSS merits further study. Silica fume concretes (as a single admixture or in combination with calcium nitrite) were prone to micro-cracking and related deterioration through the study. These problems were overcome when a third admixture of either fly ash or slag was included in the mix design, despite some small cracks that also developed in the triple combination specimens. Therefore, pending further research on DSS, either a triple combination of calcium nitrite/silica fume/fly ash, or a double combination of calcium nitrite/slag (could add silica fume as well, but at added expense for little to no

apparent benefit) is recommended. These mixes also resulted in high compressive strengths, indicating a general improvement in material quality.

## Table 6.1: Corrosion Activity - Non-Cracked Specimens

| | Mix No. | Time to Initial Activity (weeks) | Time to Elevated Readings (weeks) | Time to -0.240mV CSC (weeks) | Time to -0.350mV CSC (weeks) | Time to -0.450mV CSC (weeks) | Time to cracking (weeks) |
|---|---|---|---|---|---|---|---|
| Control | 1A1 | 1 | 1 | 1 | 1 | 1 | 11 |
| | 1A2 | 1 | 1 | 1 | 1 | 1 | |
| | 1A1-R | 4 | 32 | 4 | 5 | 50 | 12 |
| | 1A2-R | 14 | 25 | 13 | 17 | 31 | |
| | 1B1 | 1 | 1 | 1 | 1 | 1 | 9 |
| | 1B2 | 1 | 1 | 1 | 1 | 1 | |
| Single Admixtures | 2A1 | NA | NA | 104 | NA | NA | NA |
| | 2A2 | NA | NA | NA | NA | NA | |
| | 2B1 | NA | NA | NA | NA | NA | NA |
| | 2B2 | NA | NA | NA | NA | NA | |
| | 3A1 | 1 | 1 | 1 | 1 | 1 | 7 |
| | 3A2 | 1 | 1 | 1 | 1 | 1 | |
| | 3B1 | 1 | 1 | 1 | 1 | 1 | 7 |
| | 3B2 | 1 | 1 | 1 | 1 | 1 | |
| | 3B1-R | 1 | 1 | 1 | 1 | 34 | 80 |
| | 3B2-R | 1 | 1 | 1 | 1 | NA | |
| | 4A1 | 1 | 1 | 1 | 1 | 1 | 11 |
| | 4A2 | 1 | 1 | 1 | 1 | 72 | |
| | 4B1 | 1 | 1 | 1 | 1 | 1 | 0 |
| | 4B2 | 1 | 1 | 1 | 1 | 1 | |
| | 4B1-R | NA | NA | NA | NA | NA | NA |
| | 4B2-R | 105 | NA | 35 | NA | NA | |
| | 5A1 | 1 | 1 | 1 | 1 | 6 | 11 |
| | 5A2 | 1 | 1 | 1 | 1 | 41 | |
| | 5B1 | 1 | NA | 1 | NA | NA | NA |
| | 5B2 | NA | NA | 2 | NA | NA | |
| | 6A1 | NA | NA | NA | NA | NA | NA |
| | 6A2 | NA | NA | NA | NA | NA | |
| | 6B1 | NA | NA | NA | NA | NA | NA |
| | 6B2 | NA | NA | NA | NA | NA | |
| Double Combinations | 7A1 | 3 | 3 | 3 | 3 | 7 | 28 |
| | 7A2 | 7 | 9 | 7 | 8 | 14 | |
| | 7B1 | 4 | 5 | 4 | 6 | 13 | 28 |
| | 7B2 | 1 | 3 | 2 | 2 | 7 | |
| | 8A1 | NA | NA | 96 | NA | NA | NA |
| | 8A2 | 9 | NA | 9 | 81 | 99 | |
| | 8B1 | 8 | NA | 8 | NA | NA | NA |
| | 8B2 | 2 | 2 | 1 | 2 | NA | |
| | 9A1 | 1 | NA | 1 | 102 | NA | NA |
| | 9A2 | NA | NA | NA | NA | NA | |
| | 9B1 | 4 | NA | 4 | NA | NA | NA |
| | 9B2 | NA | NA | NA | NA | NA | |
| | 10A1 | NA | NA | NA | NA | NA | NA |
| | 10A2 | NA | NA | NA | NA | NA | |
| | 10B1 | NA | NA | NA | NA | NA | NA |
| | 10B2 | NA | NA | NA | NA | NA | |
| Triple Combinations | 11A1 | NA | NA | NA | NA | NA | 49 |
| | 11A2 | 4 | NA | 4 | NA | NA | |
| | 11B1 | NA | NA | NA | NA | NA | NA |
| | 11B2 | NA | NA | NA | NA | NA | |
| | 12A1 | NA | NA | NA | NA | NA | NA |
| | 12A2 | NA | NA | NA | NA | NA | |
| | 12B1 | NA | NA | NA | NA | NA | 49 |
| | 12B2 | 1 | NA | 1 | 40 | NA | |
| w/c = 0.47 | 13A1 | 49 | 99 | 48 | 51 | 98 | 79 |
| | 13A2 | 1 | 1 | 1 | 1 | 38 | |
| | 13B1 | 48 | 51 | 48 | 51 | NA | NA |
| | 13B2 | 55 | NA | 54 | 58 | NA | |
| | 14A1 | 1 | 2 | 1 | 2 | NA | NA |
| | 14A2 | 1 | NA | 1 | 2 | NA | |
| | 14B1 | 69 | NA | 56 | 72 | NA | 108 |
| | 14B2 | 1 | NA | 1 | 4 | NA | |

## Table 6.2: Corrosion Activity - Pre-Cracked Specimens

| | Mix No. | Time to Initial Activity (weeks) | Time to Elevated Readings (weeks) | Time to -0.240mV CSC (weeks) | Time to -0.350mV CSC (weeks) | Time to -0.450mV CSC (weeks) | Time to crack extension (weeks) |
|---|---|---|---|---|---|---|---|
| Control | 1C1 | 1 | 1 | 1 | 1 | 1 | 11 |
| | 1C2 | 1 | 1 | 1 | 1 | 1 | |
| Single Admixtures | 2C1 | 1 | 1 | 1 | 1 | 1 | 10 |
| | 2C2 | 1 | 1 | 1 | 1 | 1 | |
| | 3C1 | 1 | 1 | 1 | 1 | 1 | 11 |
| | 3C2 | 1 | 1 | 1 | 1 | 1 | |
| | 4C1 | 1 | 1 | 1 | 1 | 1 | 11 |
| | 4C2 | 1 | 1 | 1 | 1 | 1 | |
| | 5C1 | 1 | 1 | 1 | 1 | 1 | 11 |
| | 5C2 | 1 | 1 | 1 | 1 | 1 | |
| | 6C1 | 24 | NA | 24 | 24 | 26 | NA |
| | 6C2 | 4 | NA | 5 | 10 | 25 | |
| Double Combinations | 7C1 | 1 | 1 | 1 | 1 | 1 | 10 |
| | 7C2 | 1 | 1 | 1 | 1 | 1 | |
| | 8C1 | 1 | 1 | 1 | 1 | 1 | 11 |
| | 8C2 | 1 | 1 | 1 | 1 | 1 | |
| | 9C1 | 1 | 1 | 1 | 1 | 9 | 10 |
| | 9C2 | 1 | 1 | 1 | 1 | 1 | |
| | 10C1 | 3 | 50 | 2 | 4 | 6 | NA |
| | 10C2 | 8 | NA | 7 | 9 | 18 | |
| Triple Combinations | 11C1 | 1 | 1 | 1 | 1 | 1 | 80 |
| | 11C2 | 1 | 1 | 1 | 1 | 1 | |
| | 12C1 | 1 | 1 | 1 | 1 | 1 | 11 |
| | 12C2 | 1 | 1 | 1 | 1 | 1 | |
| w/c = 0.47 | 13C1 | 1 | 1 | 1 | 1 | 1 | 63 |
| | 13C2 | 1 | 1 | 1 | 1 | 1 | |
| | 14C1 | 1 | 1 | 1 | 1 | 1 | 11 |
| | 14C2 | 1 | 1 | 1 | 1 | 1 | |

**Table 6.3: Percent Area Corroded – Non-Cracked Specimens**

| Specimen | Area Corrosion (%) |
|---|---|
| M1B1 | 17 |
| M1B2 | 16 |
| M2A1 | 0 |
| M2A2 | 0 |
| M3A1 | 58 |
| M3A2 | 65 |
| M4A1 | 16 |
| M4A2 | 15 |
| M5A1 | 7 |
| M5A2 | 7 |
| M6A1 | 0 |
| M6A2 | 0 |
| M7A1 | 70 |
| M7A2 | 46 |
| M8A1 | 0 |
| M8A2 | 7 |
| M9B1 | 8 |
| M9B2 | 0 |
| M10A1 | 1 |
| M10A2 | 0 |
| M11A1 | 0 |
| M11A2 | 6 |
| M12A1 | 0 |
| M12A2 | 0 |
| M13A1 | 27 |
| M13A2 | 14 |
| M14B1 | 1 |
| M14B2 | 3 |
| M14B1 Bottom | 5 |
| M14B2 Bottom | 4 |

**Table 6.4: Percent Area Corroded – Pre-Cracked Specimens**

| Specimen | Area Corrosion (%) |
|---|---|
| M1C1 | 28 |
| M1C2 | 47 |
| M2C1 | 23 |
| M2C2 | 23 |
| M3C1 | 62 |
| M3C2 | 44 |
| M4C1 | 34 |
| M4C2 | 30 |
| M5C1 | 27 |
| M5C2 | 53 |
| M7C1 | 60 |
| M7C2 | 25 |
| M8C1 | 35 |
| M8C2 | 52 |
| M9C1 | 9 |
| M9C2 | 41 |
| M11C1 | 67 |
| M11C2 | 21 |
| M12C1 | 40 |
| M12C2 | 19 |
| M13C1 | 48 |
| M13C2 | 33 |
| M14C1 | 69 |
| M14C2 | 64 |
| M14C1 Bottom | 2 |
| M14C2 Bottom | 1 |

**Table 6.5: Percent Area Corroded – Replaced Specimens**

| Specimen Label | Area Corrosion (%) |
|---|---|
| M1A1 | 5 |
| M1A2 | 10 |
| M3B1 | 10 |
| M3B2 | 10 |
| M4B1 | 15 |
| M4B2 | 10 |

## Table 6.6: Chloride Content of Replaced Specimens

| Mix No. | Depth Range | Water-soluble chloride, % by weight of sample |
|---|---|---|
| 1 | 0 - $^{3}/_{8}$" | 0.473 |
| 1 | $^{1}/_{2}$ - $^{7}/_{8}$" | 0.261 |
| 1 | 1 - 1$^{1}/_{2}$" | 0.146 |
| 1 | 3$^{1}/_{2}$ - 3$^{7}/_{8}$" | <0.008 |
| 3 | 0 - $^{3}/_{8}$" | 0.686 |
| 3 | $^{1}/_{2}$ - $^{7}/_{8}$" | 0.375 |
| 3 | 1 - 1$^{1}/_{2}$" | 0.229 |
| 3 | 3$^{1}/_{2}$ - 3$^{7}/_{8}$" | <0.008 |
| 4 | 0 - $^{3}/_{8}$" | 0.608 |
| 4 | $^{1}/_{2}$ - $^{7}/_{8}$" | 0.253 |
| 4 | 1 - 1$^{1}/_{2}$" | 0.025 |
| 4 | 3$^{1}/_{2}$ - 3$^{7}/_{8}$" | <0.008 |

## Table 6.7: Rating of Non-Cracked Specimens

| | Time | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Mix | 12 weeks | 24 weeks | 36 weeks | 48 weeks | 60 weeks | 72 weeks | 84 weeks | 96 weeks | 108 weeks | NOTES |
| M1AB | NA | NA | NA | NA | NA | NA | NA | NA | NA | |
| M2AB | A | A | A | A | A | A | A | A | A | |
| M3AB | F | F | F | F | F | F | F | F | F | >>Control |
| M3RB only | D | D | D | C | C | C | C | C | C | improving |
| M4AB | D | D | C | C | C | C | C | C | C | improving |
| M5AB | D | D | C | C | C | C | C | C | C | improving |
| M6AB | A | A | A | A | A | A | A | A | A | |
| M7AB | E | F | F | F | F | F | F | F | F | >Control |
| M8AB | C | C | B | B | B | B | B | B | B | improving |
| M9AB | A | A | A | A | A | A | A | A | A | |
| M10AB | A | A | A | A | A | A | A | A | A | |
| M11AB | A | A | A | A | A | A | A | A | A | |
| M12AB | B | A | A | A | B | B | B | B | B | |
| M13AB | C | C | C | C | C | C | C | C | C | |
| M14AB | C | C | C | C | C | C | C | C | C | |

| | |
|---|---|
| A | Excellent <0.05 |
| B | Very Good 0.05 to 0.10 |
| C | Good 0.11 to 0.33 |
| D | Fair 0.34 to 0.50 |
| E | Marginal 0.51 to 0.90 |
| F | Poor >0.91 |

## Table 6.8: Rating of Pre-Cracked Specimens

| | Time | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Mix | 12 weeks | 24 weeks | 36 weeks | 48 weeks | 60 weeks | 72 weeks | 84 weeks | 96 weeks | 108 weeks | NOTES |
| M1C | NA | NA | NA | NA | NA | NA | NA | NA | NA | |
| M2C | E | E | E | E | E | E | E | E | E | |
| M3C | F | F | E | E | E | E | E | E | E | improving |
| M4C | D | D | D | D | D | D | C | C | C | improving |
| M5C | E | E | E | E | E | E | E | E | E | improving slightly |
| M6C | A | A | B | B | B | B | C | C | C | |
| M7C | F | F | E | E | E | E | E | E | E | improving |
| M8C | E | E | E | E | D | D | D | D | D | improving |
| M9C | D | D | D | D | C | C | C | C | C | improving slightly |
| M10C | A | B | B | C | C | C | C | C | C | |
| M11C | C | D | C | C | C | C | C | C | C | |
| M12C | C | C | C | C | C | D | D | D | D | |
| M13C | E | E | E | E | E | E | E | E | E | |
| M14C | D | C | C | C | C | C | C | C | C | improving |

| | |
|---|---|
| A | Excellent <0.05 |
| B | Very Good 0.05 to 0.10 |
| C | Good 0.11 to 0.33 |
| D | Fair 0.34 to 0.50 |
| E | Marginal 0.51 to 0.90 |
| F | Poor >0.91 |

## Table 6.9: Rating of Pre-Cracked Specimens to Non-Cracked Control

| | Time | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Mix | 12 weeks | 24 weeks | 36 weeks | 48 weeks | 60 weeks | 72 weeks | 84 weeks | 96 weeks | 108 weeks | NOTES |
| M1A/B | NA | NA | NA | NA | NA | NA | NA | NA | NA | |
| M1C | F | F | F | F | F | F | F | F | F | improving |
| M2C | F | F | F | F | F | F | F | F | F | improving |
| M3C | F | F | F | F | F | F | F | F | F | improving |
| M4C | F | F | F | F | F | F | E | E | E | improving |
| M5C | F | F | F | F | F | F | F | F | F | improving |
| M6C | B | C | C | C | C | C | C | C | C | |
| M7C | F | F | F | F | F | F | F | F | F | improving |
| M8C | F | F | F | F | F | F | F | F | F | improving |
| M9C | F | F | F | F | E | E | E | E | E | improving |
| M10C | C | C | C | C | C | C | C | C | C | |
| M11C | F | F | F | E | E | E | E | E | E | improving |
| M12C | F | F | F | F | F | F | F | F | F | |
| M13C | F | F | F | F | F | F | F | F | F | improving |
| M14C | F | F | E | E | E | E | E | E | E | improving |

| | |
|---|---|
| A | Excellent <0.05 |
| B | Very Good 0.05 to 0.10 |
| C | Good 0.11 to 0.33 |
| D | Fair 0.34 to 0.50 |
| E | Marginal 0.51 to 0.90 |
| F | Poor >0.91 |

**Table 6.10: Ranking of all Mix Designs**

| Mix | Average Cumulative Iron Loss (%) Through 108 Weeks | Magnifier Over M10AB | Notes |
|---|---|---|---|
| M10AB | 4.93E-03 | 1X | No Cracking |
| M6AB | 5.39E-03 | 1X | No Cracking |
| M2AB | 5.45E-03 | 1X | No Cracking |
| M11AB | 6.80E-03 | 1X | Cracking in one specimen only |
| M9AB | 9.54E-03 | 2X | No Cracking |
| M12AB | 2.22E-02 | 4X | Cracking in one specimen only |
| M8AB | 2.33E-02 | 5X | No Cracking |
| M14AB | 3.78E-02 | 8X | Cracking in one specimen only |
| M3RB only | 6.52E-02 | 13X | Specimen with no initial cracking |
| M4AB | 7.82E-02 | 16X | Cracking in one specimen only |
| M5AB | 8.13E-02 | 16X | Cracking in one specimen only |
| M10C | 8.54E-02 | 17X | No Additional Cracking |
| M6C | 8.88E-02 | 18X | No Additional Cracking |
| M13AB | 9.54E-02 | 19X | Cracking in one specimen only |
| M14C | 2.51E-01 | 51X | |
| M4C | 2.52E-01 | 51X | |
| M11C | 2.54E-01 | 51X | |
| M9C | 2.55E-01 | 52X | |
| M12C | 2.96E-01 | 60X | |
| M1AB | 3.22E-01 | 65X | *Control* |
| M8C | 3.84E-01 | 78X | |
| M7AB | 3.96E-01 | 80X | |
| M3AB | 4.86E-01 | 98X | Premature Cracking in A |
| M7C | 5.31E-01 | 108X | |
| M5C | 5.67E-01 | 115X | |
| M13C | 5.76E-01 | 117X | |
| M3C | 5.80E-01 | 118X | |
| M2C | 6.65E-01 | 135X | |
| M1C | 8.11E-01 | 164X | *Control* |

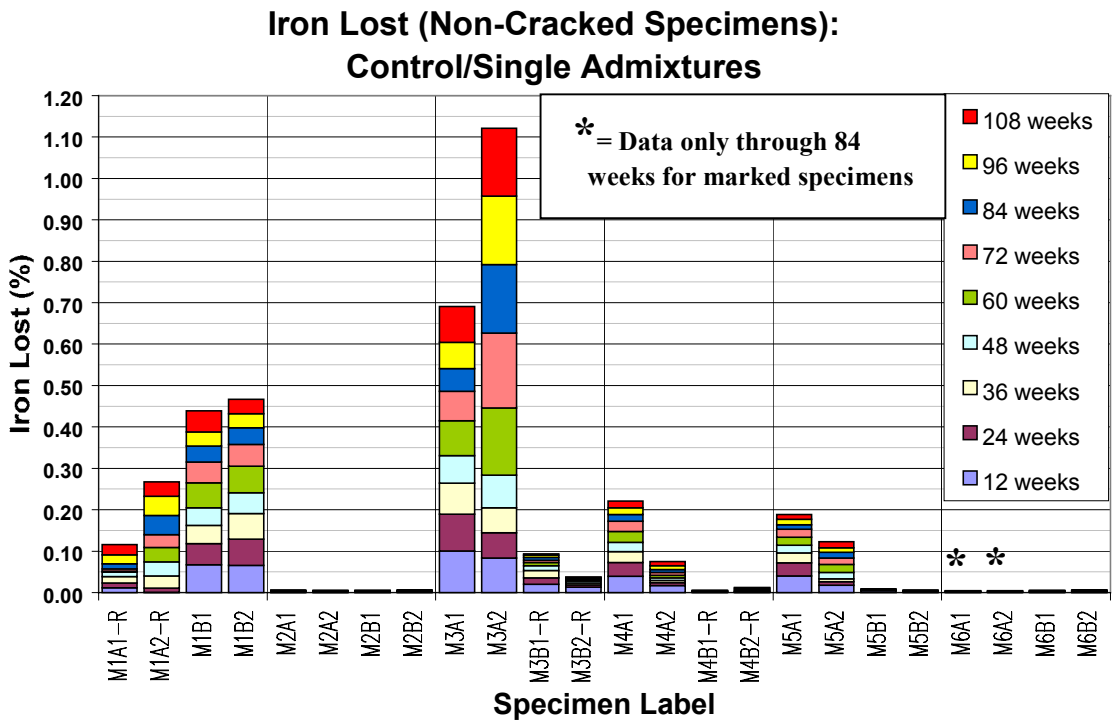


**Figure 6.1: Iron Lost Data – Control and Single Admixtures**

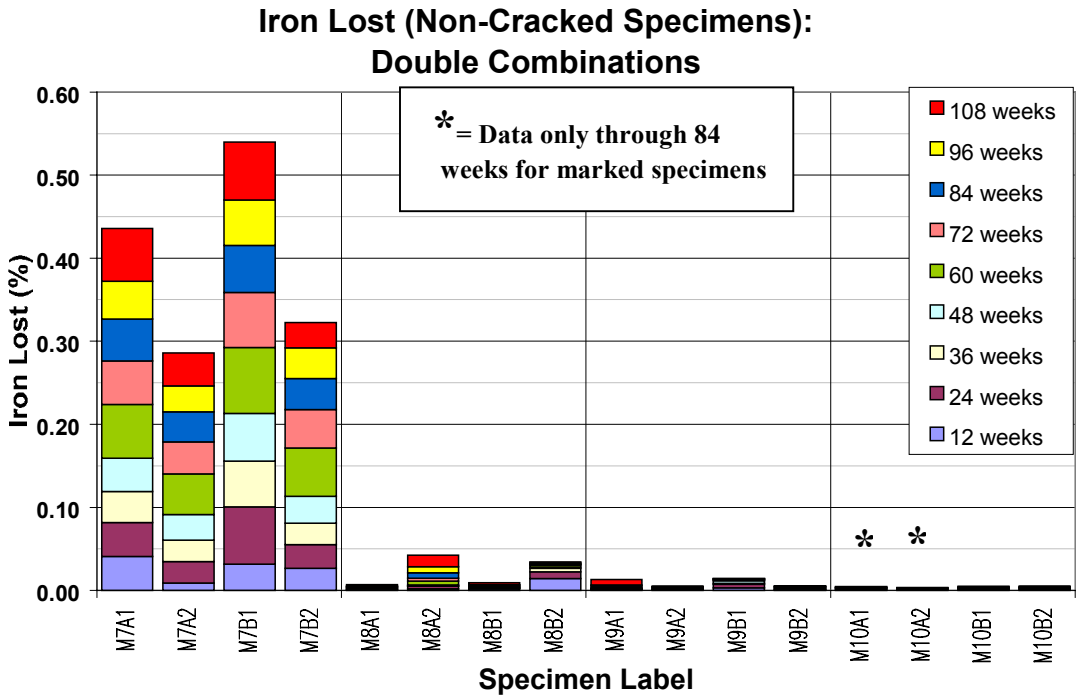


**Figure 6.2: Iron Lost Data – Double Admixtures**

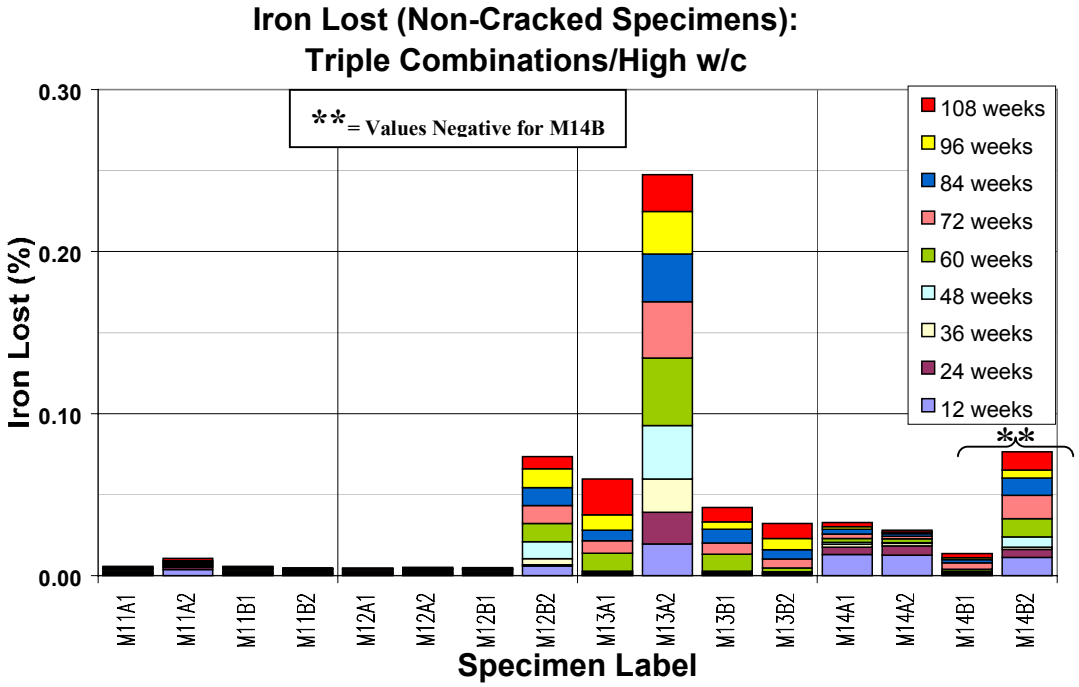


**Figure 6.3: Iron Lost Data – Triple Admixtures and Higher w/c**

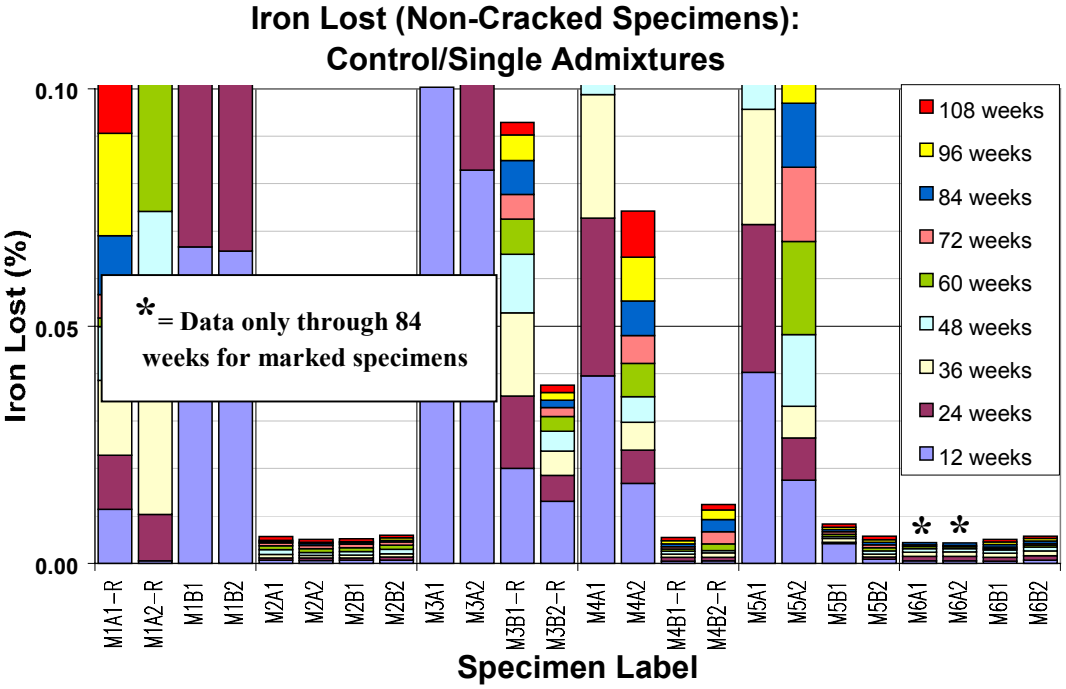


**Figure 6.4: Iron Lost Data Detail– Control and Single Admixtures**

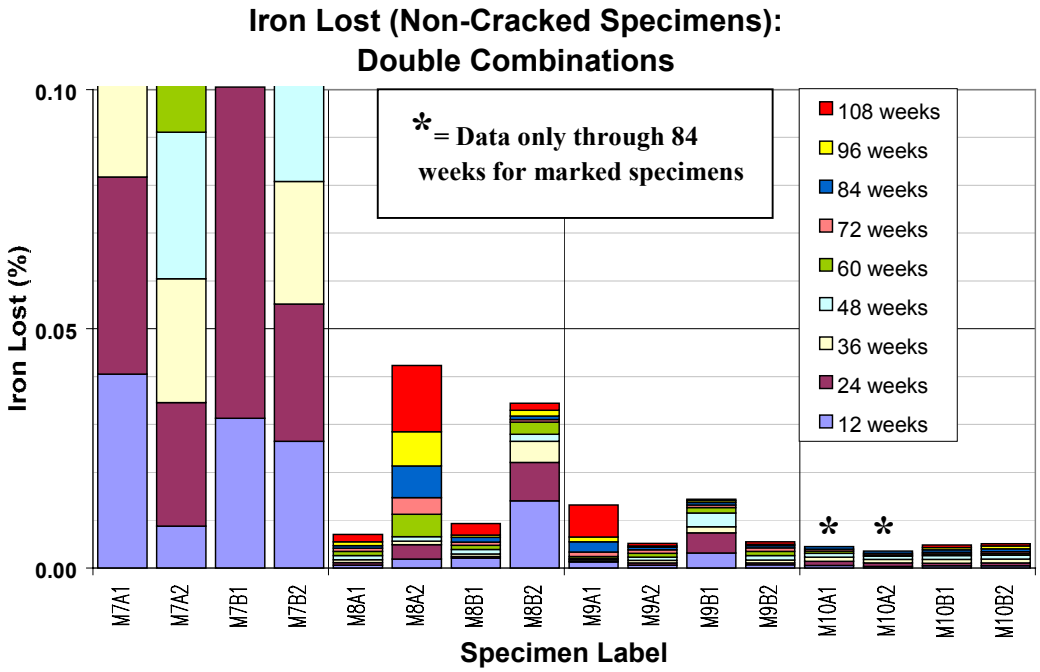


**Figure 6.5: Iron Lost Data Detail– Double Admixtures**

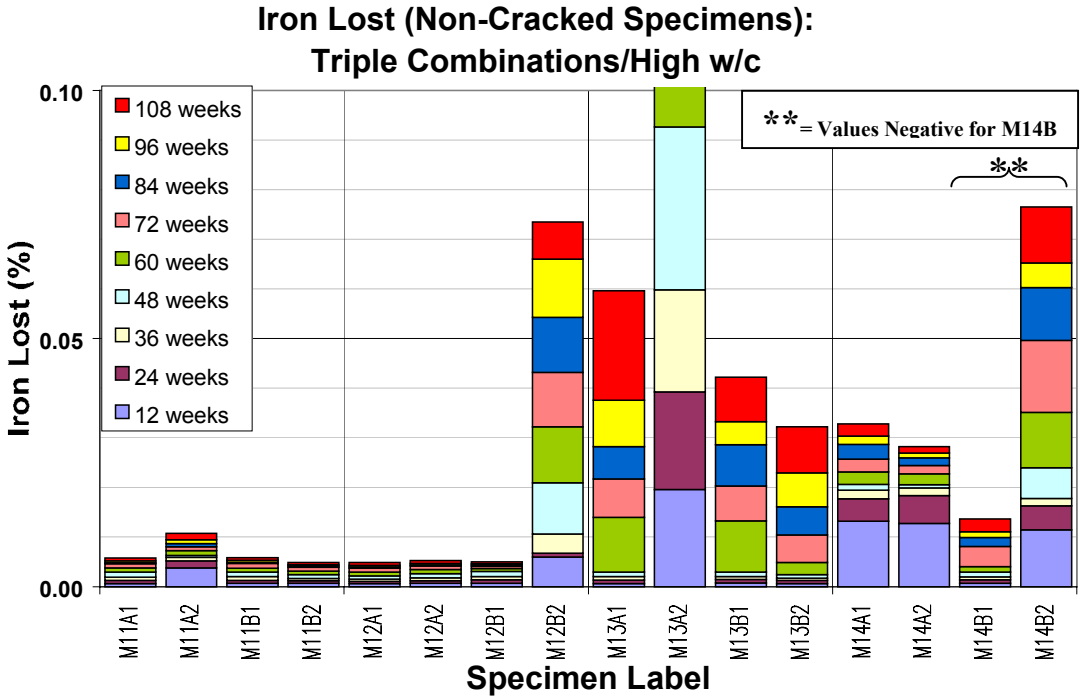


**Figure 6.6: Iron Lost Data Detail – Triple Admixtures and High w/c**

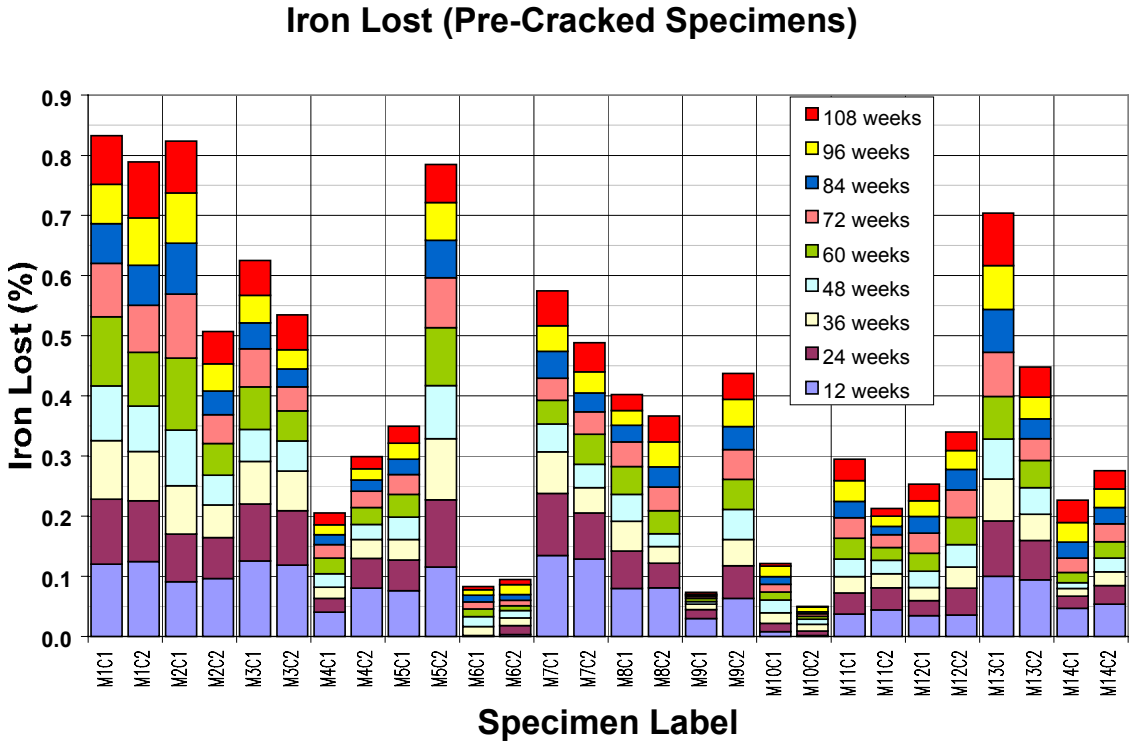


**Figure 6.7: Iron Lost Data – Pre-Cracked Specimens**

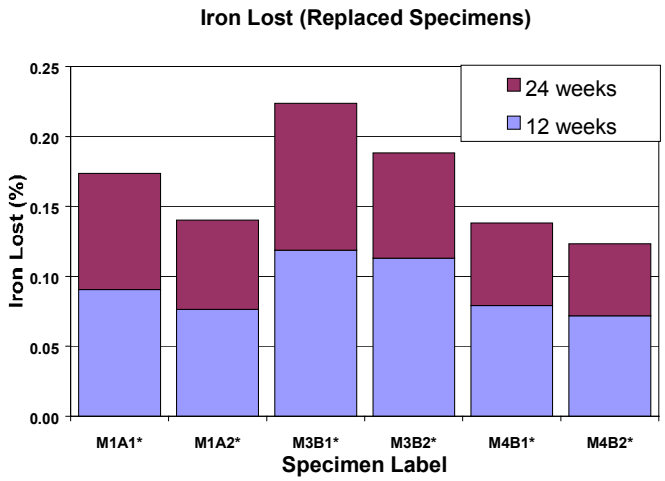


**Figure 6.8: Iron Lost Data – Replaced Specimens**

## 7. SUMMARY AND CONCLUSIONS

Corrosion of steel reinforcing bars in concrete structures is widespread in the New England area. Resulting structural deterioration costs millions of dollars in repairs and replacement. Corrosion inhibiting admixtures are typically included in the mix design to prevent this deterioration. However, there is very little data on the performance of these admixtures in the actual combinations and dosages used in practice. The five admixtures chosen for study in this project were calcium nitrite, silica fume, fly ash, slag, and DSS. The admixtures in the current project were tested individually and in double and triple combinations.

Results of the literature review showed favorable corrosion inhibiting properties for all five admixtures. Silica fume has been shown to potentially cause the concrete to crack if not consolidated and cured under more rigorous standards than typical mix designs, and cause more corrosion to develop. Potential negative aspects of the other four admixtures include a reduction of late age strength with calcium nitrite, a delayed setting time with slag, a decrease in compressive strength with DSS, and a decrease in chloride threshold with fly ash. There is very limited information regarding the effectiveness of combinations of admixtures in the literature. However, a survey of New England DOT's verified that such mix designs are common in the region.

A two-year corrosion testing protocol was established to compare 14 mix designs incorporating various combinations of admixtures. The specimens were designed to simulate the conditions of cyclically ponded salt water on a bridge deck, although at an accelerated rate. The mix designs (containing single, double, or triple combinations of admixtures) were evaluated using visual evaluation, half-cell potential readings, macrocell readings, and autopsies.

Although the original project scope included a life-cycle cost analysis of the different admixtures, unforeseen circumstances prevented their inclusion. A change in test protocol and the lack of corrosion in many of the specimens in the first half of the study mandated a decision to extend the cyclic ponding to maximize corrosion activity over the course of the project. This came at the expense of chloride diffusion analysis. Therefore data on chloride diffusion and other information typically used in an economic analysis was not obtained. However, it can be estimated that a structure's service life is a function

of the cumulative corrosion activity. Data presented in Chapter 6 specifically related corrosion activity as a fraction of activity in the control specimens (1/20, 1/10, 1/3, 1/2, 9/10).

Over the course of 108 weeks of cyclic ponding, minimal corrosion was detected in non-cracked specimens containing calcium nitrite (M2), DSS (M6), or a combination of the two (M10). Triple combinations of calcium nitrite, silica fume, and either fly ash or slag (M11 and M12), and a double combination of calcium nitrite and slag (M9), also performed very well. No benefit was realized from adding silica fume to the calcium nitrite and slag mix, so the added expense does not appear to be warranted. The recommended mixes of M11, M12, and M9 also resulted in high compression strengths, indicating an overall improvement in material performance and quality. A double combination of calcium nitrite and fly ash showed improvements over the control specimens. When specimens were pre-cracked, allowing chloride access directly to the reinforcing bar anode, DSS specimens (M6 and M10) once again outperformed all other specimens. Triple combinations (M11, M12, and M14), a double combination of calcium nitrite and slag (M9), and fly ash alone (M5) were greatly improved over the control, with the calcium nitrite and fly ash combination (M8) also improving performance.

Overall, significant improvement in minimizing corrosion was realized through the use of triple admixture combinations, a double combination of calcium nitrite and slag, or DSS. Double combinations also typically outperformed single admixtures. For non-cracked concrete, calcium nitrite as a single admixture provided excellent protection, but was not effective in pre-cracked specimens. DSS had excellent corrosion prevention properties and merits further study. DSS appeared to have mechanisms of protection quite different from the other admixtures included as part of this study. Its current availability, negative impact on mix strength, and unknown impacts on other concrete properties and interactions with admixtures remain issues that need to be resolved prior to widespread acceptance. The potential for early micro-cracking in silica fume concrete was minimized when fly ash or slag was included in the mix design.

All admixtures and combinations studied have merit. For optimal protection against corrosion in structures a triple combination of calcium nitrite, silica fume, and fly ash, or a double combination of calcium nitrite and slag (all at moderate dosages) is recommended

at this time. The triple combination of calcium nitrite, silica fume, and slag also would also be effective, although the addition of silica fume would add cost without any discernible improvement in performance. With further verification of its effects on material properties and chemical interactions, DSS could be an extremely effective admixture to prevent corrosion of transportation structures.

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# APPENDIX A

# LITERATURE REVIEW SUMMARIES

**Reference:** Al-Amoudi, O. S. B., Rasheeduzzafar, and Maslehuddin, M., "Permeability and Corrosion Resisting Characteristics of Fly Ash Concrete in Arabian Gulf Countries." *Fly Ash, Silica Fume, Slag, and Natural Pozzolans in Concrete* (Proceedings Third International Conference Trondheim, Norway), ACI SP-114, V. 1, 1989, pp. 295-313.

**Variables:** Class F fly ash (20% cement replacement, w/c of 0.35, 0.39, 0.45, 0.5, and 0.55).

**Specimens:** Concrete prisms with embedded reinforcing steel, partially immersed in 5% NaCl solution.
Concrete beams with top and bottom reinforcing steel, partially immersed in 5% NaCl solution.

**Test Methods:** Half-cell potential (similar to ASTM C876).
Linear polarization resistance (similar to ASTM G59).
Porosity (using helium gas expansion Boyle's Law porosimeter).
Water permeability.
Chloride concentration.
Time to cracking and weight loss of prism at exposure site.

**Results:** The fly ash concrete had a 16% improvement in porosity and a 33% improvement in permeability after one year with respect to the control.
The reaction between fly ash and calcium hydroxide in hydration did not reduce the pH value below the alkalinity of pure saturated calcium hydroxide (pH=12.5); the passivation threshold level is 11.5.
After four years of immersion in the salt solution, the fly ash concrete showed lower half-cell potential values when compared to plain concrete. The corrosion rates for the rebars in plain concrete were two to six times that of the fly ash concrete.

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**Reference:** Al-Amoudi, O. S. B., Rasheeduzzafar, Maslehuddin, M., and Abduljauwad, S. N., "Influence of Sulfate Ions on Chloride-Induced Reinforcement Corrosion in Portland and Blended Cement Concrete." *Cement, Concrete, and Aggregates*, V. 16, No. 1, June 1994, pp. 3-11.

**Variables:** Silica fume (10% cement replacement, w/c of 0.5).
Class F fly ash (20% cement replacement, w/c of 0.5).
Slag (60% cement replacement, w/c of 0.5).

**Specimens:** Concrete cylinders with embedded/protruding reinforcing steel, partially immersed in chloride and/or sulfate solutions.

**Test Methods:** Half-cell potential (similar to ASTM C876).
Linear polarization resistance (similar to ASTM G59).
Pore solution analysis.

**Results:** Time to initiation of corrosion in all mixes was not influenced by the concomitant presence of chloride and sulfate ions. The time to corrosion initiation where aggressive ions diffuse from the external environment depended on the microstructure of the cement matrix that controls diffusion.
When chlorides and sulfates reached the steel, the presence of the sulfates increased the corrosion current density in all the mixes.
Silica fume cement concrete performed 5 times better than Type I and Type V cement concretes in terms of time to initiation of corrosion. Corrosion current density was lower in the silica fume concrete than in the other concretes and below the threshold value. Its good performance was due to its dense structure, low oxygen diffusion, and high electrical resistivity.
Fly ash cement concrete performed 1.5 times better than the Type I cement concrete in

terms of time to initiation of corrosion.
Type I cement concrete performed better than Type V cement concrete because of the chloride binding ability of the $C_3A$.
The presence of chlorides at the time of mixing changed the pore solution by increasing the concentration of free chlorides and the $Cl^-/OH^-$ ratio, thereby creating a more aggressive corrosive environment.

**Drawback:** Tests only used relatively high w/c concrete.

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**Reference:** Alonso, C., and Andrade, C., "Effect of Nitrite as a Corrosion Inhibitor in Contaminated and Chloride Free Carbonated Mortars." *ACI Materials Journal*, V. 87, No. 2, March-April 1990, pp. 130-137.

**Variables:** Sodium nitrite (2% and 3% addition by weight of cement, w/c of 0.50 with admixed NaCl).

**Specimens:** Concrete beams with two embedded reinforcing steel bars (carbonated prior to testing).

**Test Methods:** Corrosion potential.
Polarization resistance (similar to ASTM G59).
Electrochemical weight loss.

**Results:** Sodium nitrite at these concentrations reduced the effect of carbonation; however, this protection was not effective when concrete was under both carbonation and chloride attack.
Nitrites' inhibiting effects were enhanced in cured concrete that was wet.
The higher the concentration of nitrites, the higher the protection level.

**Drawback:** Tests only used relatively high w/c concrete.

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**Reference:** Al-Saadoun, S. S., Rasheeduzzafar, and Al-Gahtani, A. S., "Corrosion of Reinforcing Steel in Fly Ash Blended Cement Concrete." *Journal of Materials in Civil Engineering*, V. 5, No. 3, Aug. 1993, pp. 356-371.

Hussain, S. E., and Rasheeduzzafar, "Corrosion Resistance Performance of Fly Ash Blended Cement Concrete." *ACI Materials Journal*, V. 91, No. 3, May-June 1994, pp. 264-272.

**Variables:** Fly ash (10%, 20%, and 30% cement replacement, w/c of 0.50)

**Specimens:** Concrete prisms with embedded/protruding reinforcing steel, partially immersed in 5% NaCl solution.
Cement past disks

**Test Methods:** Half-cell potential (similar to ASTM C876).
Visual examination/weight loss.
Electrical resistivity.
Permeability.
Chloride diffusion on the paste.
Pore size distribution on paste.

**Results:** Best performance in terms of corrosion initiation time was with the 30% replacement, which improved the corrosion resistance two and three times over that of Type I and Type V cements, respectively.
Lignite fly ash provided better impermeability and corrosion resistance than the

bituminous and sub-bituminous fly ashes.

Unbound chlorides in the pore solution decreased with fly ash cement replacements on the order of 30%. This indicated that fly ash may have bound itself with the free chlorides.

The fly ash blending with Type I cement showed a reduced corrosion rate of 1.6 times.

The 30% fly ash with Type I cement improved the physical structure of the concrete, refined the pore size distribution, reduced the coefficient of permeability and chloride diffusion by 5 times, and increased electrical resistivity of concrete 2.2 times.

Hydroxyl ion concentrations in the pore solutions of fly ash/Type V and Type I cements were less than in corresponding plain cements. The Type V cement and 30% fly ash decreased the $OH^-$ by an average of 21%. The Type I cement and 30% fly ash had a decrease of $OH^-$ by an average of 40%.

Fly ash caused small changes in the $Cl^-/OH^-$ ratio of pore solutions. The Type V cement and fly ash caused a maximum reduction of 30% in the $Cl^-/OH^-$ ratio. The Type I cement and fly ash increased the $Cl^-/OH^-$ ratio by a maximum of 40%.

**Drawback:** Tests only used relatively high w/c concrete.

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**Reference:** Andrade, C., Alonso, C., Acha, M., and Malric, B., "Preliminary Testing of $Na_2PO_3F$ as a Curative Corrosion Inhibitor for Steel Reinforcements in Concrete." *Cement and Concrete Research*, V. 22, No. 5, 1992, pp. 869-881.

**Variables:** $Na_2PO_3F$ (MFP) (0, 0.05, 0.1, and 0.5 M, in solution and added to concrete mixing water with 0.5 M NaCl, w/c of 0.50).

MFP (0.1 and 0.5 M in immersion solution with 0.5 M NaCl to penetrate the specimens, no chlorides in mixing water, w/c of 0.50).

MFP (0.1 and 0.5 M in immersion solution to penetrate the specimens, 0.5 M NaCl in mixing water, w/c of 0.50).

**Specimens:** Mortar beams with two reinforcing steel bars and one graphite bar, submitted to cyclic wetting/drying cycles and/or immersion.

Steel specimens in solution.

**Test Methods:** Corrosion potential.

Polarization resistance (similar to ASTM G59).

**Results:** $Na_2PO_3F$ (MFP) seemed to act as an anodic inhibitor in the presence of NaCl when added in alkaline solutions to the mortar mix.

The inhibitor was more effective in the same proportions when added to the mortar mix than in the solutions.

When MFP was added to the mortar mix, it was able to resist chloride attack when the ratio of concentrations of MFP to chloride was greater than 1.

The inhibitor was also effective when it penetrated through the pores of hardened concrete; this could reduce or stop corrosion.

**Drawbacks:** Tests only conducted in solution and on relatively high w/c mortar.

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**Reference:** Anqi, L., Baoyu, L., Gouping, H., Yeibo, C., and Guolian, S., "Study on Corrosion Prevention in Reinforced Concrete Containing Condensed Silica Fume and Its Application." *Durability of Concrete* (Second International Conference, Montreal, Canada), ACI SP-126, V. 1, 1991, pp. 499-509.

**Variables:** Silica fume (0%, 6%, 8.5%, 9.5%, 11.5%, and 14.5% addition by weight of cement, w/c

of 0.45 and 0.55).

**Specimens:** Concrete beams and cylinders subjected to cyclic ponding with 3.5% NaCl solution.
Concrete beams with an embedded steel reinforcing bar subjected to cyclic ponding with 3.5% NaCl solution.

**Test Methods:** Resistance to chloride ion penetration.
Rapid electrochemical chloride penetration.
Electrical resistivity of concrete.
Gravimetric weight loss.
Compressive strength.

**Results:** Silica fume showed improvements in concrete strength and impermeability; these properties also more than doubled as w/c decreased.
Tests indicated that using silica fume was more effective than a decrease in the w/c of conventional concrete to improve durability.
Silica fume increased impermeability by 4 to 46 times.
Silica fume increased electrical resistivity by 2 to 9 times.
Silica fume decreased the chloride ion ($Cl^-$) concentration surrounding the rebar (at 3 cm cover) by 9 times after seawater cycles.
The 14.5% silica fume concrete performed better than the 6% silica fume concrete; there was little difference between the 11.5% and 14.5% silica fume concrete mixes.

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**Reference:** Batis, G., Kouloumbi, N., and Katsiamboulas, A., "Durability of Reinforced Lightweight Mortars with Corrosion Inhibitors." *Cement, Concrete, and Aggregates*, V. 18, No. 2, Dec. 1996, pp. 118-125.

**Variables:** Sodium nitrite (2% and 5% by weight of cement, w/c of 0.50 - 0.90)
Sodium benzoate (1% and 2% by weight of cement, w/c of 0.50 - 0.90)
Iron oxides (5% and 10% by weight of cement, w/c of 0.50 - 0.90)

**Specimens:** Mortar beams with reinforcing steel in the corners, partially immersed in NaCl solution.

**Test Methods:** Half-cell potential (similar to ASTM C876) .
Gravimetric mass loss.

**Results:** Sodium nitrite offered superior protection, lowering the steel mass loss after 8 months exposure by 47% to 55%, depending on the concentration.
All the inhibitors tested had a protective effect on the steel.
The most efficient inhibitor tested was the sodium nitrite at the 2% and 5% concentrations.

**Drawback:** Tests only used high w/c concrete.

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**Reference:** Berke, N. S., "The Effects of Calcium Nitrite and Mix Design on the Corrosion Resistance of Steel in Concrete (Part 2, Long-Term) Results." *Corrosion/87* (Papers of the International Corrosion Forum Devoted Exclusively to the Protection and Performance of Materials, March 9-13, 1987, Moscone Center, San Francisco, California), Paper Number 132, 1987, pp. 132/1-132/11.

**Variables:** Calcium nitrite (30% solution, 14.9-30.2 $l/m^3$, w/c of 0.38-0.64).

**Specimens:** Concrete cylinders with embedded/protruding reinforcing steel, partially submerged in 3% NaCl solution.

**Test Methods:** Polarization resistance (similar to ASTM G59).
AC impedance measurements.
Total chloride/nitrite analysis (similar to Florida DOT Research Report 203 PB 289620).
Visual survey.

**Results:** Up to 2.5 years of testing, a 0.49 w/c concrete with 14.9 $l/m^3$ of 30% calcium nitrite outperformed a 0.38 w/c concrete without calcium nitrite.
Calcium nitrite improved the corrosion resistance of steel in concrete with w/c less than 0.50.
Chloride concentration levels were reduced when the w/c was decreased.
Polarization resistance and AC impedance testing methods accurately predicted the corrosion rates in concrete, with polarization resistance being the less complicated and lower cost method.
Even after corrosion had started, calcium nitrite lowered the rate of corrosion over that of the control specimens.

**Drawback:** Research conducted/reported only by W.R. Grace personnel.

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**Reference:** Berke, N. S., "Resistance of Microsilica Concrete to Steel Corrosion, Erosion, and Chemical Attack." *Fly Ash, Silica Fume, Slag, and Natural Pozzolans in Concrete* (Proceedings Third International Conference Trondheim, Norway), ACI SP-114, V. 2, 1989, pp. 861-886.

**Variables:** Silica fume (3.75%, 7.5%, and 15% cement replacement, w/c of 0.38, 0.43, and 0.48).
Silica fume/calcium nitrite (6.5% / 2 $gal/yd^3$ and 15% / 4 $gal/yd^3$, w/c of 0.38, 0.43, and 0.48).

**Specimens:** Concrete beam with top and bottom reinforcing bars, cyclically ponded with 3% NaCl solution.
Concrete cylinders partially submerged in 3% NaCl solution.
Concrete cylinders with embedded/protruding reinforcing steel, partially submerged in 3% NaCl solution.

**Test Methods:** Rapid chloride permeability (AASHTO T277).
Polarization resistance (ASTM G59).
Macrocell corrosion (similar to ASTM G109).
A.C. impedance.
Compressive strength.

**Results:** Silica fume and calcium nitrite mixes improved compressive strength and long-term corrosion resistance.
Silica fume reduced the electrical charge passed; calcium nitrite added to silica fume concrete increased coulombs present but did not increase permeability.
Silica fume significantly increased concrete resistivity; calcium nitrite slightly reduced resistivity.
Silica fume, with and without calcium nitrite, increased the time to corrosion initiation at a given water-cement ratio.
Silica fume reduced chloride ingress; calcium nitrite enhanced the reduction of chloride ingress at 0.48 water-cement ratio when used with silica fume.
Diffusion results indicated that silica fume reduced chloride ingress, and calcium nitrite for the protection against chlorides that did ingress.
Silica fume additions improved resistance with increasing silica fume content.

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**Reference:** Berke, N. S., and Hicks, M. C. "Estimating the Life Cycle of Reinforced Concrete Decks and Marine Piles Using Laboratory Diffusion and Corrosion Data." *Corrosion Forms and Control for Infrastructure*, STP-1137, 1992, pp. 207-231.

**Variables:** Calcium nitrite (30% solution, 20 l/m$^3$, w/c of 0.38 and 0.48)
Silica fume (15% cement replacements, w/c of 0.48).
Silica fume/calcium nitrite (15% / 20 l/m$^3$ and 7.5% / 20 l/m$^3$, w/c of 0.38, 0.43, and 0.48).

**Specimens:** Concrete beam with top and bottom reinforcing bars, cyclically ponded with 3% NaCl solution.
Concrete cylinders partially submerged in 3% NaCl solution.
Concrete cylinders with embedded/protruding reinforcing steel, partially submerged in 3% NaCl solution.

**Test Methods:** Rapid chloride permeability (AASHTO T277).
Polarization resistance (ASTM G59).
Macrocell corrosion (similar to ASTM G109).
Chloride analysis.
Compressive strength.

**Results:** Silica fume decreased permeability and slowed down chloride ingress, but eventually chloride reached the steel and corrosion took place.
Calcium nitrite reduced total macrocell corrosion four fold in comparison with the control concrete.
Calcium nitrite and silica fume concrete initially had reduced resistivity and increased rapid chloride permeability values, but this had no adverse effect on the actual concrete permeability; calcium nitrite and silica fume improved the durability of concrete in corrosive environments.

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**Reference:** Berke, N. S., Hicks, M. C., and Tourney, P. G., "Evaluation of Concrete Corrosion Inhibitors." *Proceedings, 12$^{th}$ International Corrosion Congress, Houston, Texas*, 1993, pp. 3271-3286.

**Variables:** Calcium nitrite (30% solution, 10 and 15 l/m$^3$, w/c of 0.40 and 0.50).
Butyl ester emulsion (5, 10, and 15 l/m$^3$ in concrete, w/c of 0.40 and 0.50).
Dimethylethanol amine [DMEA] (0.6 kg/m$^3$ in concrete, w/c of 0.40 and 0.50).

**Specimens:** Reinforcing steel immersed in sodium chloride solution saturated with calcium hydroxide.
Concrete beams with one top reinforcing bar and two bottom reinforcing bars, cyclically ponded with 3% NaCl solution.
Concrete cylinders with embedded/protruding reinforcing steel, partially immersed in 3% NaCl solution.

**Test Methods:** Cyclic polarization (similar to ASTM G61).
Macrocell corrosion (similar to ASTM G109).
Polarization resistance (similar to ASTM G59).
Visual survey.

**Results:** Cyclic polarization accurately assessed the corrosion inhibiting properties of a chemical in the presence of chlorides.
Calcium nitrite was an effective corrosion inhibitor for steel in concrete in chloride environments, even offering protection when chlorides were present at the steel.
Butyl ester emulsion reduced chloride ingress in concrete with w/c = 0.5; it had little

effect on concrete with w/c = 0.4.

Butyl ester emulsion did not prevent corrosion of reinforcing steel in the presence of chlorides; it served as a dampproofing admixture rather than a corrosion inhibitor.

It also adversely affected concrete compressive strength and the ability to entrain air.

DMEA did not appear to be an effective corrosion inhibitor in alkaline or concrete environments when chloride was present at the reinforcing steel.

Long-term corrosion testing in good quality concrete was essential for assessing the performance of "corrosion inhibitors."

**Drawback:** Research conducted/reported only by W. R. Grace personnel.

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**Reference:** Berke, N. S., Pfeifer, D. W., and Weil, T. G., "Protection Against Chloride-Induced Corrosion." *Concrete International: Design and Construction*, V. 10, No. 12, Dec. 1988, pp. 45-55.

**Variables:** Calcium nitrite (30% solution, 2, 4, and 6 gal/yd$^3$, w/c of 0.32, 0.40, and 0.50).

Silica fume (2%-6.5%, 7.5% (parking garages), 10% (marine piles), 11%-15% addition by weight of cement; w/c of 0.37, 0.43, and 0.52)

Silica fume/calcium nitrite (7.5% / 2 gal/yd$^3$, 15% / 4 gal/yd$^3$, 15% / 4 gal/yd$^3$, w/c of 0.43, 0.38, and 0.48 respectively).

**Specimens:** Literature review.

**Test Methods:** Rapid chloride permeability (AASHTO T277).

Polarization resistance (similar to ASTM G59).

**Results:** Silica fume increased concrete resistivity, decreased chloride permeability, and decreased chloride ingress.

Silica fume was more effective at low w/c, and it improved compressive strength.

Concretes with silica fume at 6.3%, 12.5%, and 15.1% by weight of cement had very low chloride permeability as based on charge passed.

Calcium nitrite was most effective in low water-cement ratio (approx. 0.34) concrete.

The corrosion rate after initiation was less severe in calcium nitrite concrete because of the reservoir of calcium nitrite still available to repassivate the steel.

Calcium nitrite at 2 gal/yd$^3$ of concrete of a 30% solution was able to protect against the corrosive action of 6 lb/yd$^3$ of chlorides.

For a parking garage, the chloride surface concentration typically increased by 2 lb/y and became constant at 30 lb/yd$^3$.

Calcium nitrite required for 50 year protection would be 5 1/2 gal/yd$^3$ to protect against 15 1/2 lb/yd$^3$ of chlorides; the reservoir of calcium nitrite would provide added passivation protection against higher chloride content, which silica fume would not. In comparison, silica fume would require 10% by weight of cement, which would allow an estimated chloride content of 6 lb/yd$^3$; the addition of 2 gal/yd$^3$ of calcium nitrite to the silica fume mix would provide extra protection for the full fifty years.

Silica fume and calcium nitrite can be used to minimize corrosion, life cycle costs and maximize structural life.

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**References:** Berke, N. S., and Rosenberg, A., "Technical Review of Calcium Nitrite Corrosion Inhibitor in Concrete." *Transportation Research Record 1211*, Transportation Research Board, National Research Council, Washington, D.C., 1989, pp. 18-27.

McDonald, D., "Design Options for Corrosion Protection." *Concrete 95 Toward Better Concrete Structures* (Brisbane, Australia, 4-7 September 1995, Conference Papers), V. 1, 1995, pp. 75-83.

**Variables:** Calcium nitrite (30% solution, 2, 3, 4, or 6 gal/yd$^3$, w/c of 0.38, 0.39, 0.43, and 0.48).
Sodium nitrite (dosage and w/c not given).

**Specimens:** Literature reviews.

**Test Methods:** Polarization resistance (similar to ASTM G59).
Electrochemical impedance.
Visual survey.

**Results:** If the chloride/nitrite is below 2.0, or below 1.5 allowing for a margin of safety, corrosion should be controlled.
In unprotected concrete, corrosion can begin if the chloride concentration is 1 to 2 lb/yd$^3$; in concrete with calcium nitrite, the concentration must reach 12.8 lb/yd$^3$.
Even in cracked samples, corrosion rates were reduced when calcium nitrite was used.
Calcium nitrite increased the AASHTO T277 Rapid Chloride Permeability coulombs; it either lowered or had no effect on the diffusion coefficient for chloride; it was compatible with concrete containing silica fume or fly ash that provided reduced permeability.
Calcium nitrite improved corrosion resistance of concrete with fly ash.
Following is a table of recommended calcium nitrite dosages:

| Chloride Content (lb/yd$^3$) | Recommended Calcium Nitrite Dose (gal/yd$^3$) |
|---|---|
| 6.0 | 2 |
| 9.9 | 3 |
| 13.0 | 4 |
| 15.0 | 5 |
| 16.0 | 6 |

Sodium nitrite reduced corrosion in cracked specimens, even at higher than recommended w/c and a low dosage rate for the exposure conditions.

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**Reference:** Berke, N. S., Scali, M. J., Regan, J. C., and Shen, D. F., "Long-Term Corrosion Resistance of Steel in Silica Fume and/or Fly Ash Containing Concretes." *Durability of Concrete* (Second International Conference, Montreal, Canada), Volume 1, ACI SP-126, V. 1, 1991, pp. 393-415.

**Variables:** Silica fume (2.5%, 5.25%, 7.5%, and 12.5% addition by weight of cement, w/c of 0.42, 0.35, 0.49, and 0.38, respectively).
Fly ash (10.75%, 15%, and 25% addition by weight of cement, w/c of 0.33, 0.45, and 0.34, respectively).
Silica fume/fly ash (2% / 21.5%, 5.25% / 21.5%, 6.25% / 12.5%, 7.5% / 30%, 10.75% / 10.75%, 12.5% / 25%, and 15% / 15% addition by weight of cement, w/c of 0.30, 0.29, 0.36, 0.38, 0.30, 0.31, and 0.40, respectively).

**Specimens:** Concrete cylinders with embedded/protruding reinforcing steel, partially immersed in 3% NaCl solution.

**Test Methods:** Rapid chloride permeability (AASHTO T277).
Concrete resistivity.

Polarization resistance (similar to ASTM G59).
Acid soluble chloride analysis.
X-ray spectrometry.
Microscopic examination.

**Results:** Silica fume and/or fly ash improved the long-term corrosion resistance of the steel in concrete; this also improved as the w/c decreased.
Fly ash additions to silica fume mixes improved corrosion protection.
Fly ash additions were less efficient in reducing chloride ingress than silica fume.
Concrete with high levels of fly ash were susceptible to carbonation at cracks.
Silica fume levels under 4% were of minimal benefit in reducing corrosion rates when w/c was greater than 0.43.
Silica fume when in sufficient quantities to achieve 1000 coulombs or less in the Rapid Chloride Permeability Test, substantially reduced corrosion activity.
Silica fume decreased concrete porosity at the aggregate-paste level.
Silica fume at 7.5%, or fly ash at 15%, with a high w/c, were not effective in preventing corrosion.
Combinations of 15% silica fume and 15% fly ash, or 7.5% silica fume and 30% fly ash, were effective in lowering corrosion rates.
Low rapid chloride permeability (less than 1000 coulombs) and high resistivities were indicators of good corrosion performance.
Moderately high permeability (1000 to 4000 coulombs) were not necessarily indicators of poor corrosion performance. Resistivity alone was not a good measure of corrosion rates. There was very good agreement between resistivity and coulomb data.

**Drawback:** Research conducted/reported only by W.R. Grace personnel.

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**Reference:** Berke, N. S. and Weil, T. G., "World-Wide Review of Corrosion Inhibitors in Concrete." *Advances in Concrete Technology*, Energy, Mines and Resources, Ottawa, Canada MSL 92-6(R), 1992, pp. 899-924.

**Variables:** Calcium nitrite (30% solution, 2.4, 3, 4.7, 6 and 7.1 gal/yd$^3$, and 10, 20, 30 l/m$^3$, w/c of 0.34, 0.45, 0.48, 0.50, and 0.60).
Silica fume (3.75% and 7.5% addition by weight of cement, w/c of 0.48).
Silica fume/calcium nitrite (3.75% / 10 l/m$^3$, 3.75% / 20 l/m$^3$, 7.5% / 10 l/m$^3$, and 7.5% / 20 l/m$^3$, w/c of 0.48)
Sodium nitrite (no dosage or w/c given).
Potassium chromate (no dosage or w/c given).
Sodium benzoate (no dosage or w/c given).
Stannic chloride (no dosage or w/c given).
Stannous chloride (no dosage or w/c given).

**Specimens:** Literature review.

**Test Methods:** Rapid chloride permeability (AASHTO T277).
Polarization resistance (similar to ASTM G59).
Macrocell corrosion (similar to ASTM G109).
Chloride analysis (similar to ASTM C114).
Half-cell potential (similar to ASTM C876).

**Results:** Sodium nitrite acted as a corrosion inhibitor, but potassium chromate, sodium benzoate, and calcium chloride did not perform well as inhibitors.
Stannic chloride and stannous chloride did not act as corrosion inhibitors.
Calcium nitrite delayed corrosion with admixed chloride up to 700 days in concrete

cylinders with embedded rebar; calcium nitrite improved corrosion resistance, preventing corrosion at chloride to nitrite ratios of 1.6 to 2.2. Nitrite at the reinforcement level remained high after 4 years of severe chloride exposure.

Under wet/dry cycling, calcium nitrite was an effective inhibitor, even at high w/c ratios. A 4 gal/yd$^3$ addition of a 30% calcium nitrite solution resulted in a reduction in corrosion.

Sodium nitrite was effective in reducing corrosion in cracked specimens, even at higher than recommended w/c ratios and low inhibitor dosages.

Core samples from bridge decks up to eight years old have shown that calcium nitrite was still effective in maintaining passivity and controlling corrosion.

An ocean fishing pier showed no sign of corrosion after 11 years, using calcium nitrite as the only means of corrosion protection.

Parking garages in a severe exposure environment, using concrete containing 30% calcium nitrite (3.5 gal/yd$^3$ and w/c of 0.45), showed no signs of corrosion after 10 years of service.

Corrosion resistance improved with a fly ash and calcium nitrite combination.

Calcium nitrite was compatible with silica fume and should provide protection in the presence of chlorides.

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**Reference:** Bobrowski, G., and Youn, D. J., "Corrosion Inhibition in Cracked Concrete: An Admixture Solution." *Concrete 2000: Economic and Durable Construction Through Excellence* (Proceedings of the International Conference held at the University of Dundee Scotland, UK on 7-9 September 1993. Volume 2, Infrastructure, Research, New Applications. E & FN SPON), 1993, pp. 1249-1261.

**Variables:** Rheocrete 222, amines and esters (dosage and w/c not given).

**Specimens:** Cracked beams with one top and two bottom reinforcing steel bars, cyclically ponded with 6% NaCl solution.

**Test Methods:** Macrocell corrosion (similar to ASTM G109)

**Results:** The treated samples delayed corrosion by 6 months in comparison to the untreated samples.

Corrosion was inhibited by the formation of a chelating organic layer protecting the steel.

Current through the resistor wired in the testing configuration was a reliable method to determine the commencement of corrosion.

The test procedure was a good indicator of overall corrosion activity occurring in the specimen.

**Drawback:** Research conducted/reported only by Master Builders personnel.

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**Reference:** Buerge, T. A., "Corrosion Inhibiting Admixture for High Durability Concrete." *Concrete Under Severe Conditions: Environmental and Loading,* (International Conference on Concrete Under Severe Conditions, Sapporo, Japan), 1995, pp. 574-585.

**Variables:** Alkanolamine (amine with a pH of 10, 0%, 3%, and 4% by weight of cement, w/c of 0.55).

Alkanolamine (amine with a pH of 10, 0%, 1.12%, 2.25%, and 4.50% in solution).

**Specimens:** Mortar cylinders with embedded/protruding reinforcing steel, cyclically partially submerged/dried in 1% NaCl solution.

Steel plates immersed in a potassium hydroxide and potassium chloride solution.

**Test Methods:** Potentiostatic (corrosion cell) with an electrode immersed in a solution containing 3% inhibitor, 0.09 m/l NaCl, and a pH of 10.5.
XPS (X-ray photoelectron spectroscopy).

**Results:** The steel plate and lollipop tests showed that alkanolamine protected the steel from corrosion.
The potentiostatic test showed that the pitting potential of mortar containing alkanolamine could be shifted towards the positive side.
XPS indicated that alkanolamines interacted with the hydroxyl group on the steel surface to form insoluble iron oxide complexes that stabilized the oxide surface and inhibited further corrosion.
Alkanolamine appeared to have the ability to diffuse considerable distances through concrete because of its vapor pressure, so it did not have to be initially in contact with the steel and could work well for rehabilitation.

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**Reference:** Deja, J., Malolepszy, J., and Jaskiewicz, G., "Influence of Chloride Corrosion on the Durability of Reinforcement in the Concrete." *Durability of Concrete* (Second International Conference, Montreal, Canada), ACI SP-126, V. 1, 1991, pp.511-525.

**Variables:** Silica fume (10% addition by weight of cement, w/c of 0.45).
Slag (100% cement replacement, w/c of 0.34 and 0.41).
Limestone (5% addition by weight of cement, w/c of 0.48).

**Specimens:** Mortar prisms, immersed in NaCl solution.
Mortar cylinders with an embedded/protruding reinforcing steel bar, immersed in NaCl solution.
Mortar beams with an embedded steel plate, immersed in NaCl solution.

**Test Methods:** Corrosion resistance of mortars.
Corrosion potential.
Compressive strength.
Gravimetric weight loss.

**Results:** Slag prevented mortar strength loss in a chloride environment.
Slag provided increased corrosion resistance due to a passivation of the steel.
Silica fume or limestone inhibited the corrosion of the reinforcing steel.

**Drawback:** Tests were only conducted on mortar specimens.

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**Reference:** El-Jazairi, B., and Berke, N. S., "The Use of Calcium Nitrite as a Corrosion Inhibiting Admixture to Steel Reinforcement in Concrete." *Corrosion of Reinforcement in Concrete Construction* (Third International Symposium ),Wishaw, England, 1990, pp. 571-585.

**Variables:** Calcium nitrite (0.5% - 2% by weight of cement, no w/c given).

**Specimens:** Literature review.

**Results:** For calcium nitrite to have long term effectiveness in an aggressive environment it should be in good quality concrete as follows:

| | | |
|---|---|---|
| Max. w/c: | 0.50 | (Preferably 0.40) |
| Min. cement content: | 300 kg/m$^3$ | (Preferably 350) |

| | | |
|---|---|---|
| Min. cover: | 30 mm | (Preferably 38 mm or max. agg. size + 18 mm) |

Adequate dosages of calcium nitrite in good quality concrete can provide safeguards and protection against corrosion of reinforcing steel in an aggressive environment.
Calcium nitrite also provides early strength development in concrete and has no detrimental effects on the durability of concrete.

**Drawback:** Research conducted/reported only by W.R. Grace personnel.

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**Reference:** Ellis, Jr., W. E., Riggs, E. H., and Butler, W. B., "Comparative Results of Utilization of Fly Ash, Silica Fume, and GGBFS in Reducing the Chloride Permeability of Concrete." *Durability of Concrete* (Second International Conference, Montreal, Canada), ACI SP-126, V. 1, 1991, pp.443-458.

**Variables:** Fly ash Class F1 (23%, 33%, 47%, and 71% addition by weight of cement, w/c of 0.37, 0.28, 0.30, and 0.30, respectively).
Fly ash Class F1 (50% cement replacement, w/c of 0.33).
Fly ash Class F2 (23%, 47%, and 71% addition by weight of cement, w/c of 0.35, 0.29, and 0.31, respectively).
Fly ash Class C (23% and 47% addition by weight of cement, w/c of 0.41 and 0.30, respectively).
Slag (50% cement replacement, w/c of 0.47).
Silica fume (10% addition by weight of cement, w/c of 0.39).
Silica fume/fly ash (10% / 30% addition by weight of cement, w/c of 0.29).

**Specimens:** Concrete cylinders partially immersed in NaCl solution.

**Test Methods:** Rapid chloride permeability (AASHTO T277).
Compressive strength (ASTM C39).

**Results:** Class F fly ash concretes had superior chloride reducing permeability in comparison with Class C fly ash, silica fume, and slag concretes.
Class F fly ash improved concrete strength and impermeability with increased additions.
Addition of fly ash to silica fume concretes improved concrete strength and impermeability.
Concretes with fly ash Class F2 at 47% and 71% addition by weight of cement had higher compressive strengths and lower permeability than the 10% silica fume concrete.

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**Reference:** Gaidis, J. M., and Rosenberg, A. M., "The Inhibition of Chloride-Induced Corrosion in Reinforced Concrete by Calcium Nitrite." *Cement, Concrete, and Aggregates*, V. 9, No. 1, 1987, pp. 30-33.

**Variables:** Calcium nitrite (2% by weight of cement (30% solution, 2.5-5 gal/yd$^3$), w/c not given).

**Specimens:** Steel reinforcing bars immersed in aqueous solutions of NaCl, calcium nitrite, and calcium hydroxide (limewater).
Concrete cylinders with embedded/protruding reinforcing steel with calcium nitrite and with NaCl mixed in to give chloride/nitrite of 1.0, 1.5, 2.5, and 3.0 by weight.
Concrete beams with top and bottom reinforcing steel, salted daily.

**Test Methods:** Half-cell potential (similar to ASTM C876).
Visual survey.

**Results:** Limewater samples showed passivity was provided by nitrite for chloride/nitrite weight ratios up to 0.87 and as high as 2.61.
The cylinder samples showed passivity was provided by nitrite for chloride/nitrite weight ratios greater than 1.5 but less than 2.5.
The slab samples showed that for calcium nitrite in a 4 gal/yd$^3$ mix, the threshold for corrosion was 13.72 lb/yd$^3$ of chloride ion, with a chloride/nitrite weight ratio of 1.61; ratios higher than this resulted in corrosion.
For a chloride/nitrite weight ratio less than 1.5, calcium nitrite provided protection and inhibited corrosion.

**Drawback:** Research conducted/reported only by W.R. Grace personnel.

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**Reference:** Gautefall, O., and Havdahl, J., "Effect of Condensed Silica Fume on the Mechanism of Chloride Diffusion into Hardened Cement Paste." *Fly Ash, Silica Fume, Slag, and Natural Pozzolans in Concrete* (Proceedings Third International Conference Trondheim, Norway), ACI SP-114, V. 2, 1989, pp. 849-860.

**Variables:** Silica fume (5%, 10%, and 15% cement replacement, w/c of 0.50, 0.70, and 0.90).
Fly ash (10% cement replacement), blended with the clinker at the cement plant.

**Specimens:** Cement paste cylinders immersed in stagnant seawater.

**Test Methods:** Potentiometric determination of chloride content.

**Results:** The effective diffusion coefficient was reduced in the silica fume blends. This effect was more distinct for the ordinary Portland cement mix than the 10% fly ash blend, but the fly ash still outperformed the ordinary Portland cement mix.

**Drawbacks:** Tests were conducted in cement paste and used only relatively high w/c.

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**Reference:** Gjorv, O. E., "Effect of Condensed Silica Fume on Steel Corrosion in Concrete." *ACI Materials Journal*, V. 92, No. 6, 1995, pp. 591-598.

**Variables:** Silica fume (9% - 30% cement replacement, w/c of 0.35 - 0.70).
Fly ash (0% - 30% cement replacement, w/c of 0.37 - 1.10).
Slag (65% cement replacement, w/c of 0.40 and 0.70).
Fly ash/silica fume (10% / 5%, 10% / 10%, 25% / 5%, 25% / 10%, and 0% - 30% / 0% - 15%, w/c of 0.37 - 1.30).

**Specimens:** Literature review.

**Test Methods:** Rapid chloride permeability (AASHTO T277).

**Results:** Silica fume up to 20% did not reduce the pH below 12.5. Even 30% replacement did not reduce the pH below 11.5, the threshold level to maintain passivity of embedded steel.
Silica fume of 5% to 15% replacement of cement decreases chloride permeability. A 10% replacement of cement reduced chloride penetration by 68% to 84%. Even a 9% replacement of cement with silica fume reduced chloride diffusion by a factor of five.
Silica fume in conjunction with low w/c increased electrical resistivity to inhibit corrosion.
Silica fume addition of 10% to 20% increased resistivity by from 60% to 190%.

Proper curing was essential to prevent cracking and subsequent corrosion.
A well mixed concrete with silica fume that was properly cured and has a low w/c gives a structure an excellent performance, even in hostile environments, per field performance of over 20 years.
Silica fume reduced chloride diffusion, by itself and in combination with fly ash.
Silica fume contributed the most to increasing resistivity when in combination with fly ash.
Fly ash had no early effect on resistivity, but effect increased over time. Fly ash was not as effective as silica fume.
Slag significantly reduced oxygen diffusion when compared to conventional concrete.

**Drawback:** Tests used relatively high w/c mortar.

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**Reference:** Harrt, W. H., and Rosenberg, A. M., "Influence of $Ca(NO_2)_2$ on Sea Water Corrosion of Reinforcing Steel in Concrete." *Performance of Concrete in Marine Environment,* ACI SP-65, 1980, pp. 609-623.

**Variables:** Calcium nitrite (0-4% by weight of cement, with and without a water reducing agent (WRA), w/c of 0.50).

**Specimens:** Concrete cylinders with embedded/protruding reinforcing steel , partially submerged in seawater.

**Test Methods:** Half-cell potential (similar to ASTM C876).

**Results:** The addition of calcium nitrite retarded the onset of corrosion.
For the no WRA mix, the time to the onset of corrosion increased 50% by adding 2% calcium nitrite and 100% by adding 4% calcium nitrite.
For the concrete with WRA, the time to corrosion was increased by 80% for the 2% calcium nitrite.

**Drawback:** Tests only used relatively high w/c concrete.

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**Reference:** Hope, B. B., and Ip, A. K. C., "Corrosion Inhibitors for Use in Concrete." *ACI Materials Journal*, V. 86, No. 6, Nov.-Dec. 1989, pp. 602-608.

**Variables:** Calcium nitrite (0.1%-0.3% in solution).
Stannous chloride (0.1%-0.3% in solution).

**Specimens:** Steel samples submerged in oxygenated lime water containing calcium chloride in a test cell similar to ASTM G 5-78.

**Test Methods:** Half-cell potential (similar to ASTM C876).
AC impedance.
Polarization resistance (similar to ASTM G 5-78).
Tafel plot.
Visual survey.

**Results:** Calcium nitrite appeared to be promising as a corrosion inhibitor.
Stannous chloride did not show promise as a corrosion inhibitor.
A critical threshold of nitrite/chloride ions appeared to exist (0.07-0.09).
Steel could be repassivated by adding calcium nitrite after corrosion initiation.

**Drawbacks:** No tests performed in actual concrete; no long term tests.

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**Reference:** Hussain, S. E., and Rasheeduzzafar, "Corrosion Resistance Performance of Fly Ash Blended Cement Concrete." *ACI Materials Journal*, V. 91, No. 3, May-June 1994, pp. 264-272.

See Al-Saadoun, S. S., Rasheeduzzafar, and Al-Gahtani, A. S.

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**Reference:** Incorvia, M. J., "Corrosion Inhibitive Admixtures for Concrete." *Corrosion 96* (The NACE International Annual Conference and Exposition), Paper No. 239, 1996, pp. 239/1-239/12.

**Variables:** Calcium nitrite alone and in combination with sodium molybdate (4.5 parts and 1 part respectively, w/c not given).
Lead nitrate and calcium nitrate alone and blended with zinc or lead oxides (dosage and w/c not given).
Silica fume (15% addition by weight of cement, w/c of 0.44 and 0.48).
Superplasticizers (w/c of 0.28 and 0.40 - 0.51).
Butyl esters and amines (5 $l/m^3$, w/c of 0.50).
Phosphonic acid derivatives containing hydroxyl or amino groups (0.005%-5% by weight of cement, w/c not given).
Carboxylic acids: malonate, formate, acetate, and propionate (dosage and w/c not given).
Sodium chromate and polysiloxane (dosage and w/c not given).

**Specimens:** Literature review.

**Test Methods:** Macrocell corrosion (similar to ASTM G109).
Half-cell potential (similar to ASTM C876).
Chloride analysis (ASTM C114).

**Results:** Silica fume decreased the chloride diffusion coefficient, after 2 years cyclical ponding with chloride solution, by about 15 times in comparison with the control.
Silica fume reduced chloride content by 98% at the 1 in. level (w/c = 0.44).
Superplasticizers reduced concrete porosity and chloride permeability, but not enough to provide protection against chloride induced corrosion.
Butyl esters and amines reduced chloride permeability; the chloride content was reduced by 85% in comparison with a control.
Other corrosion protecting combinations:
- Calcium nitrite and sodium molybdate was better than calcium nitrite alone.
- Lead nitrate and calcium nitrate alone and blended with zinc or lead oxides passivated steel in concrete. Zinc oxide alone did not passivate.
- Phosphonic acid derivatives containing hydroxyl or amino groups provided protection.
- Carboxylic acids provided corrosion protection; malonate was the most efficient acid of malonate, formate, acetate, and propionate.
- Sodium chromate and polysiloxane did not provide reduced chloride penetration.

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**Reference:** Kayyali, O. A., and Haque, M. N., "The $Cl^-/OH^-$ Ratio in Chloride-Contaminated Concrete - A Most Important Criterion." *Magazine of Concrete Research*, V. 47, No. 172, 1995, pp. 235-242.

**Variables:** Fly ash (15% addition by weight of cement and 30% cement replacement, w/c of 0.31, 0.36, 0.45, and 0.56)

**Specimens:** Concrete cylinders with admixed NaCl at chloride ion concentrations of 0.2% - 2.0% and/or immersed in NaCl solution.

**Test Methods:** Chloride ion concentration in pore solution.
Hydroxyl ion concentration in pore solution.

**Results:** Concrete without superplasticizers and with fly ash resulted in a large reduction of free chloride ion content, for both admixed chlorides and externally applied chlorides.
Concrete with fly ash and superplasticizers showed a release of free chloride ions into the pore solution that resulted in a detrimental corrosive environment.
The $Cl^-/OH^-$ ratio and the source of chloride contamination (admixed or external) were indicative factors in the prediction of chloride induced corrosion of reinforcing steel. The concentration of free chloride ions in pore solution alone was not a sufficient indication of chloride induced corrosion.
Charts were developed that indicated the threshold values of $Cl^-/OH^-$ for chloride induced corrosion; they indicate the equivalence of admixed chloride to externally applied chloride and could be used to predict the occurrence of chloride initiated corrosion of reinforcing steel.

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**Reference:** Khedr, S. A., and Idriss, A. F., "Resistance of Silica-Fume Concrete to Corrosion Related Damage." *Journal of Materials in Civil Engineering*, V. 7, No. 2, May 1995, pp. 102-107.

**Variables:** Silica fume (10%, 15%, 20% and 25% cement replacement, w/c of 0.44).

**Specimens:** Concrete cylinders with embedded/protruding reinforcing steel, some samples cured in 4% NaCl solution.

**Test Methods:** Impressed voltage (with current measurements).
pH of fresh concrete.
Absorption.
Compressive/tensile strength.

**Results:** The 28 day strength of silica fume concrete showed higher compressive strength than the control. Maximum compressive strength was for 20% replacement of cement.
Silica fume concrete had a lower susceptibility to corrosion rates than the control. The least susceptible was for 15% silica fume at 28 day curing; beyond this optimal dosage, the susceptibility to corrosion increased.
For the optimum of 15% silica fume replacement of cement, the susceptibility to corrosion was several times that of the control mix.
The 10% and 20% dosages for saline-water curing had nearly identical susceptibility to corrosion, indicating there was little difference in performance of the mixes.

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**Reference:** Kouloumbi, N., and Batis, G., "Chloride Corrosion of Steel Rebars in Mortars with Fly Ash Admixtures." *Cement and Concrete Composites*, V. 14, No. 3, 1992, pp. 199-207.

**Variables:** Greek fly ash (15% and 30% cement replacement, w/c of 0.50 and 0.55).

**Specimens:** Mortar cylinders with embedded/protruding reinforcing steel, partially immersed in 3.5% NaCl solution.

**Test Methods:** Polarization resistance (similar to ASTM G59).
Gravimetric weight loss.
Total and free chloride content.

**Results:** The porosity and consequently the free chlorides in the pore solution, increased with

increasing w/c.
Total chloride content of the fly ash specimens was higher than the control, but the free chloride content was lower, resulting in an improved corrosion resistance; it was believed that the fly ash and chlorides chemically bonded.
The decrease in permeability of the fly ash concrete was due to the reduction in pore size.

**Drawback:** Tests only used relatively high w/c mortar.

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**Reference:** Kouloumbi, N., Batis, G., and Malami, C., "The Anticorrosive Effect of Fly Ash, Slag, and a Greek Pozzolan in Reinforced Concrete." *Cement and Concrete Composites*, V. 16, No. 4, 1994, pp. 253-260.

**Variables:** Greek fly ash (15% and 30% cement replacement, w/c of 0.50 and 0.55).
Blast furnace slag (50% cement replacement, w/c of 0.50 and 0.55).
Greek natural pozzolan (15% and 30% cement replacement, w/c of 0.50 and 0.55).

**Specimens:** Mortar cylinders with embedded/protruding reinforcing steel, ponded long term with 3.5% NaCl solution.

**Test Methods:** Half-cell potential (similar to ASTM C876).
Chloride analysis.
Gravimetric weight loss.

**Results:** The fly ash concrete had lower chloride penetration, expressed as concentrations of chlorides.
The chloride binding capacity of the fly ash concrete resulted in lower free chlorides that could cause corrosion; the 30% fly ash mix had the greatest ability to bind chlorides.
The most effective corrosion protection was from the 30% fly ash mix.
Fly ash and slag improved the long-term corrosion resistance of concrete by lowering the corrosion rates due to decreased permeability.

**Drawbacks:** Tests only used relatively high w/c mortar.

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**Reference:** Krauss, P. D. and Nmai, C. K., "Preliminary Corrosion Investigation of Prestressed Concrete Piles in a Marine Environment: Deerfield Beach Fishing Pier." *Techniques to Assess the Corrosion Activity of Steel Reinforced Concrete Structures,* ASTM STP 1276, 1996, pp. 161-172.

**Variables:** Water based organic corrosion inhibitor of amines and fatty acid esters (similar to Rheocrete) and Class F fly ash (1 gal/yd$^3$ and 22% by weight of cement, respectively, w/c of 0.34).

**Specimens:** In-service evaluation of a corrosion inhibitor consisting of amines and esters on an ocean fishing pier.

**Test Methods:** Half-cell potential (similar to ASTM C876).
Chloride analysis (similar to ASTM C114).
Visual survey.

**Results:** Half-cell potentials were high near ground level and decreased towards the top of the pile.
The readings did not indicate corrosion, which was confirmed by exposing a section of

spiral steel, by coring, that was found not to be corroding.
Chloride ion content data indicated that the pile caps (containing no inhibitors) had high chloride levels at 1 1/2 in. to 3 in. depths compared to the pile samples, even though the pile caps had the least exposure to saltwater splash.

**Drawback:** Only two years exposure as of the reporting date.

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**Reference:** Lee, C., and Lee, M. G., "Effect of Fly Ash and Corrosion Inhibitor on Reinforced Concrete in Marine Environments." *Durability of Concrete* (Proceedings Fourth CANMET/ACI International Conference), ACI SP-170, V. 1, 1997, pp. 141-156.

**Variables:** Calcium nitrite (3% by weight of cement, w/c of 0.45 and 0.60).
Class F fly ash (10% sand replacement, and 20% and 30% cement replacement, w/c of 0.45 and 0.60).
Class F fly ash and calcium nitrite (fly ash with 10% sand replacement, and 20% and 30% cement replacement, calcium nitrite 3% addition by weight of cement, w/c of 0.45 and 0.60).

**Specimens:** Mortar cubes mixed with artificial salt water and immersed in saturated lime water or artificial sea water.
Concrete cylinders with embedded/protruding reinforcing steel, mixed with artificial salt water and partially immersed in saturated lime water or artificial sea water.

**Test Methods:** Compressive strength.
Half-cell potential (ASTM C876).

**Results:** The fly ash concretes had lower early strengths but normal late strengths with respect to the control mix.
The calcium nitrite concretes had higher early strengths but lower late strengths with respect to the control mix.
Calcium nitrite and fly ash concrete mix prevented the corrosion of steel.
Calcium nitrite appeared to be a low cost, effective method to protect the reinforcing steel from corrosion under aggressive sea water exposure.
Ten percent sand replacement with fly ash was beneficial in preventing steel corrosion; at 20% cement replacement by fly ash, there was no apparent additional corrosion resistance.

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**Reference:** Loto, C. A., "Effect of Inhibitors and Admixed Chloride on Electrochemical Corrosion Behavior of Mild Steel Reinforcement in Concrete in Seawater." *Corrosion*, V. 48, No. 9, September 1992, pp. 759-763.

**Variables:** Sodium nitrite (1% addition by weight of cement, w/c of 0.44 with admixed NaCl).
Formaldehyde (1% addition by weight of cement, w/c of 0.44 with admixed NaCl).
Potassium dichromate (1% addition by weight of cement, w/c of 0.44 with admixed NaCl).
Potassium dichromate/formaldehyde (0.5% / 1% addition by weight of cement, w/c of 0.44 with admixed NaCl).

**Specimens:** Concrete beams with symmetrically placed reinforcing steel, with NaCl admixed and/or partially immersed in seawater.

**Test Methods:** Electrochemical potential.
Compressive strength.

**Results:** Sodium nitrite had a tendency toward effective protection, but it was minimal.
Formaldehyde and potassium dichromate, when mixed alone with the concrete, were not effective inhibitors.
Potassium dichromate and formaldehyde together provided a passivating effect up to the seventh week of testing.
Further investigation is required to determine the full extent of the effectiveness of the inhibitors that worked, especially by varying the dosages.

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**Reference:** Maslehuddin, M., Al-Manna, A., Shamin, M., and Saricimen, H., "Effect of Sand Replacement on the Early Age Strength Gain and Long Term Corrosion Resisting Characteristics of Fly Ash Concrete." *ACI Materials Journal*, V. 86, No. 1, Jan.-Feb. 1989, pp. 58-62.

**Variables:** Class F fly ash (20% and 30% sand replacement, w/c of 0.35, 0.40, 0.45, and 0.50).

**Specimens:** Concrete cylinders.
Concrete prisms with embedded reinforcing steel, partially immersed in 5% NaCl solution for 4 years.

**Test Methods:** Half-cell potential (similar to ASTM C876).
Linear polarization resistance (similar to ASTM G59).
Compressive strength (ASTM C39).

**Results:** Fly ash increased the compressive strength and long term corrosion resistance capability of the concrete.
The control concrete had 13 to 19 times the corrosion rate of the 30% fly ash concrete, and 4 to 10 times that of the 20% fly ash concrete.

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**References:** McDonald, D., "Design Options for Corrosion Protection." *Concrete 95 Toward Better Concrete Structures* (Brisbane, Australia, 4-7 September 1995, Conference Papers), V. 1, 1995, pp. 75-83.

See Berke, N. S., and Rosenberg, A.

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**Reference:** McGrath, P. F., and Hooton, R. D., "Influence of Binder Composition on Chloride Penetration Resistance of Concrete." *Durability of Concrete,* (Proceedings Fourth CANMET/ACI International Conference), ACI SP-170, V. 1, 1997, pp. 331-347.

**Variables:** <u>Concrete mixes</u>:
Silica fume (8% cement replacement, w/c of 0.31 and 0.40).
Slag (24% cement replacement, w/c of 0.40).
Class C fly ash (25% cement replacement, w/c of 0.40).
Slag/silica fume (40% / 8% cement replacement, w/c of 0.31).
Silica fume/Class F fly ash (8% / 30% cement replacement, w/c of 0.31).

<u>Mortar mixes</u>:
Silica fume (8% and 12% cement replacement, w/c of 0.30).
Slag (25% cement replacement, w/c of 0.30).
Class F fly ash (40% cement replacement, w/c of 0.30).
Slag/silica fume (25% / 8% cement replacement, w/c of 0.30).
Slag/silica fume (40% / 8% cement replacement, w/c of 0.30).
Silica fume/Class F fly ash (8% / 40% cement replacement, w/c of 0.30).

**Specimens:** Cores from slabs, and blocks of concrete and mortar, ponded with NaCl solution.

**Test Methods:** Chloride analysis using chloride migration and chloride ponding tests.

**Results:** Silica fume was essential to obtain low diffusion coefficients, particularly at early ages.
Additional reductions in the diffusion coefficients were obtained with ternary blends of silica fume/slag or silica fume/Class F fly ash; these blends were superior to silica fume alone.
Ranking of these three blends was as follows:
Diffusion of the control was greater than slag concrete, which was equal to fly ash concrete, which was greater than silica fume concrete, which was greater than slag/silica fume concrete, which was equal to fly ash/silica fume concrete. This research ranking differed from others, which typically have found that fly ash and slag concretes have similar or lower diffusion values than silica fume concrete in long duration tests.
Increasing silica fume content from 0% to 8% reduced chloride diffusion dramatically, with some additional reduction by increasing from 8% to 12%.
The ranking of materials by the chloride ponding test was similar to that of the chloride migration test.

**Drawbacks:** Short term tests of 120 days.

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**Reference:** Montani, S., "Study on (Ecotrade) Blast Furnace Slag." *World Cement*, V. 27, No. 11, Nov. 1996, pp. 58-62.

**Variables:** Blast furnace slag (25%, 50%, and 75% cement replacement, mortar w/c of 0.50, concrete w/c of 0.54 and 0.55).

**Specimens:** Mortar cylinders.
Concrete slabs (50% replacement and control only), ponded with 3% NaCl solution.

**Test Methods:** Chloride permeability (AASHTO T259-90).
Oxygen permeability on mortar specimens.
Compressive strength.

**Results:** Slag contents of 40% and greater typically had lower permeability than ordinary concrete control specimens due to refinement of the pore structure and a substantial decrease in the average pore radius.
Slag contents had to be limited to about 35% if early strength development similar to the control was needed.
Higher durability should be expected with the use of slag.

**Drawbacks:** Tests only used relatively high w/c concrete and mortar.

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**Reference:** Monticelli, C., Frignani, A., Brunoro, G., Trabanelli, G., Zucchi, F., and Tassinari, M. , "Corrosion Inhibition of Steel in Alkaline Chloride Solutions." *Corrosion Science*, V. 35, No. 5-8, 1993, pp. 1483-1489.

**Variables:** di-sodium β-glycerophosphate (GPH) (0.05 M).
di-sodium β-glycerophosphate and sodium nitrite (0.005 M of each).

**Specimens:** Rebar samples tested in a solution containing calcium hydroxide, chloride concentration of 0.1M, and the inhibitor.

**Test Methods:** Electrochemical impedance spectroscopy (EIS).
Electrochemical noise analysis (ENA).
Cathodic polarization curve analysis.

**Results:** GPH had good inhibitor efficiency towards localized attack, nearly comparable to sodium nitrite.
The GPH/sodium nitrite mixture at a concentration of 5 mM of each inhibitor efficiently inhibited localized attack.

**Drawback:** Tests only conducted in solution.

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**Reference:** Naik, T. R., Singh, S. S., and Ramme, B., "Effect of Source and Amount of Fly Ash on Mechanical and Durability Properties of Concrete." *Durability of Concrete* (Proceedings Fourth CANMET/ACI International Conference), ACI SP-170, V. 1, 1997, pp. 157-188.

**Variables:** Class C fly ash (40%, 50%, and 60% cement replacement, w/c of 0.30).

**Specimens:** Concrete cylinders.
Concrete slabs, ponded with NaCl solution.
Literature review.

**Test Methods:** Resistance to chloride penetration (ASTM C 1202).
Salt scaling resistance (ASTM C672).

**Results:** Laboratory tests:
Concrete with 40% fly ash was comparable or superior to no-fly ash concrete.
Fly ash concrete showed higher resistance to chloride penetration than no-fly ash concrete.
Concrete resistance to chloride ions increased beyond 28 days for the 40% - 60% fly ash mixes. Resistance to chloride penetration was unaffected by the source of fly ash used.
All fly ash mixtures up to 60% cement replacement showed equal or better resistance to deicing salt in comparison to the control concrete. The 40% fly ash mixture outperformed the control, but anything above 40% did not show any significant additional improvements.

Literature review:
Class C fly ash for 68% replacement had lower permeability than ordinary Portland cement concrete.
An increase in the content of Class C or F fly ash for a fixed w/c increased the concrete's resistance to chloride penetration.
Water and chloride permeability of fly ash concrete having 55% and 60% cement replacement had lower water permeability than ordinary Portland cement concrete.
Chloride permeability for the fly ash concretes were comparable to the silica fume concretes.
Class C fly ash concrete up to 60% (w/c of 0.60) showed good resistance to air and water permeability and chloride penetration. Beyond 60% fly ash content, concrete permeability increased substantially.

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**Reference:** Nmai, C. K., Farrington, S. A., and Bobrowski, G. S., "Organic-Based Corrosion-Inhibiting Admixture for Reinforced Concrete*." Concrete International: Design and Construction*, V. 14, No. 4, April 1992, pp. 45-51.

**Variables:** Organic-based corrosion-inhibiting admixture (OCIA, similar to Rheocrete, a

combination of amines and esters in a water medium, 1 gal/yd$^3$, w/c of 0.40 and 0.50).

Calcium nitrite (30% solution, 2 and 4 gal/yd$^3$, w/c of 0.40 and 0.50).

**Specimens:** Cracked and non-cracked beams with a single reinforcing steel bar, continuously ponded with 6% NaCl solution.

**Test Methods:** Half-cell potential (similar to ASTM C876).
Macrocell corrosion (similar to ASTM G109).
Mat-to-mat resistance of the concrete.

**Results:** Measurable corrosion was detected in the reference concrete after 9 weeks, compared to 36 weeks for the OCIA concrete.

Chloride ions penetrated faster into untreated and calcium nitrite concrete faster than OCIA concrete.

Chloride ion concentrations, at the top of rebar (1.5 in.) either side of the crack, were measured to be 12.0 lb/yd$^3$ for untreated concrete, 13.0 and 14.7 lb/yd$^3$ for concrete treated with calcium nitrite at 2 and 4 gal/yd$^3$, and 5.0 lb/yd$^3$ for OCIA treated concrete.

For comparison in the cracked specimens, corrosion was initiated in the reference concrete at 6 days, 17 and 39 days for concrete treated with calcium nitrite at 2 and 4 gal/yd$^3$, and 118 days for concrete treated with 1 gal/yd$^3$ of OCIA.

Adding OCIA could require increasing the air-entraining admixture (vinsol resin-based and synthetics).

The coulomb rating of concrete indicated that OCIA did not decrease the electrical resistivity of concrete.

The following table of recommended calcium nitrite dosages was provided:

| Chloride Content (lb/yd$^3$) | Recommended Calcium Nitrite Dose (gal/yd$^3$) |
|---|---|
| 4.1 | 2 |
| 6.1 | 3 |
| 8.1 | 4 |
| 10.1 | 5 |
| 12.1 | 6 |

**Drawback:** Research conducted/reported only by Master Builders personnel.

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**Reference:** Nmai, C. K., and Krauss, P. D., "Comparative Evaluation of Corrosion-Inhibiting Chemical Admixtures for Reinforced Concrete." *Durability of Concrete* (Proceedings of the 3rd CANMET/ACI International Conference), ACI SP 145, 1994, pp. 245-262.

**Variables:** Calcium nitrite (30% solution, 10, 20, and 30 l/m$^3$, w/c of 0.50)
Amines and esters, water based organic inhibitor (5 l/m$^3$, w/c of 0.50)

**Specimens:** Uncracked slabs with two layers of rebar, two bars on top and 4 bars on the bottom, cyclically ponded and dried with 15% NaCl solution.
Precracked beams with one bar on top and 2 bars on the bottom, with a 0.25 mm crack, cyclically ponded and dried with 15% NaCl solution.

**Test Methods:** Macrocell corrosion (similar to ASTM G109).
Half-cell potential (similar to ASTM C876).
Chloride analysis (ASTM C114).
Visual survey.

**Results:** The water based organic inhibitor had the lowest corrosion current and the longest time to corrosion.
Calcium nitrite at 20 and 30 l/m$^3$ had lower corrosion currents than the untreated control and at 10 l/m$^3$.
The chloride contents for the water based organic inhibitor were lower than untreated and calcium nitrite treated concrete, with significant reductions and lower than the accepted chloride ion threshold for corrosion in untreated concrete.
For the precracked beams, the chloride ion content was highest at all locations for the calcium nitrite treated concrete, followed by the untreated concrete and then the water based organic inhibitor treated concrete.
The performance of the water based organic inhibitor concrete at 5 l/m$^3$ was comparable to the calcium nitrite concrete 30 l/m$^3$.

**Drawback:** Tests only used relatively high w/c concrete.

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**Reference:** Olsen, N. H., and Summers, G. R., "Performance of Reinforced Blast Furnace Slag Cement Concrete Specimens After 10 Years' Exposure in Bahrain." *Durability of Concrete* (Proceedings Fourth CANMET/ACI International Conference), ACI SP-170, V. 1, 1997, pp. 285-308.

**Variables:** Slag (70% cement replacement, site blended and preblended mixes, w/c of 0.49-0.54 and 0.78-0.89).

**Specimens:** Concrete beams containing reinforcing steel bars, contaminated at onset with chlorides and sulfates; specimens were exposed outdoors in an ultra hot climate.

**Test Methods:** Depth of carbonation.
Weight loss due to corrosion.
Visual survey.

**Results:** Carbonation progressed faster in the slag specimens.
Carbonation progressed beyond the depth of steel at 120 months; therefore, results included both the effects of carbonation and chloride induced corrosion.
Steel reinforcement in contaminated slag concrete experienced greater corrosion loss than concrete made with normal Portland cement, in either carbonated or uncarbonated concrete, regardless of curing, cover to reinforcement, and w/c.

**Drawback:** Tests only used relatively high w/c concrete.

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**Reference:** Ozyildirim, C., "High-Performance Concrete for Transportation Structures." *Concrete International: Design and Construction*, V. 15, No. 1, Jan. 1993, pp. 33-38.

**Variables:** Silica fume (7%, 8%, and 10% addition by weight of cement, w/c of 0.36, 0.39, and 0.40).
Slag (40% and 50% addition by weight of cement, w/c of 0.33 and 0.39).
Cement/fly ash/silica fume (60% / 35% / 5% and 65% / 30% / 5% addition by weight of cement, w/c of 0.40 and 0.45).
Cement/slag/silica fume (50% / 45% / 5% and 50% / 47% / 3% addition by weight of cement, w/c of 0.40 and 0.45).

**Specimens:** Concrete slabs ponded with NaCl solution.
Concrete cylinders with embedded/protruding reinforcing steel, ponded with NaCl solution.
Review of field performance.

**Test Methods:** Chloride content (AASHTO T259, ponding test extended to 2.5 years).
Rapid chloride permeability (AASHTO T277).
Half-cell potentials (ASTM C876).
Compressive strength.

**Results:** Laboratory tests:
At the end of the ponding tests, the chloride contents of the silica fume and slag concretes at 1.75 in. were below the threshold level, for pavements and decks, of 1.3 lb/yd$^3$; the chloride contents were also lower than (or at) the threshold at the 1.4 1 in. depth.
After 28 days curing, steam cured slag concrete had a very low chloride permeability rating, and those moist cured had a low or moderate rating.
Silica fume concrete had a low chloride permeability rating.
Concrete with combinations of slag and silica fume had higher strengths and lower permeability than those containing fly ash and silica fume. Better results were also obtained with Type III over Type II cements, and lower permeability when the specimens were cured at higher temperatures for the first 3 days or when low water-cement ratios were used.
Field tests:
For conventional concrete (in a comparison of bridges built before 1965, with a 2 in. clear cover), the chloride content at 1.75 in. had a median of 6.41 lb/yd$^3$, and corrosion was confirmed by half-cell potentials. For bridges built between 1966 and 1972, the chloride content at 1.75 in. in nine of the 27 bridges exceeded the threshold, and the average content was 0.71 lb/yd$^3$. These data indicate that ordinary concrete did not provide adequate resistance to chloride penetration.

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**Reference:** Pfeifer, D. W., "Corrosion Protection for Concrete Structures - - The Past and the Future." *Bridges: Selected Topics* (Fall 1989 Lecture Series, The Structural Group, BSCES/ASCE), 1989, pp. 4a-1 - 4a-30.

**Variables:** Calcium nitrite (2.75% by weight of cement, with admixed chloride, w/c of 0.53).
Calcium nitrite (30% solution, 4 gal/yd$^3$, w/c of 0.45).

**Specimens:** Literature review.

**Test Methods:** Half-cell potential (similar to ASTM C876).

**Results:** Calcium nitrite was found effective in reducing the rate of corrosion of black steel.
The control specimen exhibited 4 times the corrosion on the fully-cracked specimen than similar fully-cracked calcium nitrite specimens.
The control had 3 times the corrosion on the partially cracked specimen and 2 times the corrosion on the non-cracked specimen than similar calcium nitrite specimens.

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**Reference:** Philipose, K. E., Feldman, R. F., and Beaudoin, J. J., "Durability Predictions from Rate of Diffusion Testing of Normal Portland Cement, Fly Ash, and Slag Concrete." *Durability of Concrete* (Second International Conference, Montreal, Canada), ACI SP-126, V. 1, 1991, pp. 335-354.

**Variables:** Fly ash/silica fume (30% / 5% cement replacement, w/c of 0.35, 0.42, 0.50, and 0.60).
Slag/silica fume (75% / 3% cement replacement, w/c of 0.35, 0.42, 0.50, and 0.60).

**Specimens:** Concrete prisms immersed in NaCl solution.

**Test Methods:** Microscopic microprobe analysis.
X-ray analysis.
Porosity.
Ionic penetration profile data.

**Results:** The addition of fly ash, silica fume, and slag decreased the rate of ingress of chloride ions, which is a diffusion controlled process; a decrease in w/c improved the resistance further. The slag systems had the highest resistance to ionic ingress.
The slag system would have an expected service life of ten times that of an ordinary Portland cement system. The fly ash system would have a service life of five times that of an ordinary Portland cement system.

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**Reference:** Pigeon, M., Garnier, F., Pleau, R., and Aitcin, P., "Influence of Drying on the Chloride Ion Permeability of HPC." *Concrete International*, V. 15, No. 2, February 1993, pp. 65-69.

**Variables:** Silica fume (10% cement replacement, w/c of 0.22, 0.25, 0.35, and 0.45; also 5%, 10%, and 15% cement replacement, w/c of 0.25).

**Specimens:** Cored cylinders from a plate (various curing and drying regimes), exposed to a NaCl solution.
Cubes (various curing and drying regimes).

**Test Methods:** Rapid chloride permeability (AASHTO T277).

**Results:** Silica fume always significantly reduced chloride ion permeability of concrete. The reduction in permeability increased with the amount of silica fume used.
The use of silica fume at w/c of 0.25 or less made high performance concretes that were extremely resistant to internal damage due to high temperature drying.

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**Reference:** Pyc, W. A., Zemajtis, J., Weyers, R. E., and Sprinkel, M. M., "Evaluating Corrosion-Inhibiting Admixtures." *Concrete International*, April 1999, pp. 39-44.

**Variables:** Calcium nitrite (30% solution DCI, 4 gal/yd$^3$, w/c of 0.45).
Amines and esters (Rheocrete 222, 1 gal/yd$^3$, w/c of 0.45).
Amines and alcohol (Armatec 2000, 0.5 gal/yd$^3$, w/c of 0.45).

**Specimens:** Reinforcing steel immersed in NaCl solution for 90-days.

Concrete prisms with embedded reinforcing steel, cyclically ponded with 6% NaCl solution

**Test Methods:** Immersion test.
Half-cell potential (ASTM C876).
Chloride analysis (ASTM C114).
Linear polarization (similar to ASTM G59).

**Results:** Calcium nitrite reduced corrosion significantly in immersion tests.
Calcium nitrite had less negative corrosion potential indicating no corrosion activity.
Calcium nitrite experienced slightly better corrosion rates than the concrete control.
Calcium nitrite resisted development of active corrosion cells below the chloride threshold limit.
Rheocrete 222 did not provide corrosion protection in the immersion tests.
Armatec 2000 provided some corrosion protection at high chloride concentrations.
Rheocrete and Armatec showed little to no corrosion inhibition.
Rheocrete and Armatec experienced more negative corrosion potential than the concrete control, indicating a higher probability of active corrosion.
Corrosion rates for Rheocrete and Armatec were higher than the concrete control suggesting more active corrosion.
After one year of ponding none of the inhibitors appeared to inhibit chloride ingress.
Calcium nitrite entered active corrosion at about 65 weeks, 40 weeks for the control, and 33 weeks for Rheocrete and Armatec.

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**Reference:** Rasheeduzzafar, Al-Saadoun, S. S., and Al-Gahtani, A. S., "Reinforcement Corrosion-Resisting Characteristics of Silica-Fume Blended-Cement Concrete." *ACI Materials Journal*, V. 89, No. 4. July-August 1992, pp. 337-344.

**Variables:** Silica fume (10% and 20% cement replacement, w/c of 0.50).

**Specimens:** Concrete prisms with embedded/protruding reinforcing steel, partially immersed in 5% NaCl solution.

**Test Methods:** Half-cell potential (similar to ASTM C876).

**Results:** Concrete made with 9%, 11%, and 14% $C_3A$ Type I cements performed respectively, 1.75, 1.93, and 2.45 times better, with respect to half-cell values, than Type V, 2% $C_3A$ concrete.
The concretes with 10% and 20% replacement of cement with silica fume performed, respectively, 3.34 and 3.83 times better than the control concrete in corrosion resistance with respect to half-cell values.
Silica fume changed the physical structure of the hardened cement paste, to a dense and highly impermeable cement matrix, as a result of a refinement and segmentation of the capillary pores, negated the increased corrosion risk introduced by the elevated $Cl^-/OH^-$ ratio of the pore solution which is a result of hydration.
There was no real advantage with respect to corrosion initiation time by increasing the cement replacement with silica fume from 10% to 20%.

**Drawback:** Tests only used relatively high w/c concrete.

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**Reference:** Rose, J., "The Effect of Cementitious Blast-Furnace Slag on Chloride Permeability of Concrete." *Corrosion, Concrete, and Chlorides--Steel Corrosion in Concrete: Causes and Restraints,* ACI SP-102, 1987, pp. 107-125.

**Variables:** Blast furnace slag (40%, 50%, and 65% cement replacement, w/c of 0.35, 0.40, 0.42, 0.55, and 0.56, Type II cement).

**Specimens:** Reinforced concrete beams immersed in NaCl solution.
Core samples immersed in NaCl solution.
Concrete cylinders immersed in NaCl solution

**Test Methods:** Half-cell potential (similar to ASTM C876).
Rapid chloride permeability (similar to AASHTO T277).
Chloride determination (ASTM C114).
Visual survey.

**Results:** Corrosion potential decreased as the slag content increased.
The half-cell test could not differentiate the effects of different blends at low w/c.
No corrosion was found in the 40% slag concrete, and the chloride level of the control was about 8 times greater than that of the 40% slag concrete at all depths.
The permeability tests indicated that as the slag content increased, the chloride permeability decreased.
The permeability of slag concrete was less affected by increases in w/c than ordinary Portland cement concrete.
Chloride ion concentration below the 1/2 in. depth was greatly reduced as the percentage of slag was increased.
The chloride ion concentration at the 1.5 in. depth increased in all concrete mixes with an increased time of exposure, but the ordinary Portland cement concretes had a greater rate of increase than the slag concretes.
Ordinary Portland cement mixes had an increased chloride concentration as the w/c increased, but the slag concretes had little change with increasing w/c.

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**Reference:** Sagoe-Crentsil, K. K., Glasser, F. P., and Yilmaz, V. T., "Corrosion Inhibitors for Mild Steel; Stannous Tin (SnII) in Ordinary Portland Cement." *Cement and Concrete Research*, V. 24, No. 2, 1994, pp. 313-318.

**Variables:** Stannous tin (SnII) (200 mM/l, w/c of 0.50).

**Specimens:** Cement paste prisms with embedded reinforcing steel bars, with 2.5% by weight of cement of NaCl admixed in some specimens.

**Test Methods:** Linear polarization (similar to ASTM G59).

**Results:** Stannous tin was a strong inhibitor of chloride induced corrosion of steel embedded in concrete; the mechanism was believed to be that tin stabilized the passivating layer on the steel.
For cements containing 0-1628 mM/l chloride, $Sn^{2+}$, but not $Sn^{4+}$, was an effective inhibitor at an initial concentration of 200 mM/l.

**Drawbacks:** Tests done on cement paste samples; tests only used relatively high w/c concrete.

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**Reference:** Sagoe-Crentsil, K. K., Yilmaz, V. T., and Glasser, F. P., "Corrosion Inhibition of Steel in Concrete by Carboxylic Acids." *Cement and Concrete Research*, V. 23, No. 6, June 1993, pp. 1380-1388.

**Variables:** Carboxylic acids (2.5% addition by weight of cement, w/c of 0.50).

**Specimens:** Mortar cylinders with embedded/protruding reinforcing steel, with 2.5% by weight of

cement of NaCl admixed.

**Test Methods:** Linear polarization (similar to ASTM G59).

**Results:** The acids remained soluble after curing in cement for up to 90 days.
Malonic acid (malonate), a dicarboxylic acid, was a very effective corrosion inhibitor, even in the presence of 2.5% chloride by weight of cement; however, it acted as a set retarder in the mortar.
Soluble dicarboxylic acids inhibited corrosion more effectively than monofunctional acids.

**Drawback:** Tests only used relatively high w/c mortar.

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**Reference:** Schiessl, P., and Wiens, U., "Long-Term Influence of Fly Ash on Chloride-Induced Corrosion." *Durability of Concrete* (Proceedings Fourth CANMET/ACI International Conference), ACI SP-170, V. 1, 1997, pp. 1-21.

**Variables:** Slag (46% and 74% cement replacement, w/c of 0.50).
Class F fly ash (0%, 20%, 40%, and 60% cement replacement, w/c of 0.50).
Slag/fly ash (46% / 20% cement replacement, w/c of 0.50).

**Specimens:** Cylinders drilled from mortar slabs (with 1% admixed chloride), immersed in NaCl solution.

**Test Methods:** Rapid chloride permeability with diffusion cells.
Calorimetric method for chloride penetration depth.
Electrolytic resistance in corrosion cells.

**Results:** There was a reduction of the diffusion coefficients when slag and fly ash were combined.
Diffusion coefficients for fly ash mixtures dropped as the fly ash content increased.
For fly ash at 20% and 40%, the diffusion coefficients fell by one (or more than one) order of magnitude; slag also increased diffusion resistance.
The rapid test (migration test) was suitable for characterizing diffusion resistance of concrete containing different additions.
Fly ash increased electrolytic resistance as its content increased, indicated by a drop of the macrocell currents.
The 40% and 60% fly ash mixes had electrolytic resistance greater than the slag concrete; the 20% fly ash mix performed the same as the slag mixes.

**Drawbacks:** Tests only used relatively high w/c mortars.

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**Reference:** Sherman, M. R., McDonald, D. B., and Pfeifer, D. W., "Durability Aspects of Precast Prestressed Concrete, Part 2: Chloride Permeability Study." *PCI Journal*, July-Aug. 1996, pp. 76-95.

**Variables:** Silica fume (5% and 7.5% addition by weight of cement, w/c of 0.32, 0.37, and 0.46, burlap cured).
Conventional concrete (w/c of 0.32, 0.37, and 0.46, tank, burlap, and heat cured).

**Specimens:** Concrete beams with top and bottom reinforcing bars, ponded with NaCl solution.
Concrete cylinders with embedded/protruding reinforcing steel, partially immersed in NaCl solution.

**Test Methods:** Chloride permeability tests (AASHTO T259, salt water ponding extended to 365 days).

Coulomb test (ASTM C1202 or AASHTO T277).
Water absorption test (ASTM C642).

**Results:** The lowest average diffusion coefficients were from the 0.32 w/c concretes with 5% and 7.5% silica fume.

The w/c was the dominant factor in reducing chloride permeability; the reductions were approx. 95% from the 0.46 w/c concrete to the 0.32 w/c concrete.

Silica fume concrete had lower chloride concentrations than conventional concrete; heat cured concrete had lower concentrations than burlap-cured concrete near the top surface, but about the same concentration at lower levels; 7.5% silica fume concrete and heat cured concrete had similar lower concentrations near the top surface. The 7.5% silica fume concrete at w/c of 0.32 had the least near surface chlorides.

Heat cured concrete had between 18% and 36% less chlorides at the surface than water tank and burlap cured conventional and silica fume concrete.

Concrete with 5% and 7.5% silica fume replacements had an average volume of permeable voids of 100% and 50%, respectively, greater than heat cured mixtures. Heat cured specimens had absorption and permeable void volume 25% to 40% lower than companion burlap cured concrete. However, with a given w/c, the silica fume concretes had lower coulomb values than heatcured slabs.

The 5% and 7.5% silica fume concretes with 0.37 - 0.46 w/c had estimated time to corrosion similar to those of heat cured 0.32 - 0.37 w/c concrete. The 7.5% silica fume mix with a low w/c had a greater time to corrosion than any of the other mixes by more than 12 times.

Using the estimated time to corrosion and long term chloride ingress, low w/c heat cured conventional concrete should perform as well as practical w/c concrete with silica fume.

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**Reference:** Valantini, C., Berardo, L., and Alanis, I., "Influence of Blast Furnace Slags on the Corrosion Rate of Steel in Concrete." *Corrosion Rates of Steel in Concrete,* ASTM STP 1065, 1990, pp. 17-28.

**Variables:** Blast furnace slag (20%, 45%, and 75% cement replacement, w/c of 0.50).

**Specimens:** Mortar prisms with embedded/protruding reinforcing steel, partially immersed in NaCl solution.

**Test Methods:** Polarization resistance (similar to ASTM G59).
Corrosion potential.
Ohmic resistance.

**Results:** Corrosion currents and potentials showed passivation trends over time for the reinforcing steel in concrete whether blended with slag up to 75% or not.

Corrosion currents immediately after curing were found to be independent of the amount of slag (from 20% to 75%) and were up to 10 times the current for pure Portland cement mortar. This difference disappeared with time. Therefore, laboratory tests performed on different ages of specimens could give contradictory results.

**Drawbacks:** Test only used relatively high w/c mortar.

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**References:** Virmani, Y. P., "Effectiveness of Calcium Nitrite Admixture as a Corrosion Inhibitor." *Public Roads*, V. 54, No. 1, June 1990, pp. 171-182.

Virmani, Y. P., "Time to Corrosion of Reinforcing Steel in Concrete Slabs, Vol VI: Calcium Nitrite Admixture." 1988, FHWA/RD-88/165, pp. 1-45.

Virmani, Y. P., Clear, K. C., and Pasko Jr., T. J., "Time to Corrosion of Reinforcing Steel in Concrete Slabs, Volume 5: Calcium Nitrite Admixture or Epoxy Coated Reinforcing Bars as Corrosion Protection Systems." 1983, FHWA/RD-83/012, pp. 1-72.

**Variables:** Calcium nitrite (2.75% by weight of cement, w/c of 0.53).
The top slab lifts mixed with calcium nitrite had nominal chloride contents of 0, 5, 10, 15, 20, 25, and 35 lb $Cl^-/yd^3$.
Control slab top lifts were mixed with 0, 5, 15, and 35 lb $Cl^-/yd^3$.

**Specimens:** Slabs of two lifts; the upper lift was 2.5 in. with 4- #5 longitudinal and 2- #4 cross rebar and typically mixed with chlorides; lower lift was 3.5 in. with 7- #5 longitudinal and 3- #4 cross rebar, cast 1 to 3 days before the top, and was chloride free. Top clear cover was 3/4 in. and bottom was 1 in.. Slabs were ponded with 3% NaCl solution until a corrosion current developed in a control slab (46 days); then slabs were exposed to climate conditions of the Washington, D.C. area.

**Test Methods:** Thermocouple readings to monitor temperature.
Voltage drop to measure current flow between the top and bottom mats.
Polarization resistance (similar to ASTM G59).
Half-cell potential (similar to ASTM C876).
Electrical resistance between top and bottom mats.
Visual survey.

**Results:** The rate of corrosion increased as the chloride/nitrite increased.
The reductions in the corrosion rate were about a factor of 10 for chloride/nitrite in the range of 0.29 to 1.11.
For a chloride/nitrite above 1.11, the corrosion rate was only reduced by a factor of 2.
The non-destructive corrosion measurement techniques and data correlated well with the visual surveys, making them reliable in situ test methods.
The magnitude of corrosion current flow between mats in chloride contaminated concrete was used to effectively monitor the performance of corrosion inhibitors.
The use of calcium nitrite was effective in reducing the rate of corrosion of steel rebar in poor quality chloride contaminated concrete up to a chloride/nitrite of 0.90.
Calcium nitrite was effective because it did not allow a large electrical potential difference to develop between adjoining mats.

**Drawback:** Tests only used relatively high w/c concrete.

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**Reference:** Wolsiefer, Jr., J. T., "Silica Fume Concrete: A Solution to Steel Reinforcement Corrosion in Concrete." *Utilization of Industrial By-Products for Construction Materials* (Proceedings of the Session Sponsored by the Materials Engineering Division in Conjunction with the ASCE National Convention in Dallas, Texas), 1993, pp. 15-29.

**Variables:** Silica fume (20% addition by weight of cement, no w/c given).

**Specimens:** Literature review.
Concrete cubes immersed in 15% NaCl solution.
Concrete cylinders partially immersed in 3% NaCl solution

**Test Methods:** Half-cell potential (similar to ASTM C876).
Rapid chloride permeability (AASHTO T277).
Macrocell corrosion (similar to ASTM G109).

NCHRP cube test.
A.C. resistivity.

**Results:** Silica fume at 20% had an absorption of 16% of the control concrete.
Silica fume at 5% to 15% had very low chloride permeability.
Permeability of silica fume concrete depends on curing. The rate of permeability decreases with time, is proportional to the moisture available and cement hydration.
Silica fume increased electrical resistivity.
Silica fume concrete will not support macrocell corrosion activity.
The high electrical resistance of silica fume concrete prevents significant corrosion current current along and between reinforcement, in the presence of chloride intrusion allowed by concrete cracking.

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**Reference:** Zhang, H., Wheat, H. G., Sennour, M. L., and Carrasquillo, R. L., "Corrosion of Steel Bars in Concrete Containing Different Chemical and Mineral Admixtures." *Materials Performance*, V. 31, No. 12, December 1992, pp. 37-43.

**Variables:** Class C and F fly ash (20%, 27.5%, and 35% cement replacement, w/c of 0.40 - 0.69).

**Specimens:** Concrete cylinders, cyclically ponded with 3.5% NaCl solution.
Concrete cylinders with embedded/protruding reinforcing steel, cyclically immersed in 3.5% NaCl solution.
Concrete beams with top and bottom reinforcing steel, cyclically ponded with 3.5% NaCl solution.
Concrete prisms, cyclically ponded with 3.5% NaCl solution.

**Test Methods:** Half-cell potential (ASTM C876).
Polarization resistance (ASTM G59).
Rapid chloride permeability (similar to AASHTO T277).
Macrocell corrosion (ASTM G109).
Compressive strength (ASTM C39).

**Results:** Concrete with Class C fly ash had the highest initial strength.
Concrete with Class F fly ash had the highest six-month strength, lowest initial permeability, and least chloride penetration.
Further long term results were pending as of publication date.

**Reference:** Baweja, D., Roper, H., Sirivivatnanon, V., "Chloride-Induced Steel Corrosion in Concrete: Part 1 – Corrosion Rates, Corrosion Activity, and Attack Areas." *ACI Materials Journal*, V. 95, No.3. May-June 1998, pp. 207-217.

**Variables:** Slag (35% cement replacement)
Fly Ash (25% cement replacement)
w/cm = 0.45, 0.55, 0.65, 0.85

**Specimens:** Concrete slabs that include mesh reinforcement, partially immersed in 3% NaCl solution.

**Test Methods:** Potential readings (mV vs. SCE)
Visual Survey of recovered reinforcement

**Results:** Fly ash blended cements had decreased 28-day strength compared to that of control and slag specimens.

Corrosion resistance was lowered with the addition of fly ash and slag, and a decreased w/cm ratio.
Slag showed the lowest corroded area percentages.

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**Reference:** Ozyildirim, C., "Laboratory Investigation of Low-Permeability Concretes Containing Slag and Silica Fume." *ACI Materials Journal*, V. 91, No. 2. March-April 1994, pp. 197-202.

**Variables:** Combinations of Portland cement, slag, and silica fume:
(PC/Slag/Silica Fume) – (100/0/0), (50/50/0), (93/0/7), (50/47/3), (50/45/5), (50/43/7), (60/37/3), (60/35/5), (60/33/7) at w/cm = 0.45, and (50/45/5), (50/47/3) at w/cm = 0.40

**Specimens:** concrete cylinders 100x200mm$^2$ and 100x100mm$^2$

**Test Methods:** Compressive Strength
Chloride permeability

**Results:** 1-day compressive strength was lower in concretes containing slag compared to those of ordinary Portland cement and silica fume concretes, this difference was reduced greatly at 7 days. At 28 days, OPC had the lowest compressive strength and the highest permeability.
The article suggests that silica fume may not be needed to reduce permeability in slag concretes that are cured properly.
Although the addition of silica fume decreases permeability, higher initial curing temperatures resulted in lower permeability.

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**Reference:** Polder, R., "The Influence of Blast Furnace Slag, Fly Ash and Silica Fume on Corrosion of Reinforced Concrete in Marine Environment." *Heron*, V. 41, No. 4. 1996, pp. 287-300

**Variables:** Ordinary Portland cement concrete (w/cm = 0.43)
Silica Fume – 5% addition by wt of cement (w/cm = 0.41)
Silica Fume – 5% and Fly Ash – 10% (w/cm = 0.37)
Slag – 70% (w/cm = 0.25)

**Specimens:** Concrete prisms (100x100x300mm$^3$ and 100x100x50mm$^3$)

**Test Methods:** Electrical Resistance
Total chloride content
Compressive and tensile strength

**Results:** The addition of silica fume increased 28-day compressive and tensile strength.
Service life calculations performed using chloride penetration and strength tests gave the following results:
Slag > SF + FA > SF > OPC

**Drawbacks:** Study used w/cm values that might not be appropriate for comparison of different percentages of admixtures.

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**Reference:** Smith, B., "Durability of Silica Fume Concrete Exposed to Chloride in Hot Climates." *Journal Materials in Civil Engineering*, V. 13, No. 1, January 2001, pp. 41-48.

**Variables:** Slag (50% replacement by weight of cement) at w/cm = 0.4
Fly Ash (25% replacement by weight of cement) at w/cm = 0.4

Silica Fume (10% and 5% replacement by weight of cement) at w/cm = 0.4

**Specimens:** not specified

**Test Methods:** not specified

**Results:** The article compares the admixtures according to the relative time to corrosion: 50% slag > 25% fly ash > 10% silica fume > 5% silica fume > OPC
Maximum amount of cement replacement with silica fume was given as 10%.
The article also gives a mathematical model of how to predict the service-life of concrete structures.

**Drawbacks:** Minimal information was given as to how the data was obtained (i.e. testing procedure and corrosion criteria).

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**Reference:** Thomas, M., "Chloride Thresholds in Marine Concrete." *Cement and Concrete Research*, V. 26, No. 4. April 1996, pp. 513-519

**Variables:** Fly Ash (design strength of 25, 35, and 45 MPa) at 15, 30, and 50% cement replacement

**Specimens:** 100x100x300mm$^3$ reinforced concrete prisms

**Test Methods:** Mass loss of reinforcing bars
Chloride content

**Results:** Fly ash specimens had more mass loss in reinforcing bars compared to control at a given chloride content. This may offset the benefit of fly ash decreasing permeability.

**Drawbacks:** The study used variable water-to-cementitious materials ratio, preventing valid comparison of mix designs.

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**Reference:** Wolsiefer, J. T. Sr., "Silica Fume Concrete: A Solution to Steel Reinforcement Corrosion in Concrete." *Utilization of Industrial By-Products for Construction Materials Proceedings of the ASCE National Convention and Exposition*, October 24-28 1993, pp. 15-29.

**Variables:** Silica Fume (10 and 20% addition by weight of cement)

**Specimens:** 20ft$^2$ concrete slabs ponded with 3% NaCl solution
4 inch cube specimens
Concrete cylinders
Concrete slabs

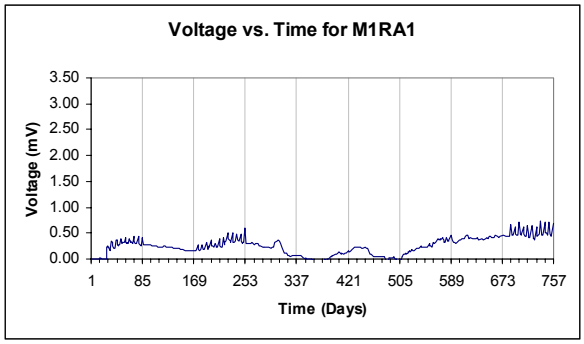
**Test Methods:** Chloride permeability
Electrical resistivity
Macrocell data
½-Cell data

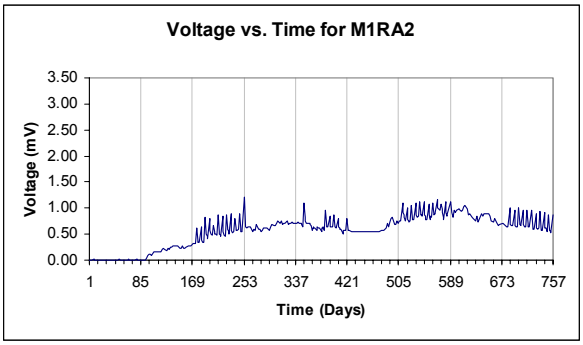
**Results:** The addition of silica fume to OPC increased the strength, increased the abrasion resistance, increased resistance to corrosion current, and decreased permeability.

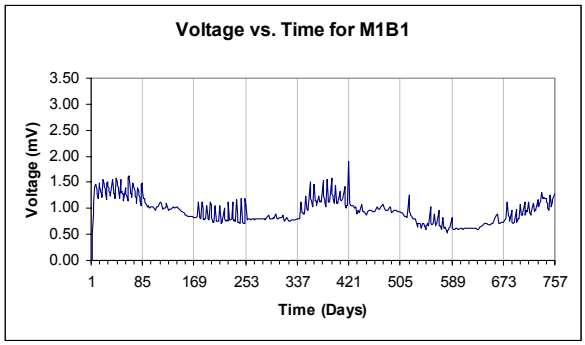
**Drawbacks:** Many different test procedures were carried out, but no detail was given about the mix designs (no w/cm or w/c was mentioned)

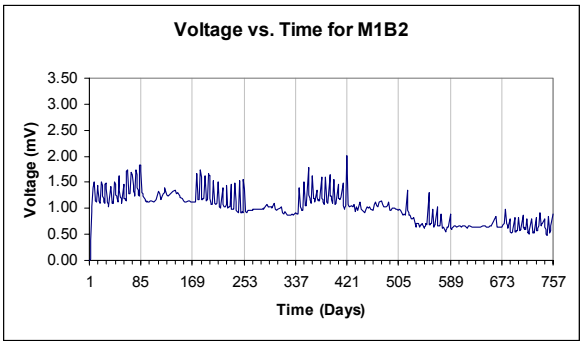
# APPENDIX B:
# MACROCELL DATA

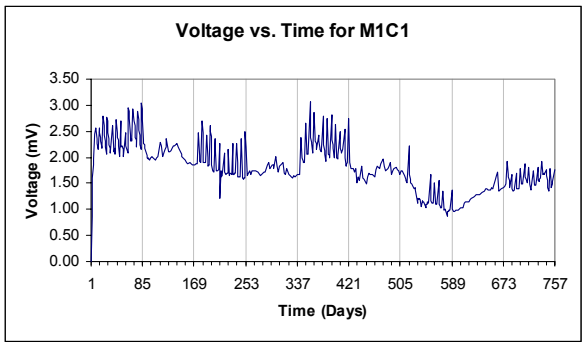
# MIX 1 Macrocell Data

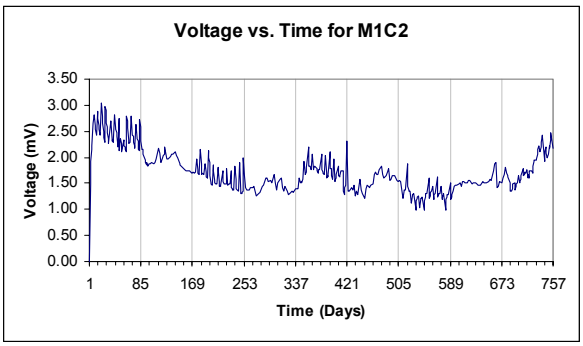


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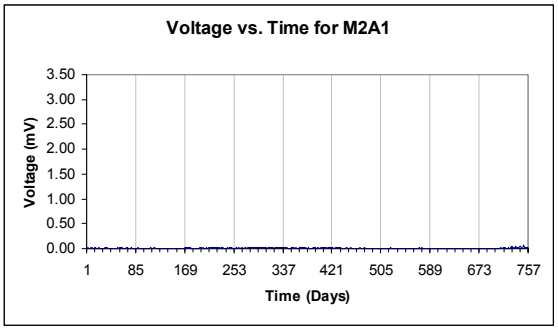


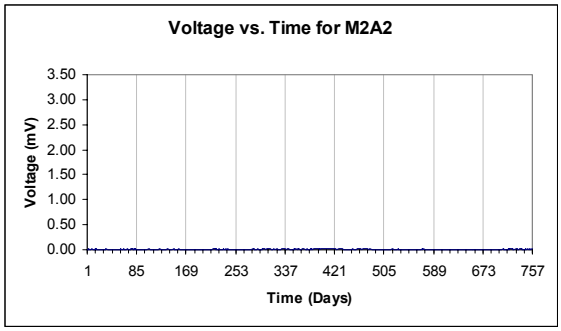


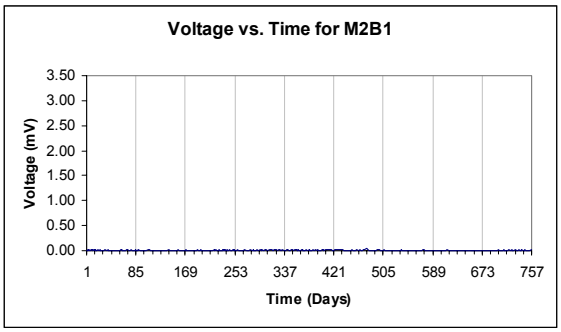


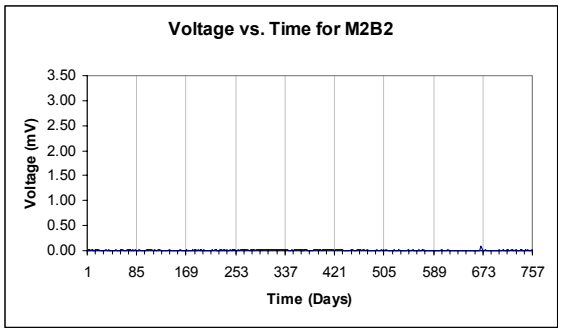


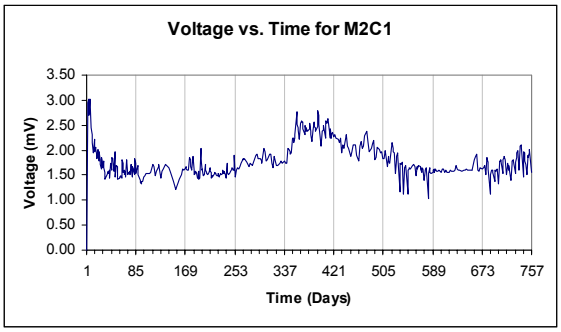


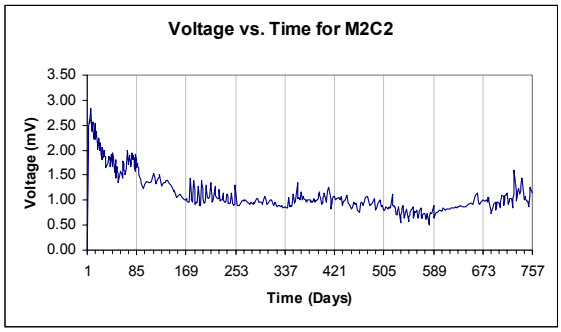

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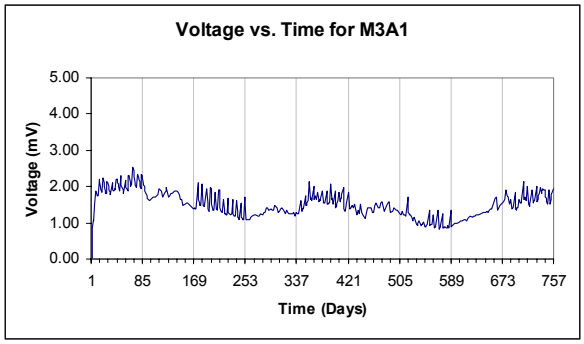


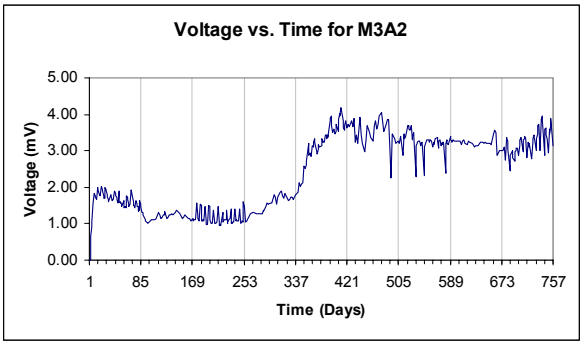


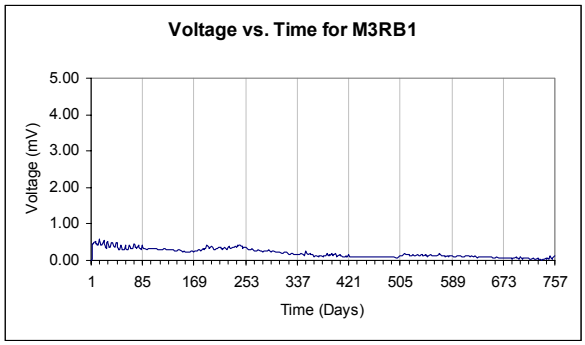


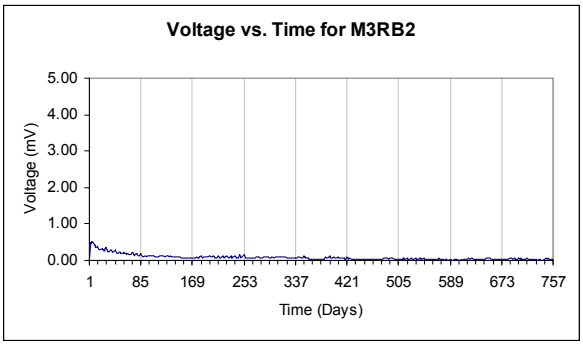


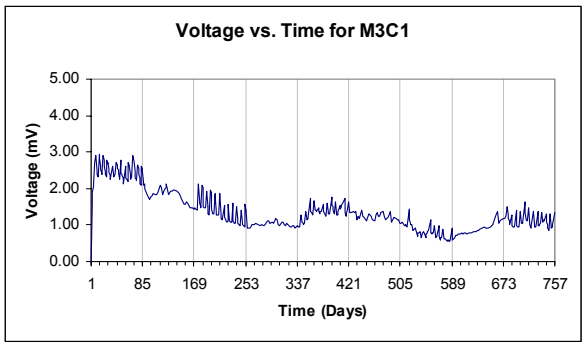


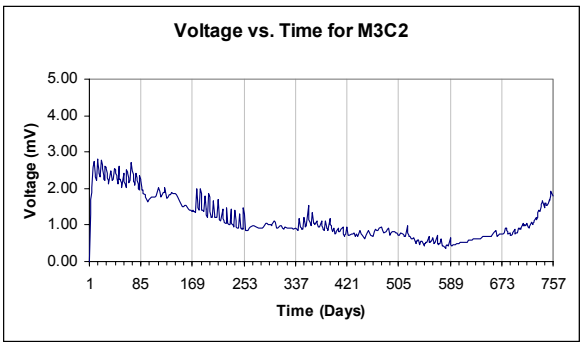

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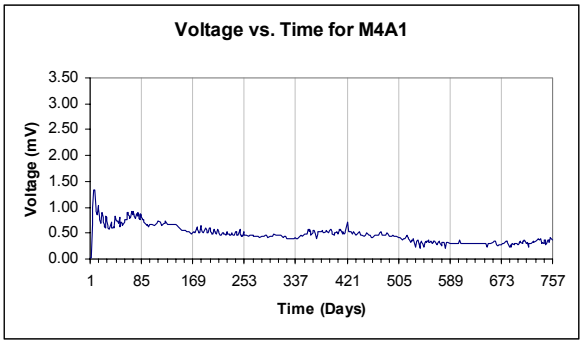


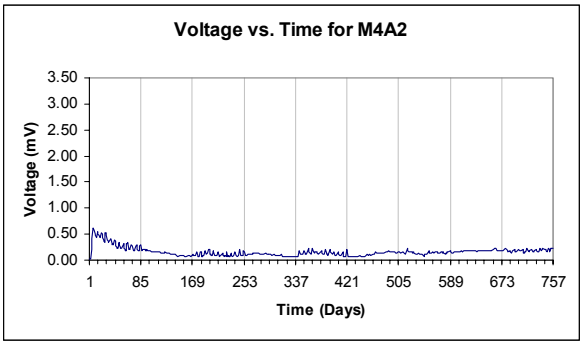


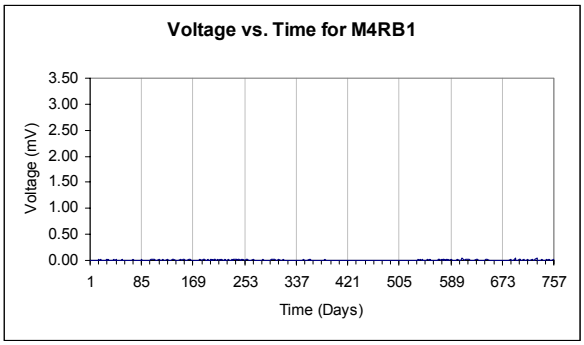


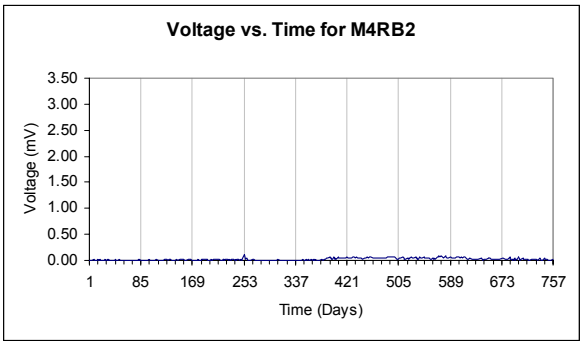


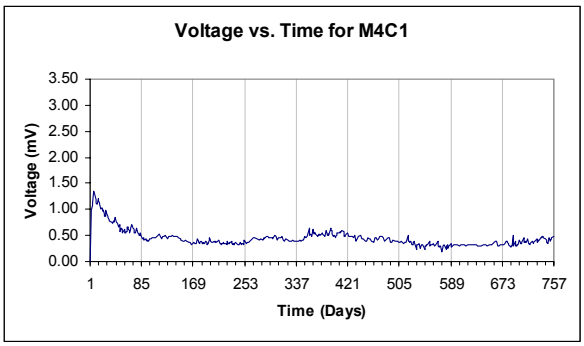


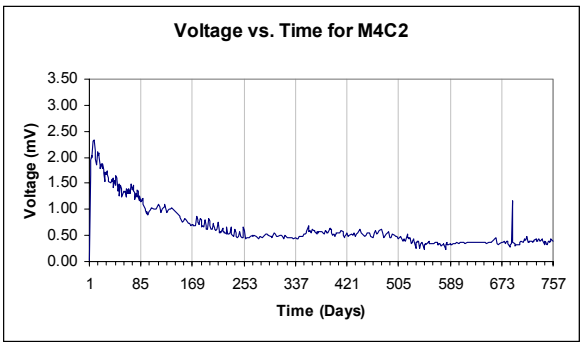

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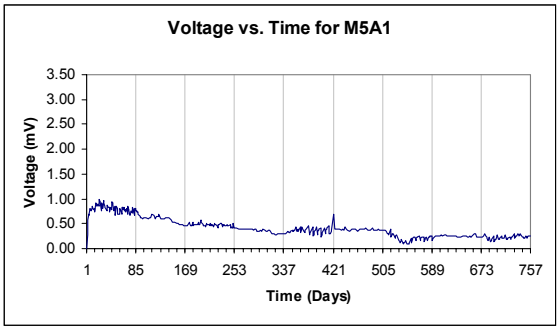


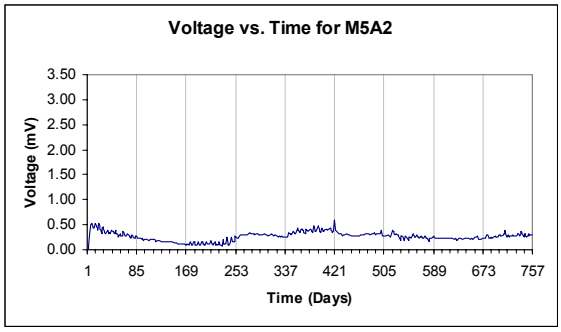


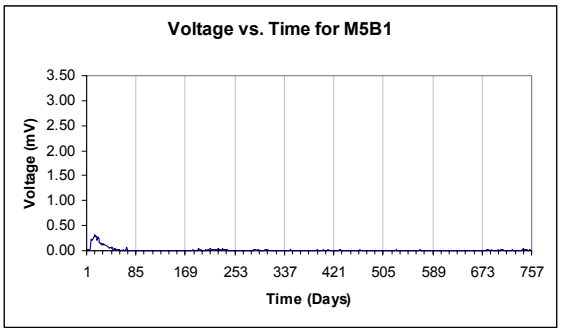


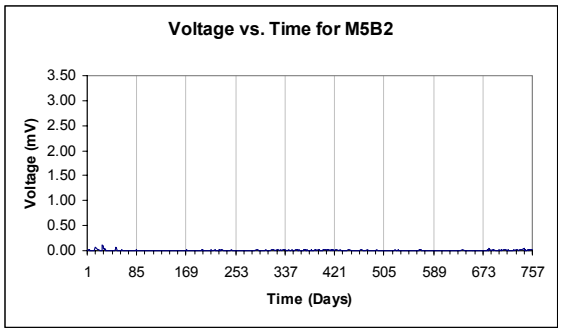


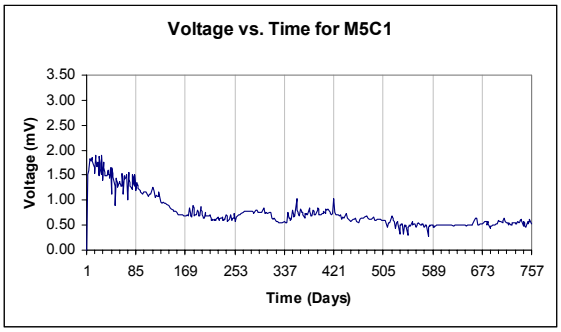


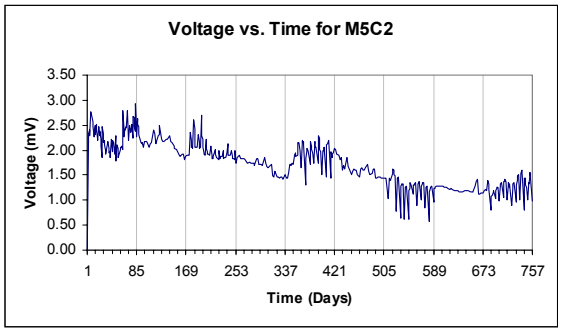

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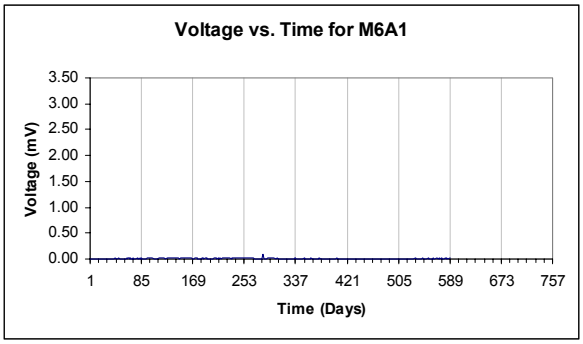


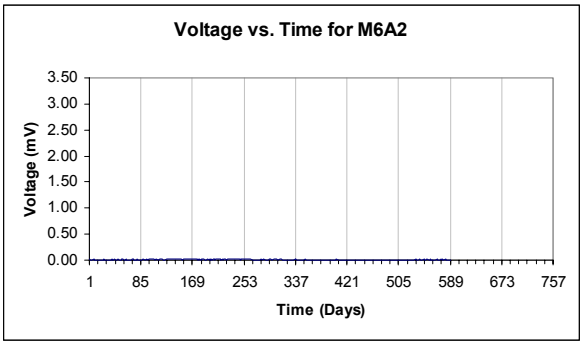


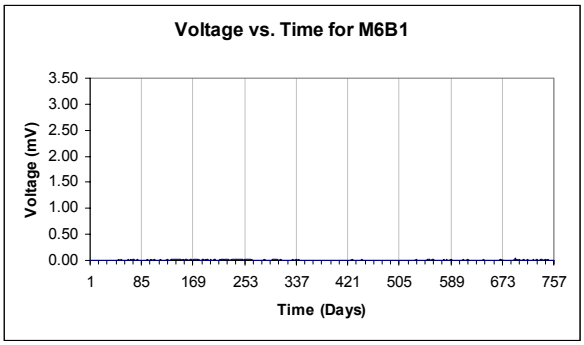


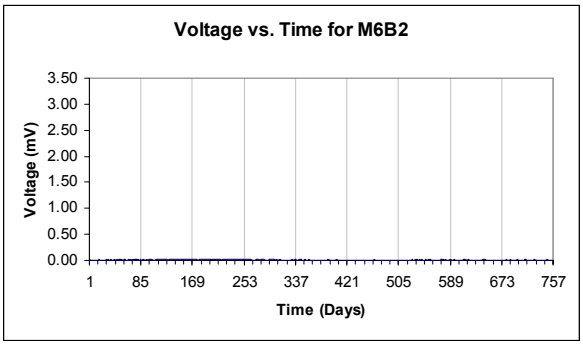


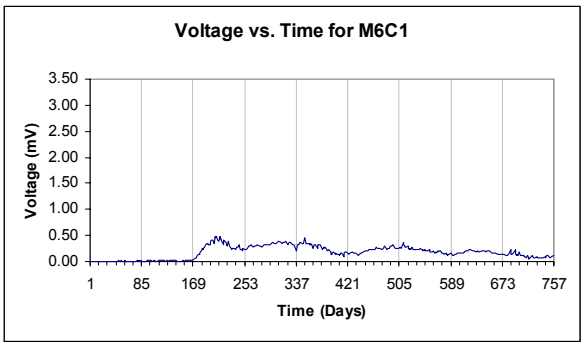


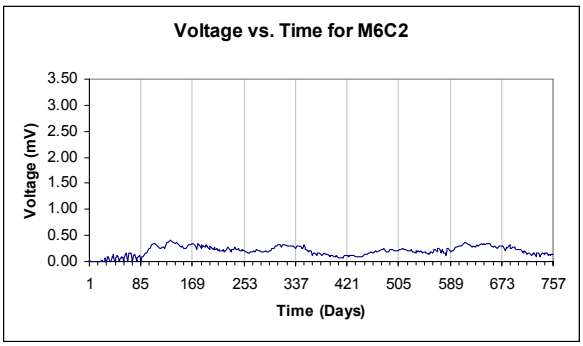

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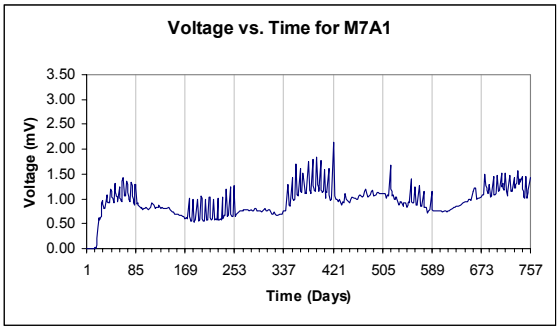


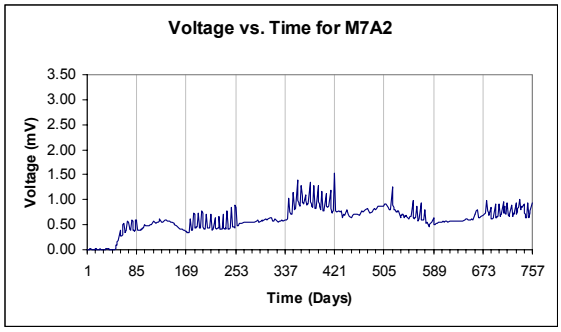


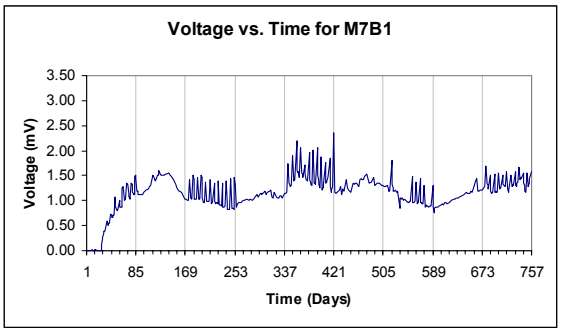


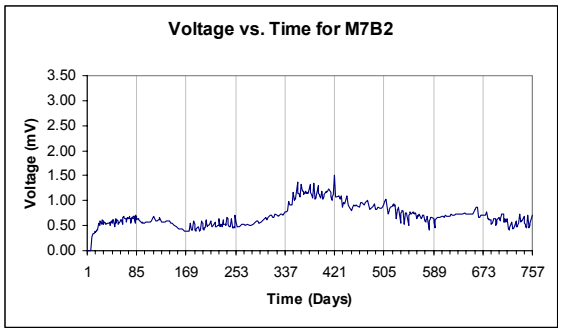


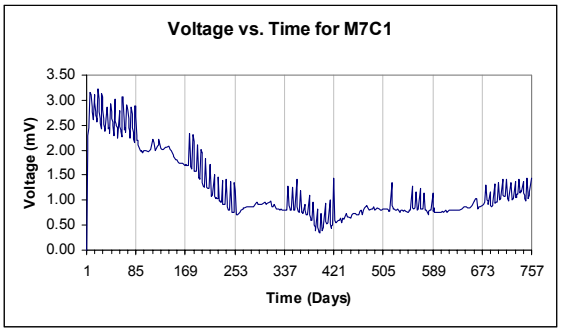


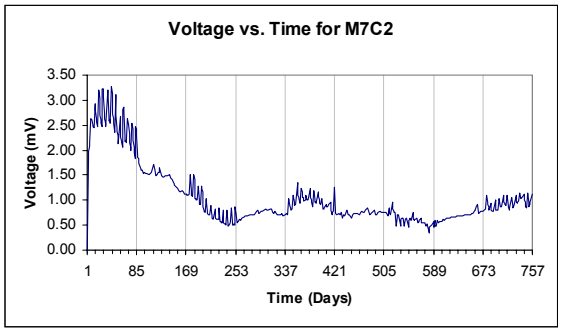

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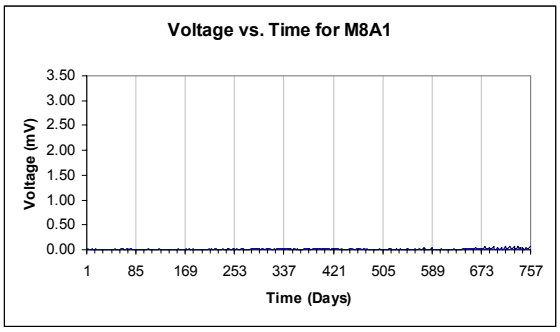


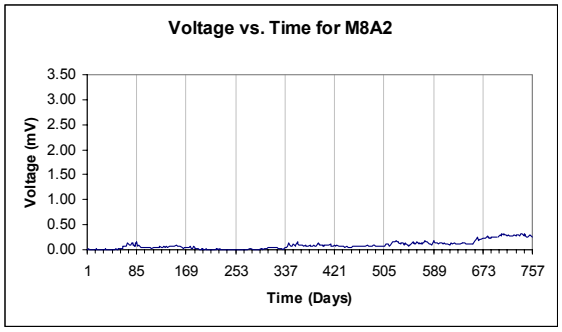


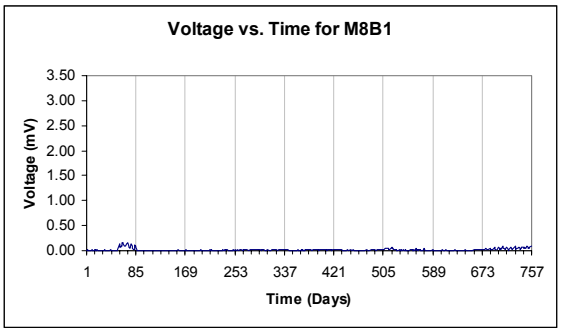


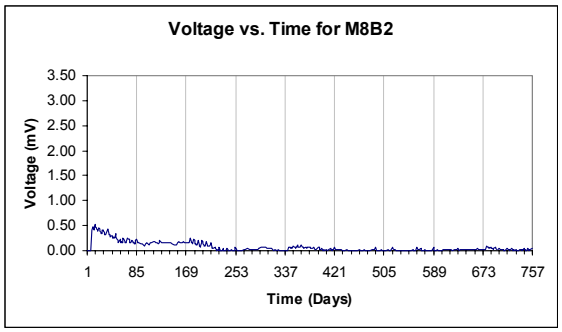


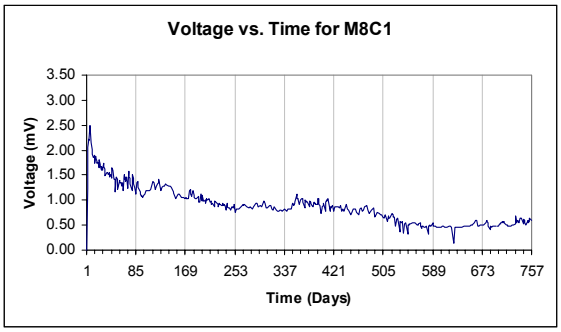


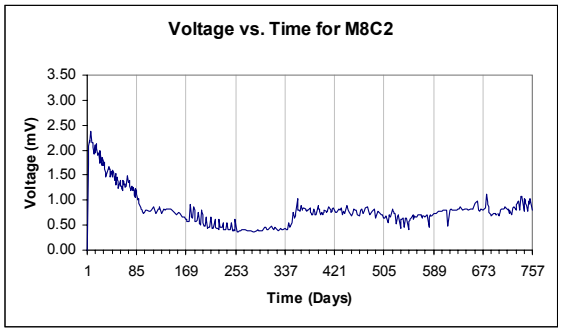

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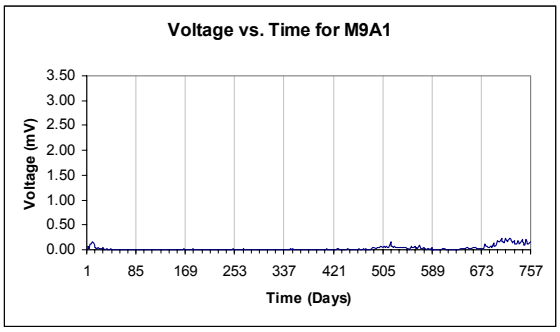


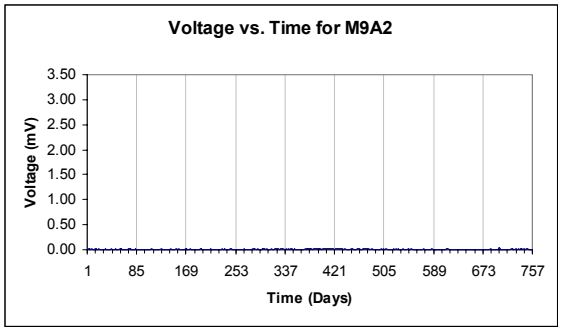


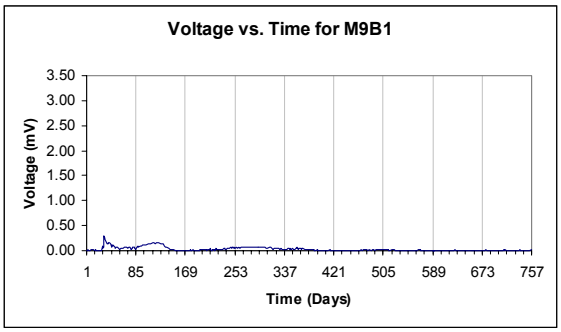


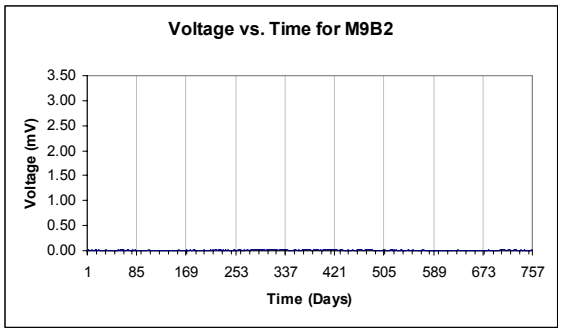


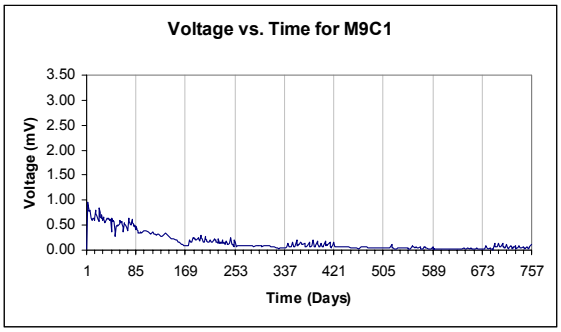


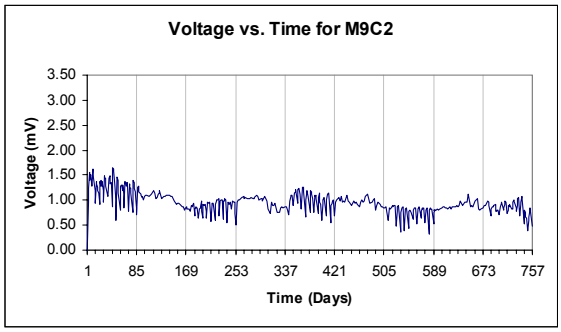

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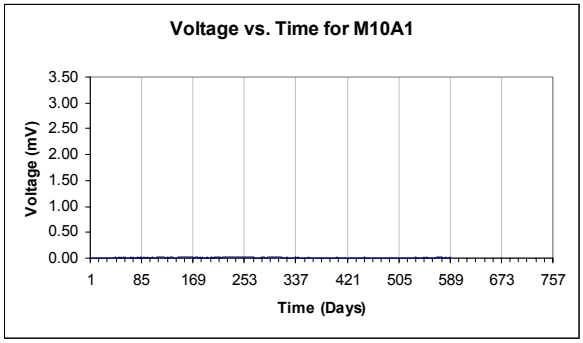
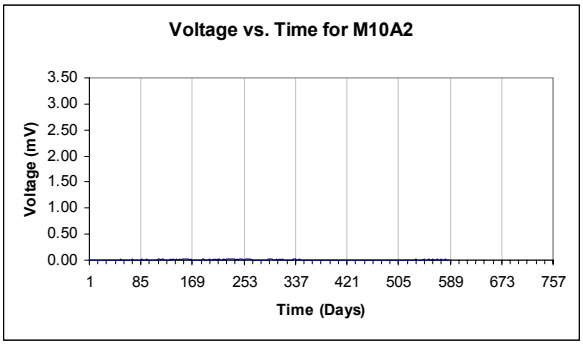
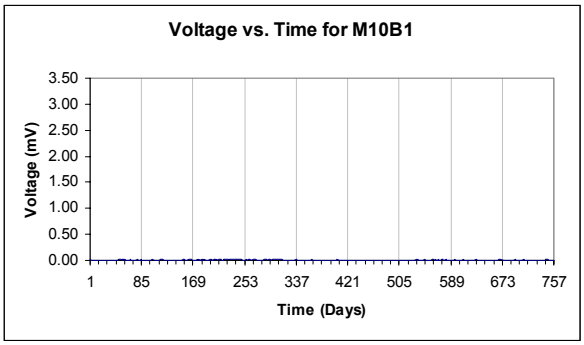
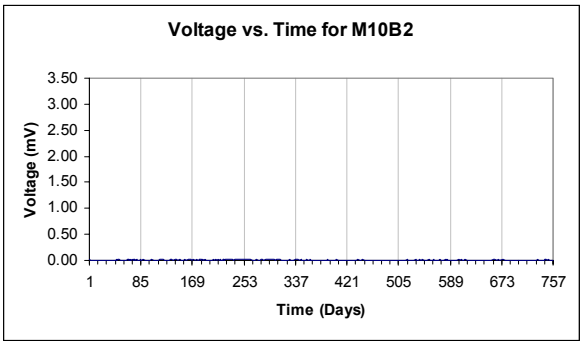
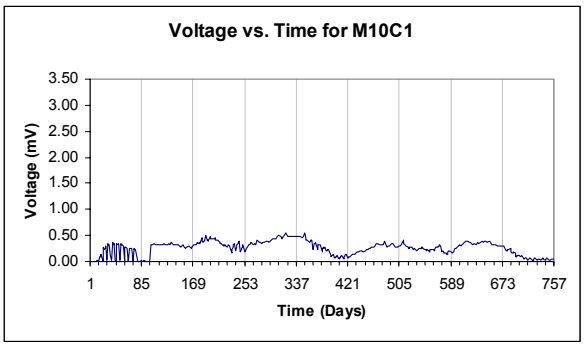
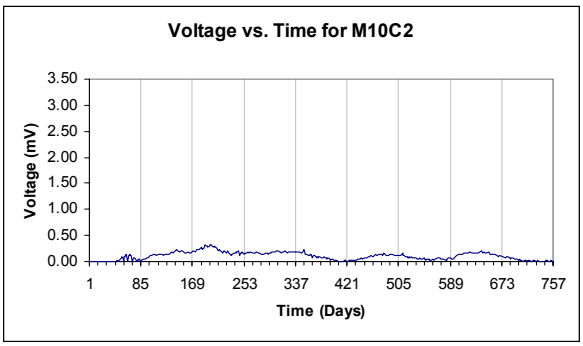


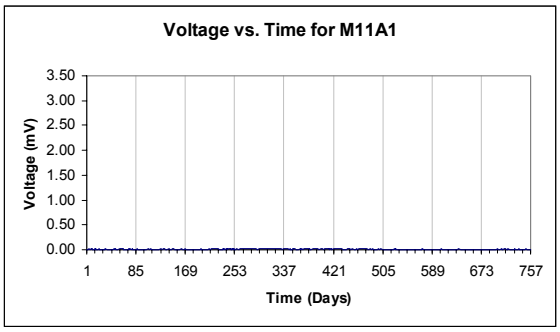



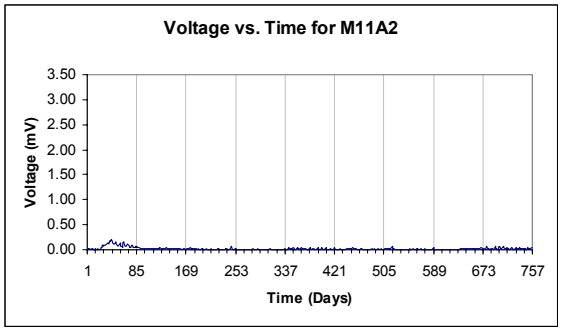



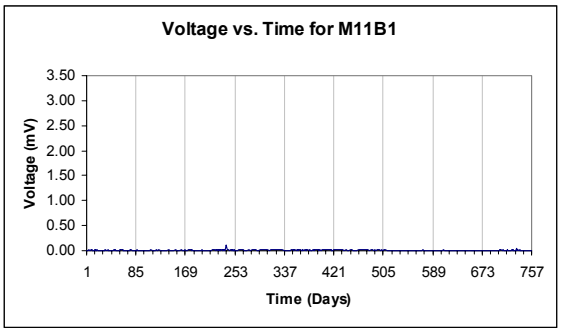



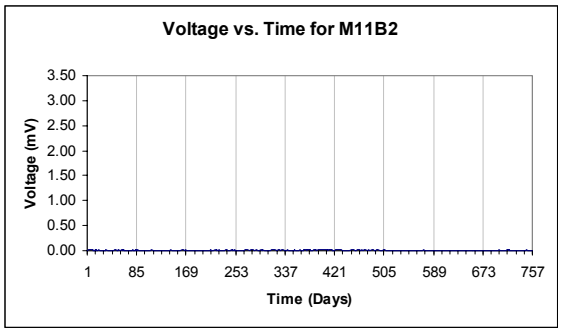



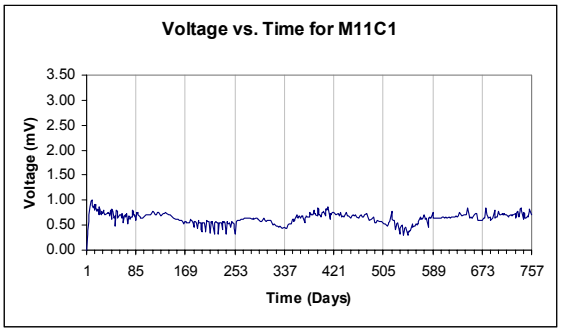
# MIX 11 Macrocell Data

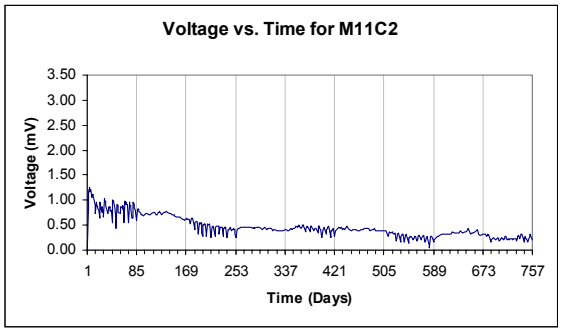


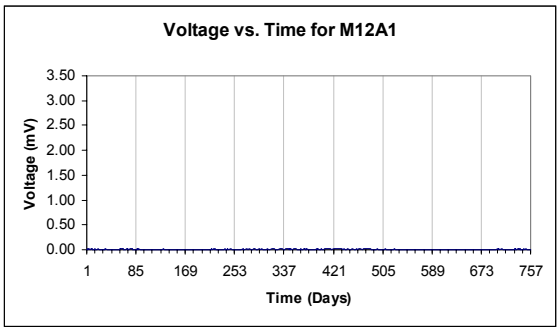



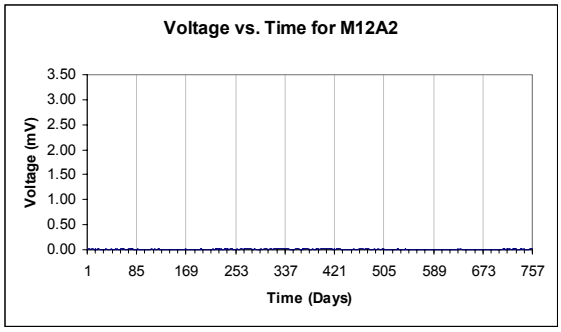



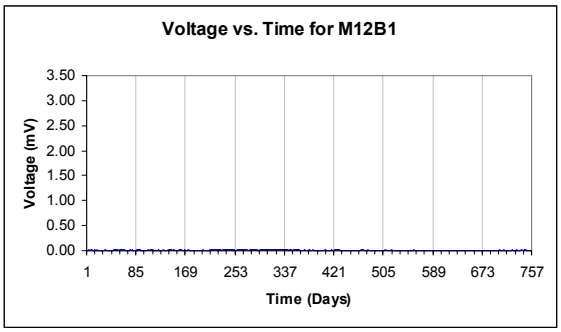



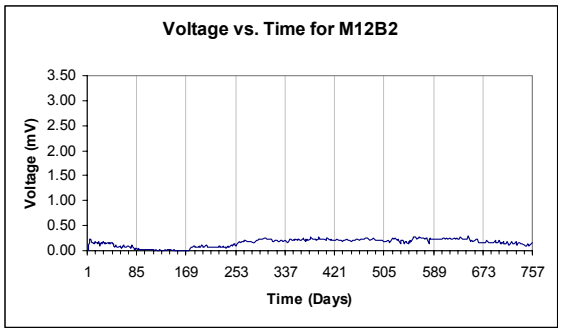



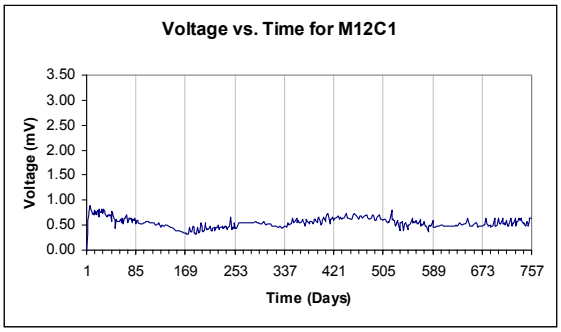
# MIX 12 Macrocell Data

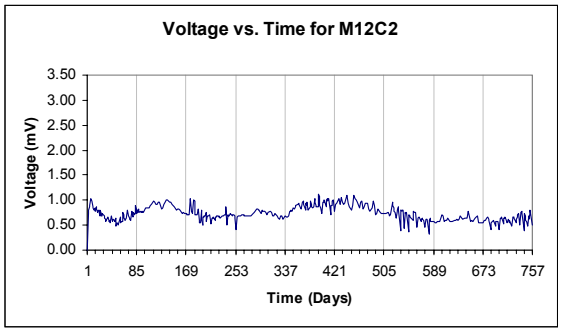


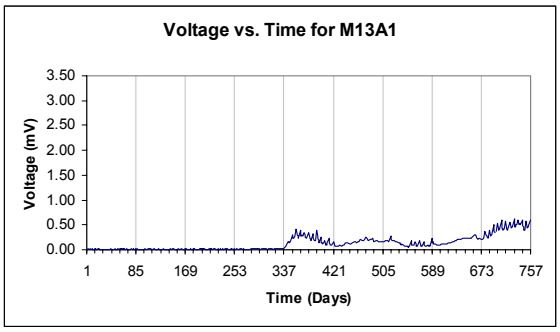



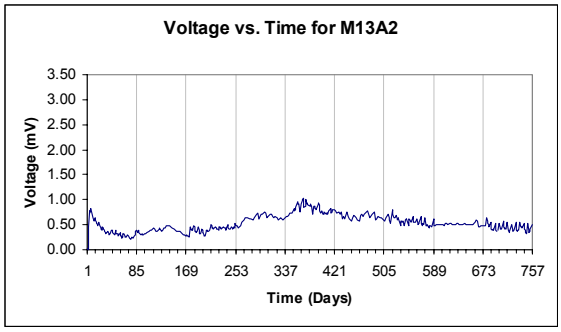



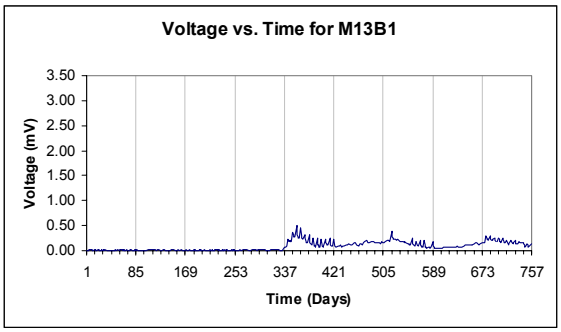



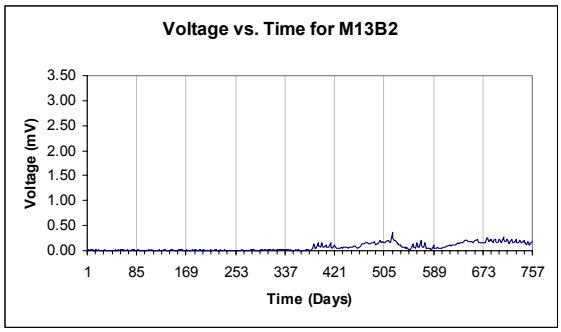



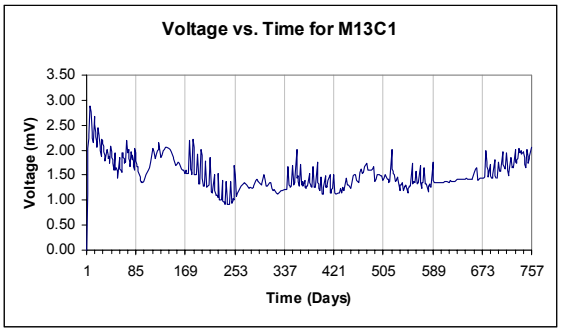
# MIX 13 Macrocell Data

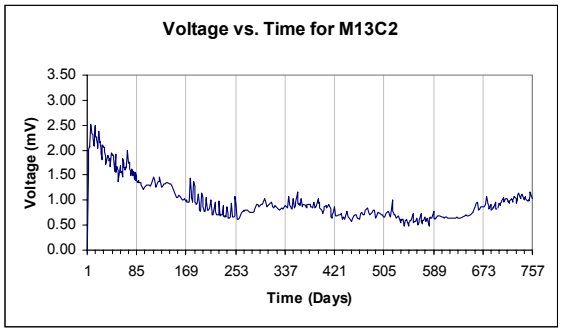


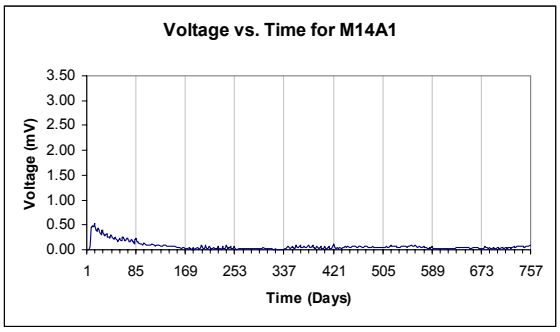



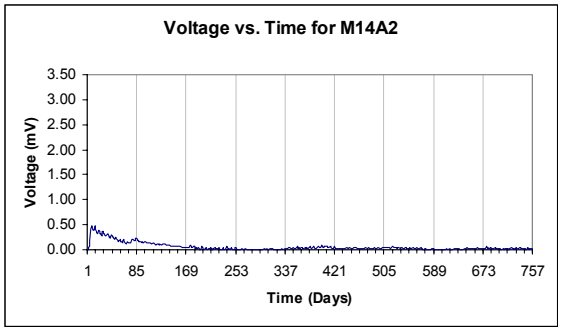



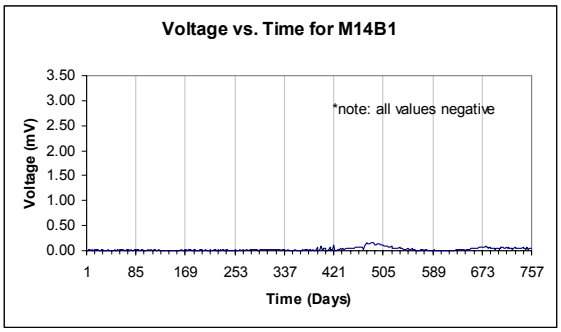



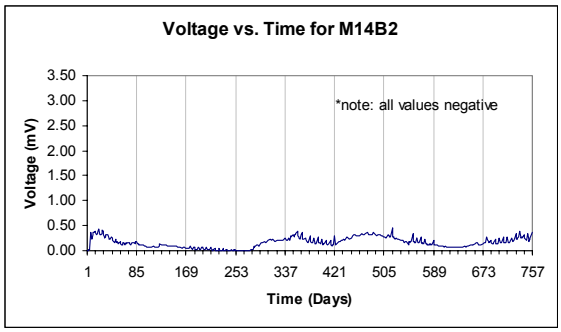



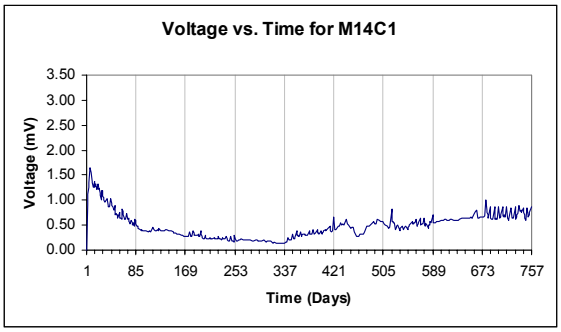
# MIX 14 Macrocell Data

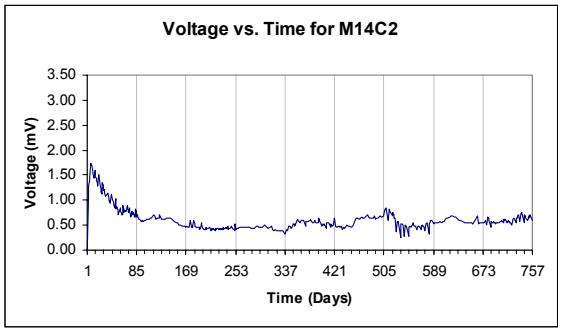


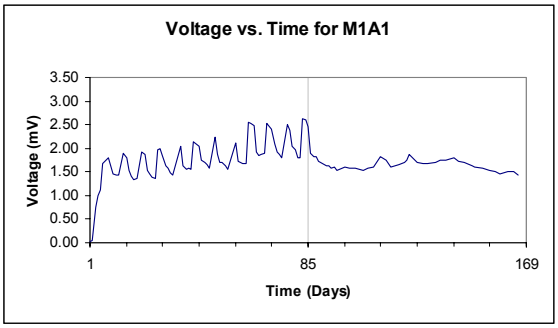



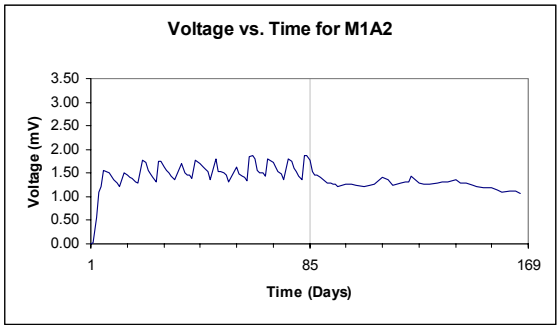



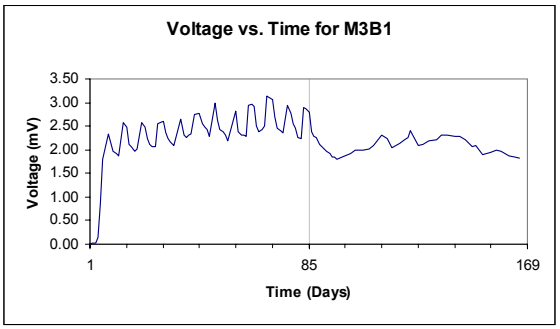



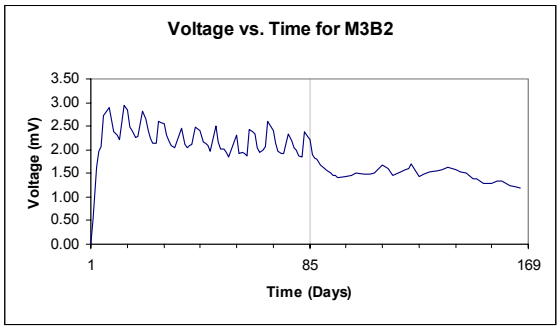



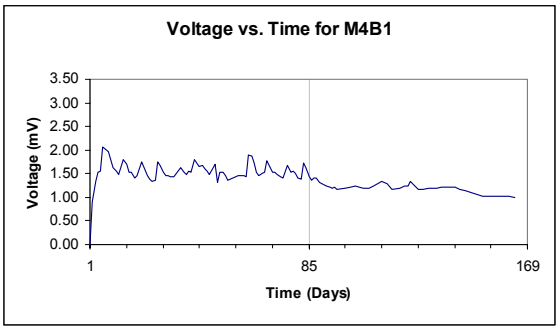
# Discontinued Specimen Macrocell Data

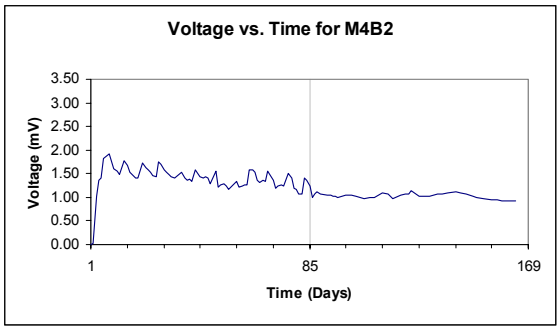


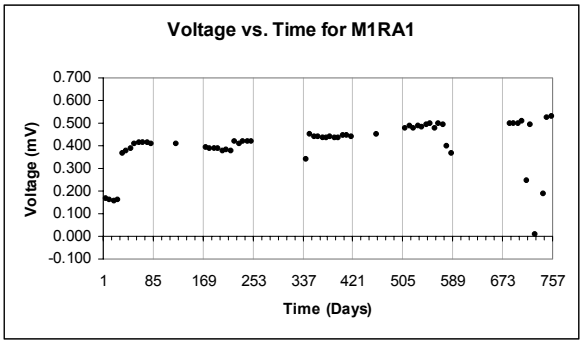



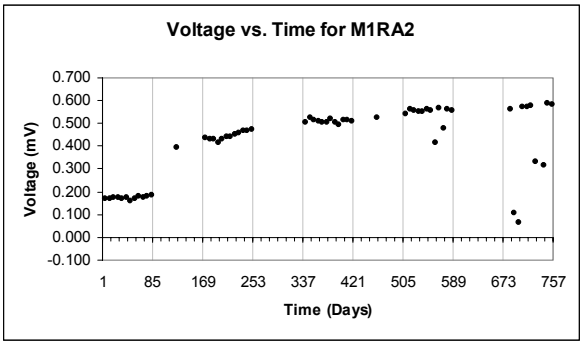



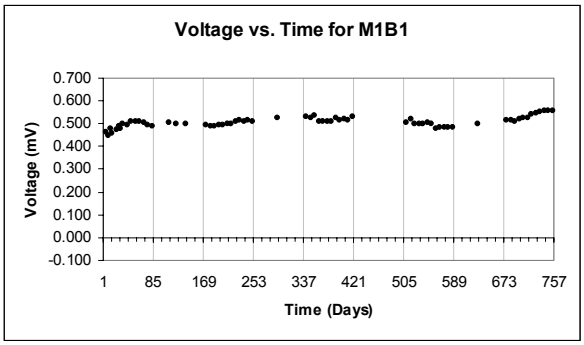



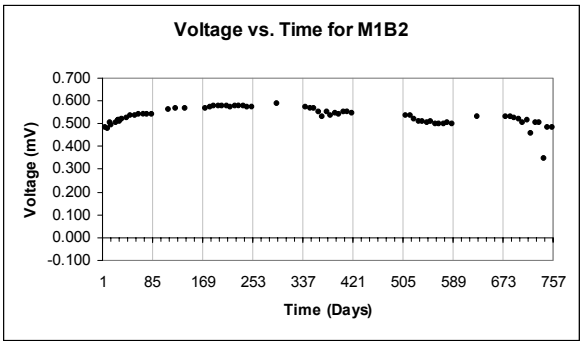
# APPENDIX C:
# HALF-CELL DATA

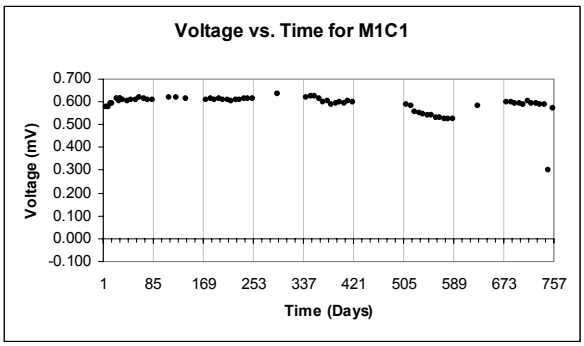
# MIX 1 Half-Cell Data

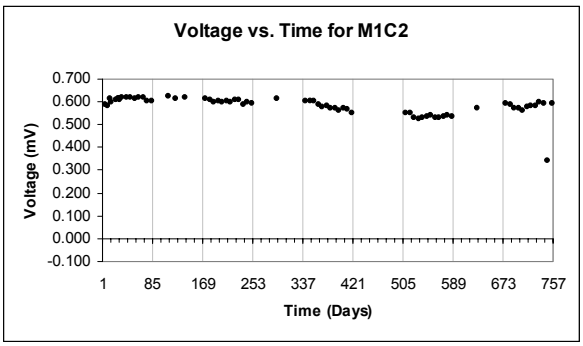


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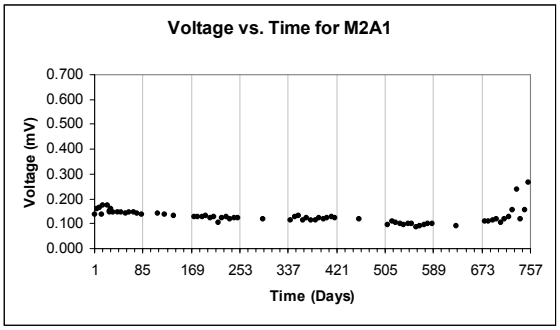
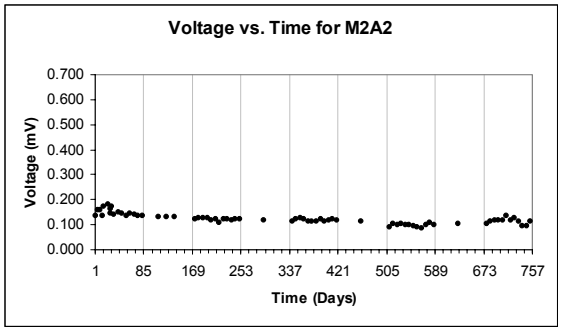
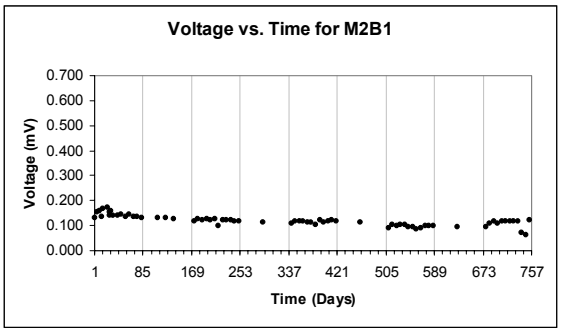
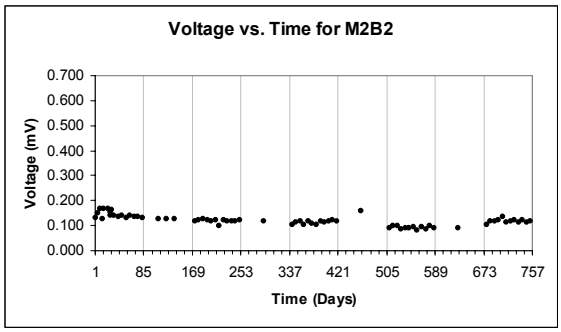
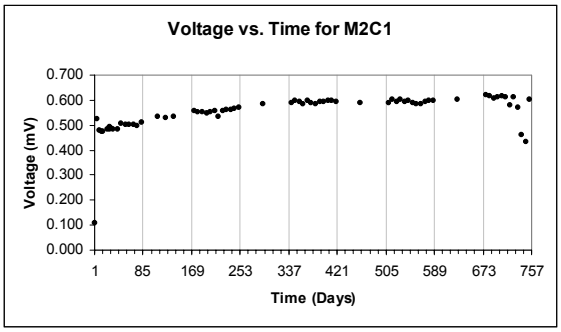
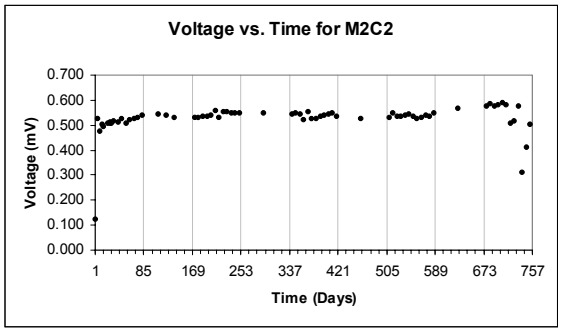


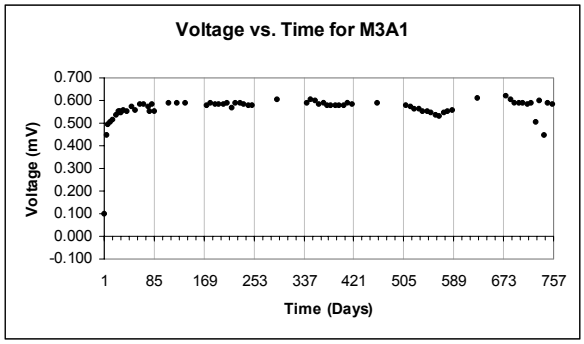



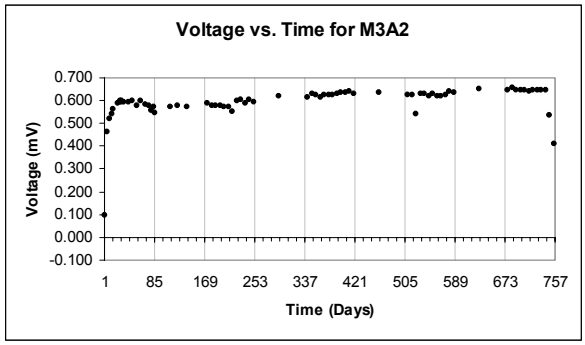



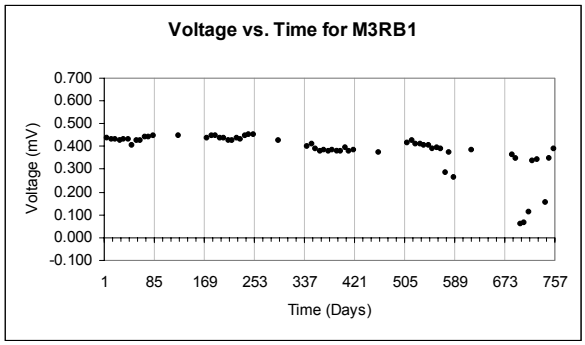



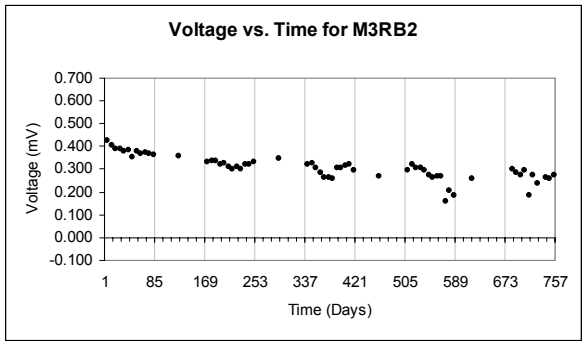



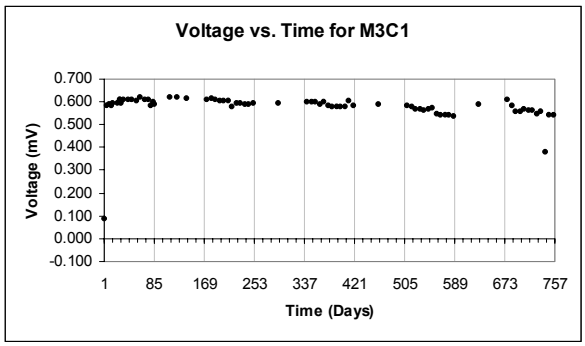
# MIX 3 Half-Cell Data

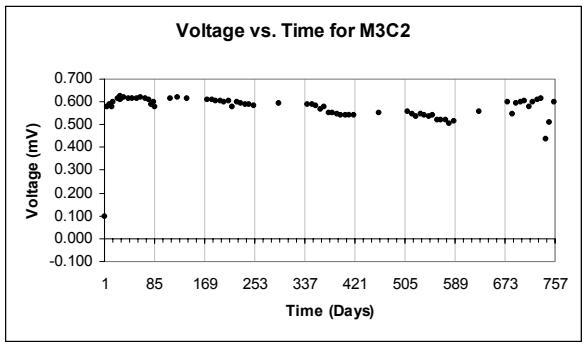


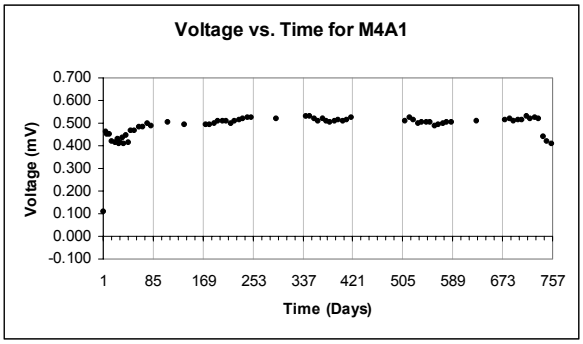



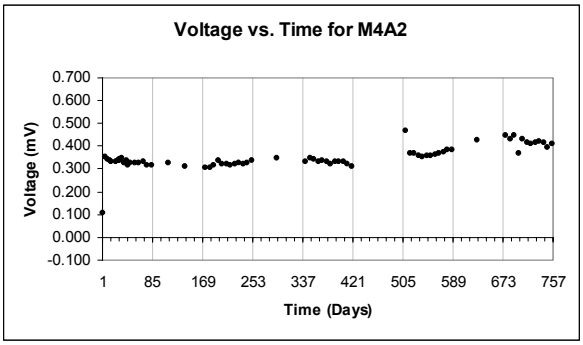



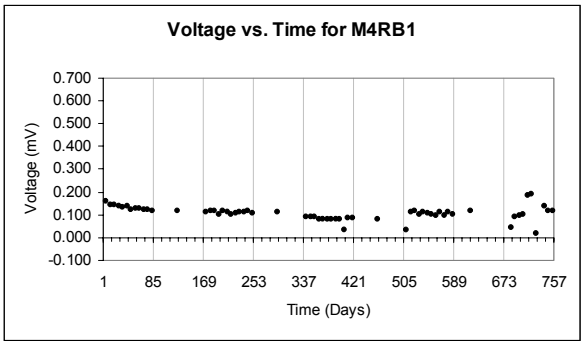



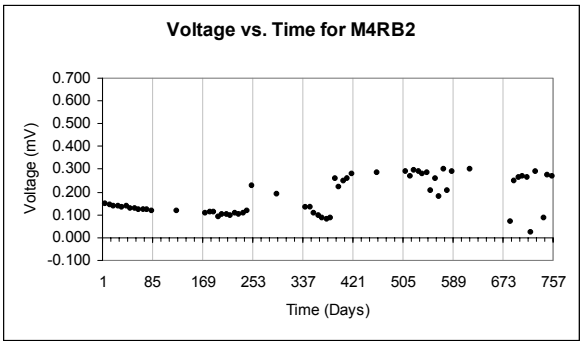



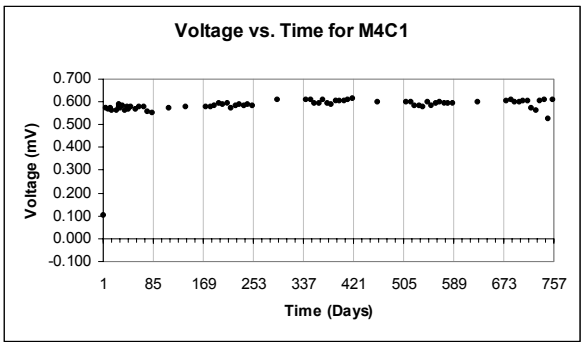
# MIX 4 Half-Cell Data

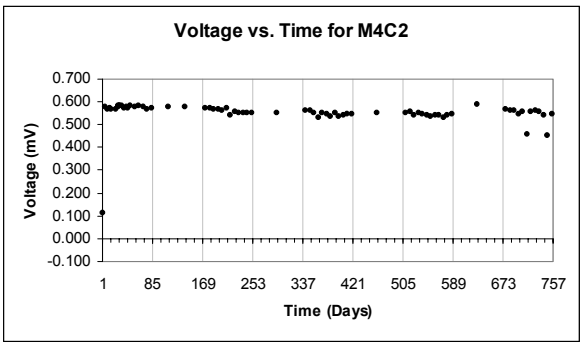


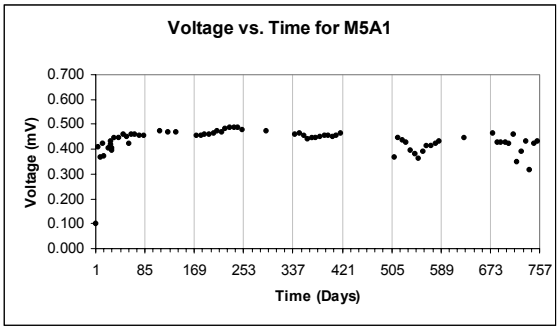



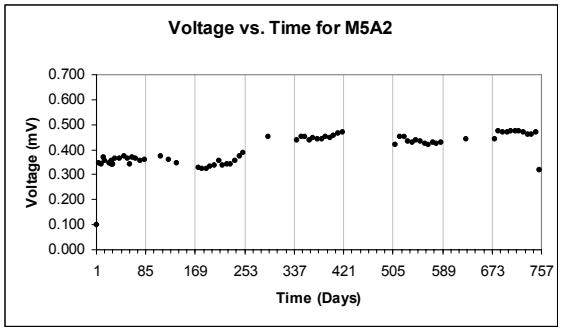



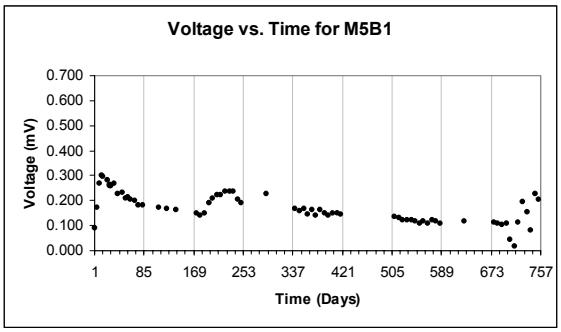



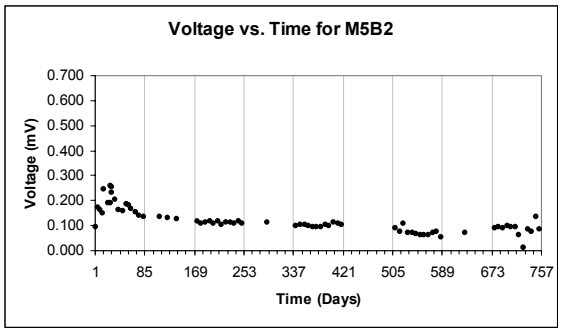



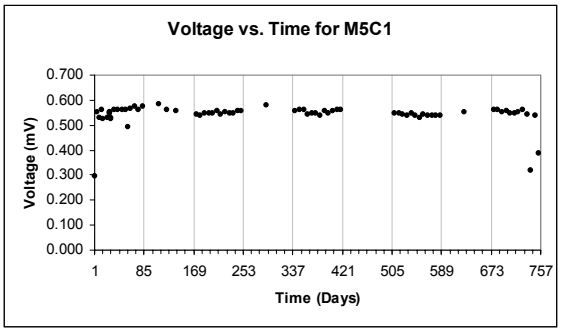
# MIX 5 Half-Cell Data

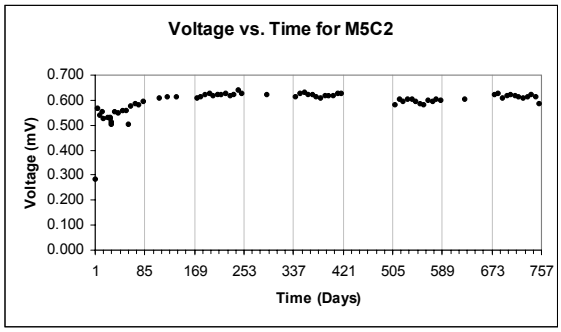


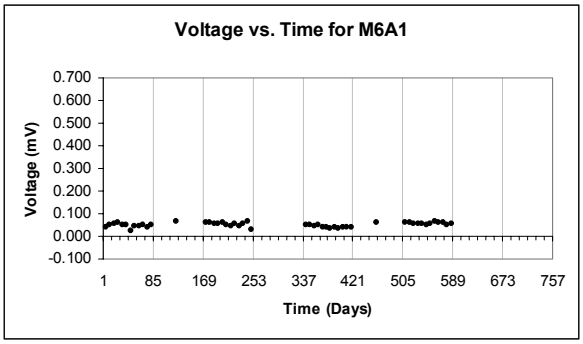



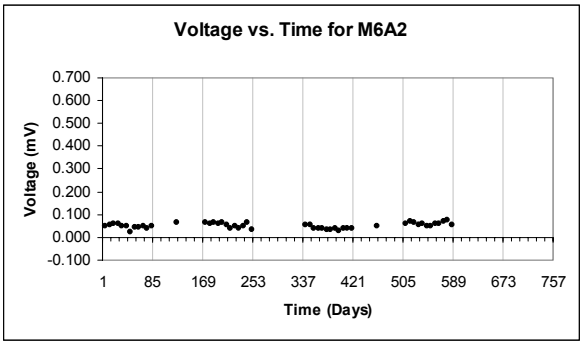



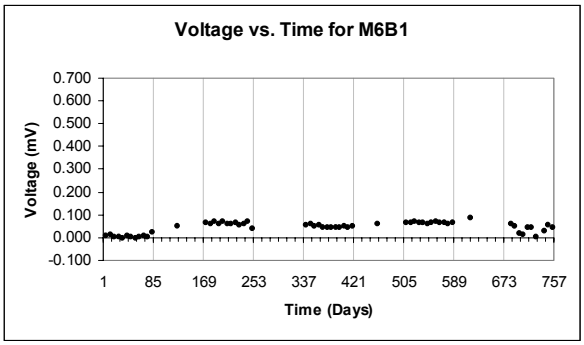



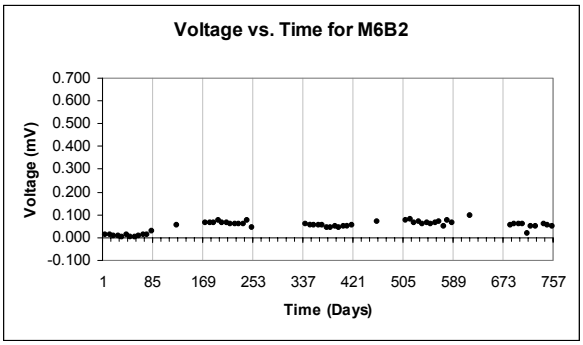



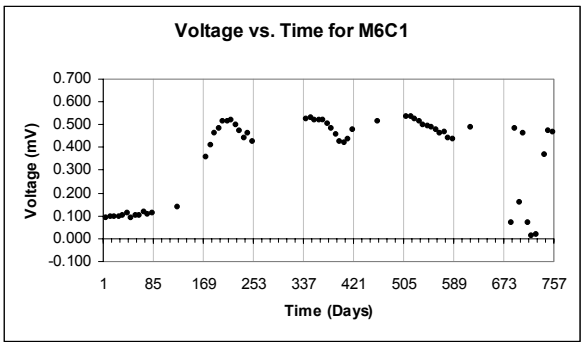
# MIX 6 Half-Cell Data

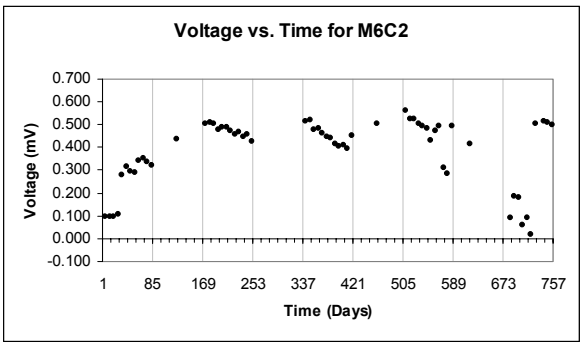


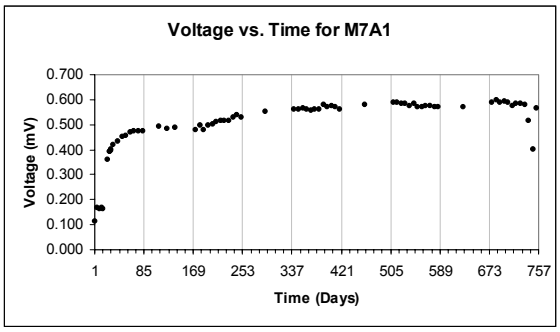



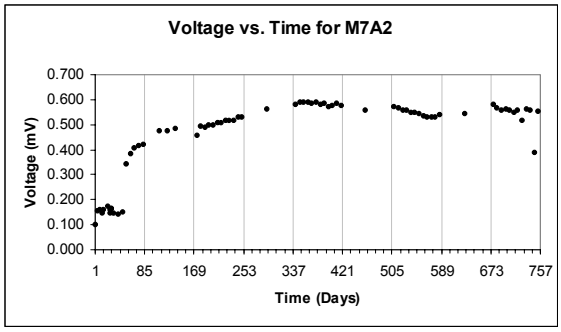



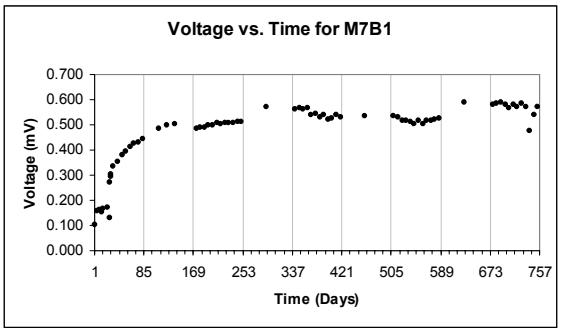



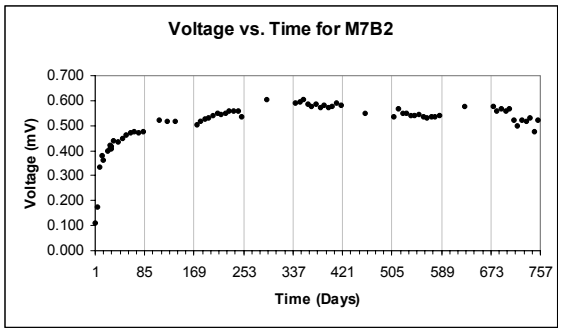



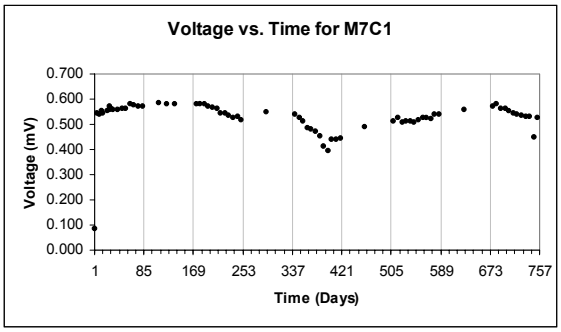
# MIX 7 Half-Cell Data

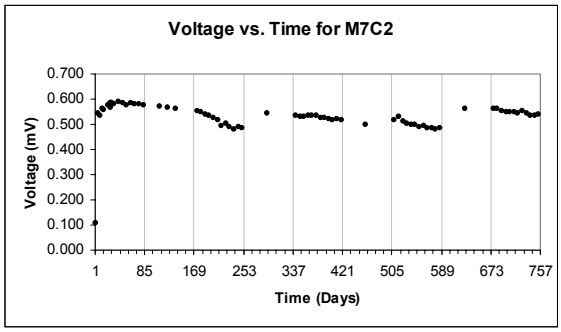


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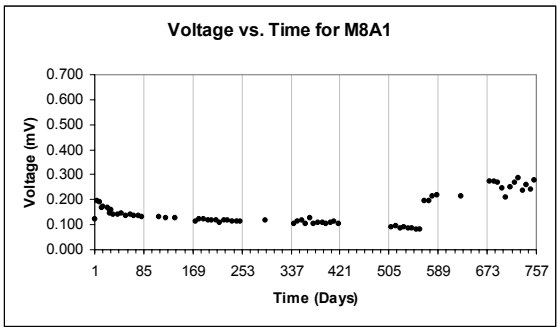
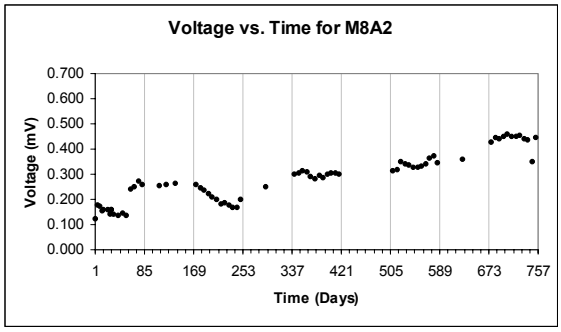
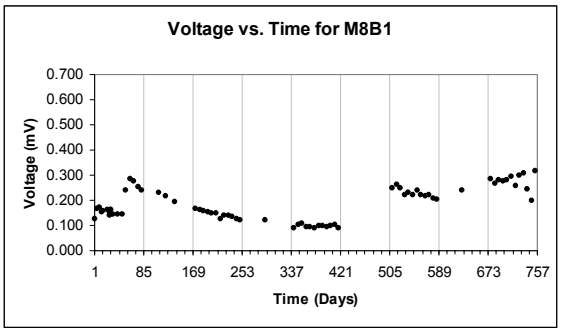
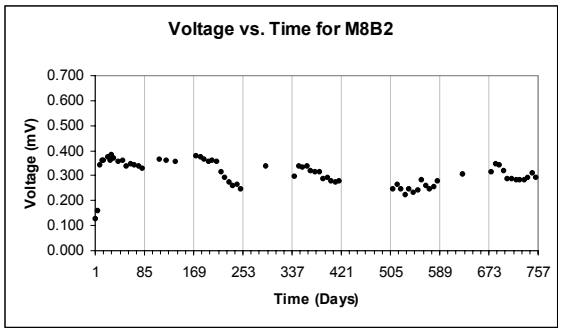
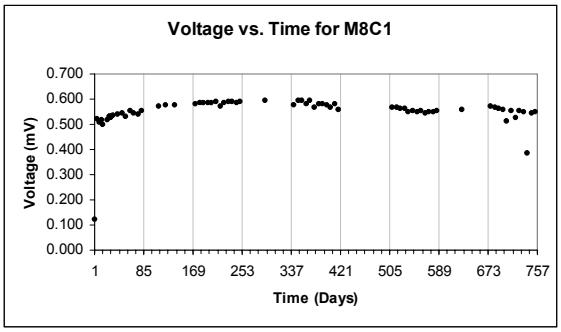
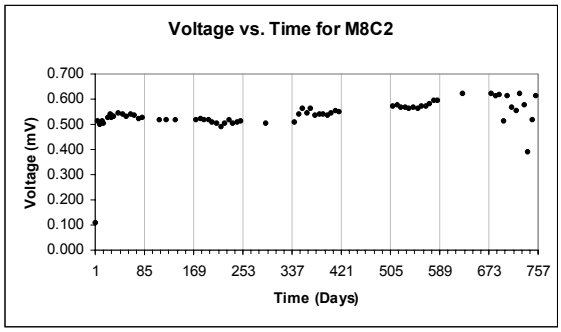


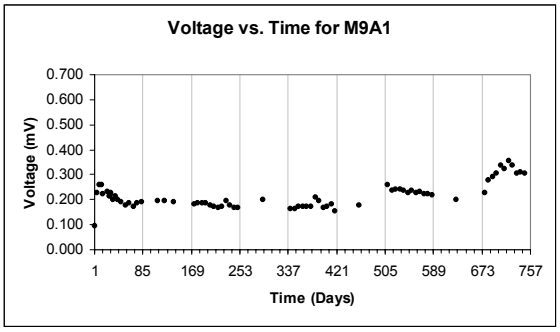



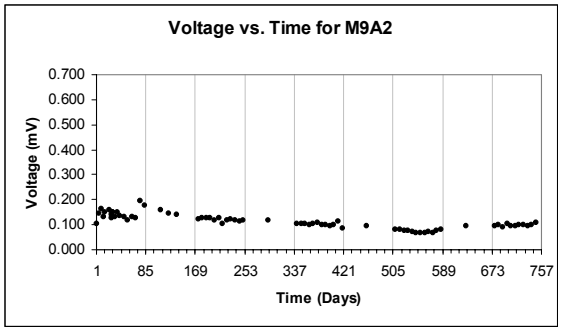



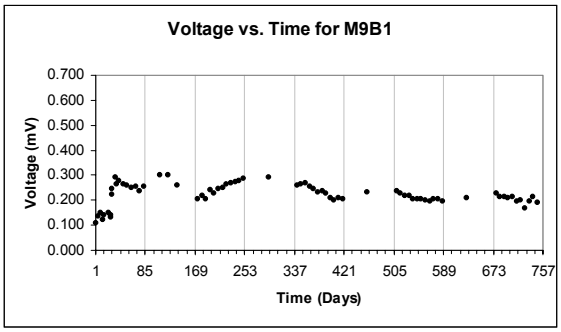



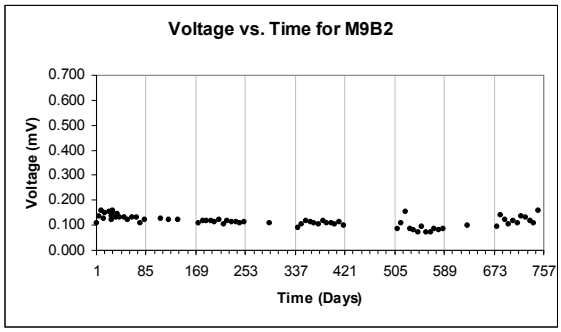



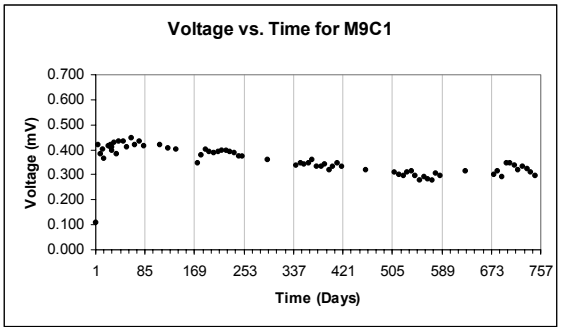
# MIX 9 Half-Cell Data

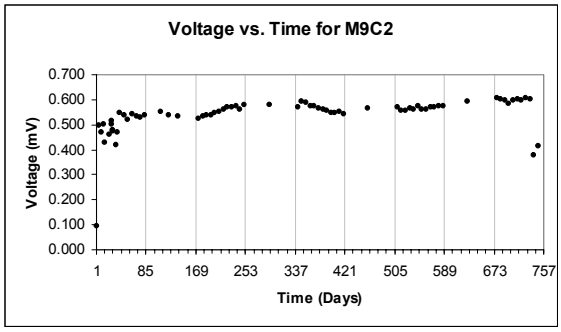


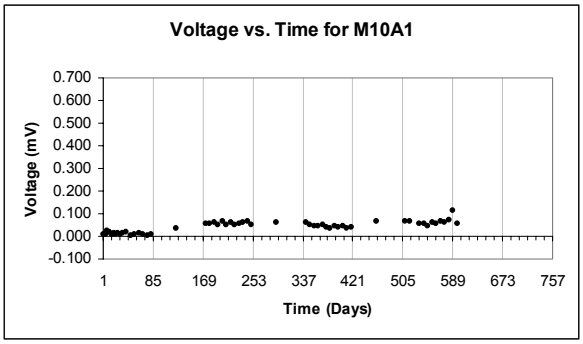



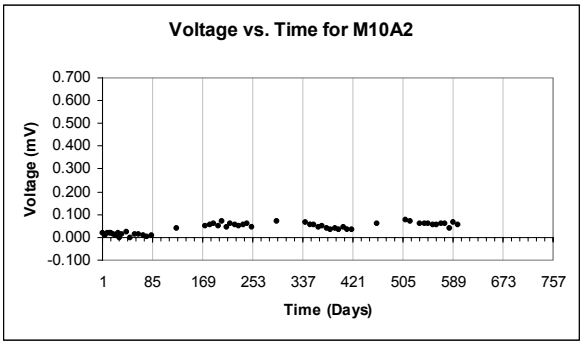



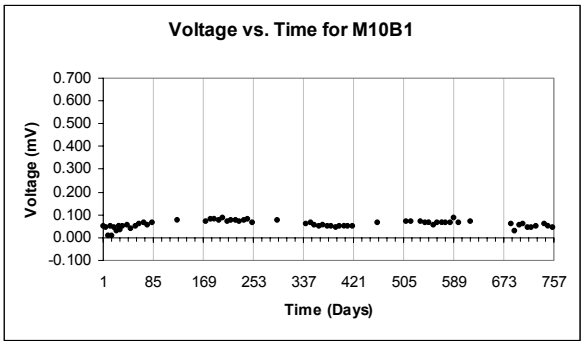



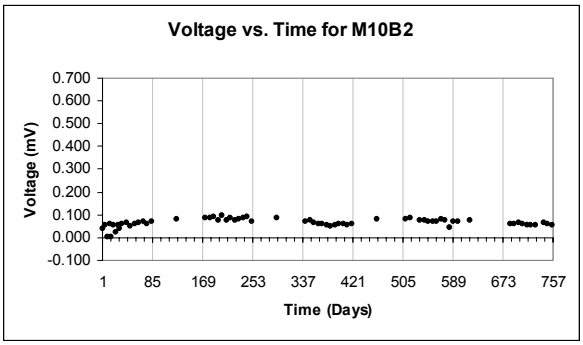



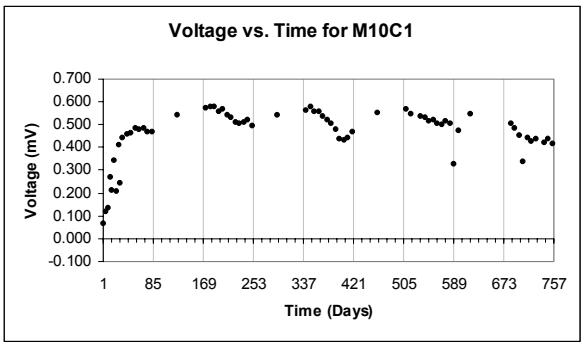
# MIX 10 Half-Cell Data

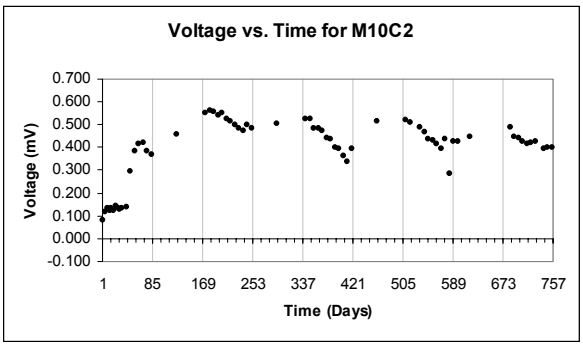


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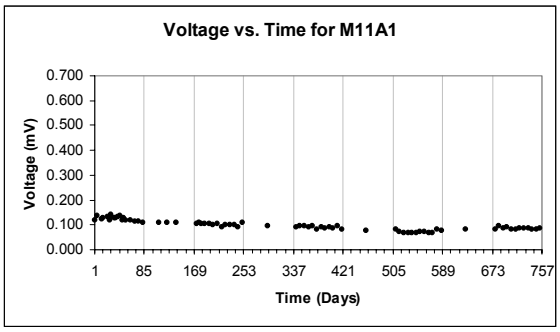


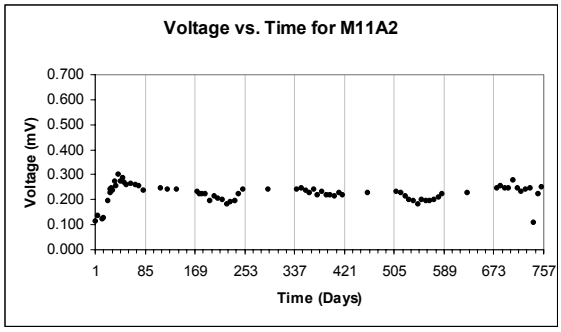


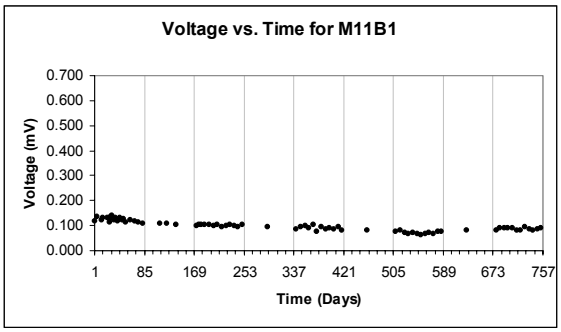


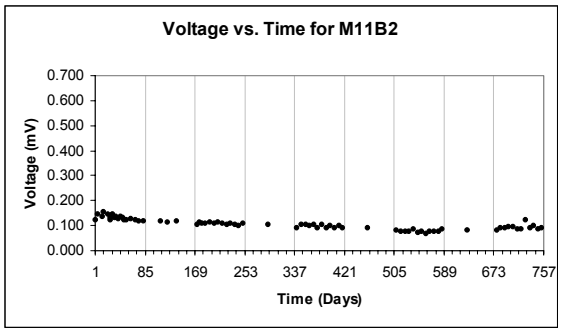


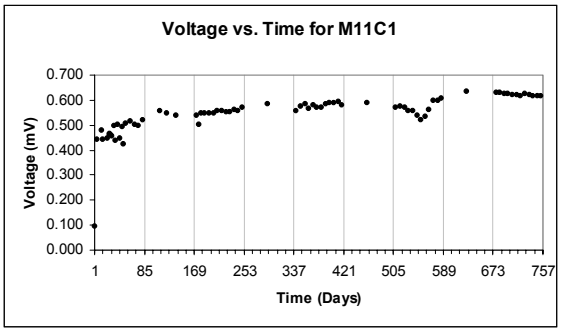


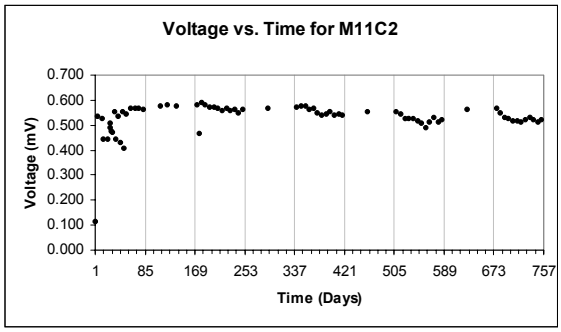

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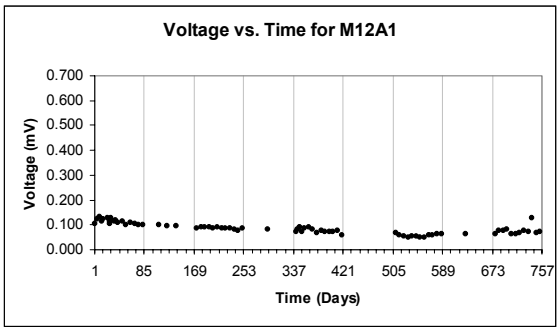
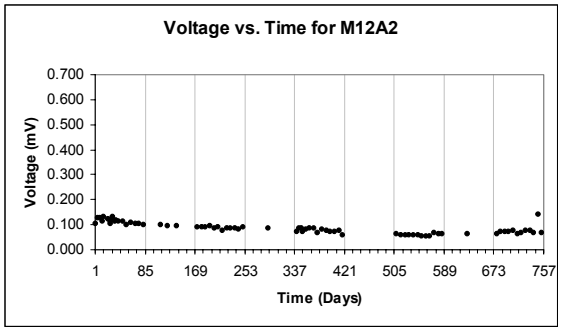
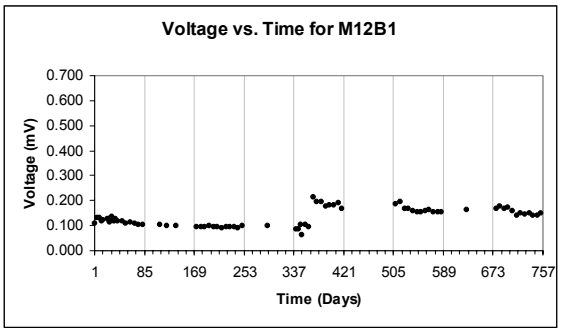
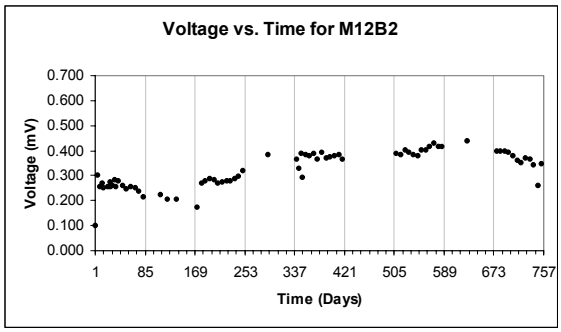
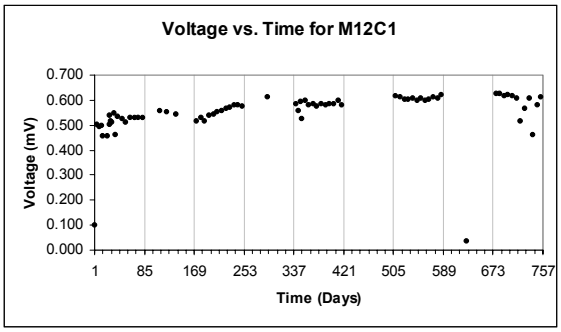
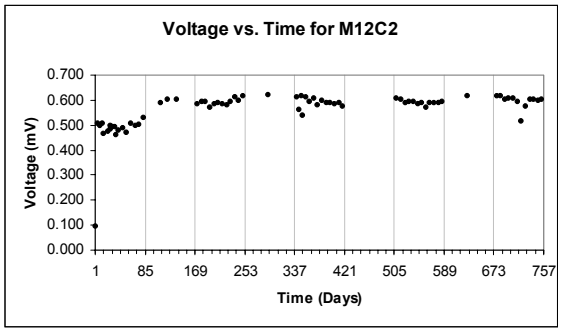


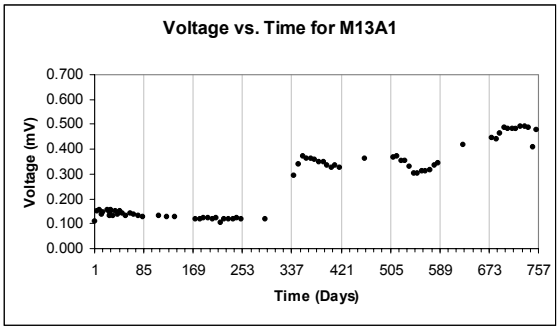



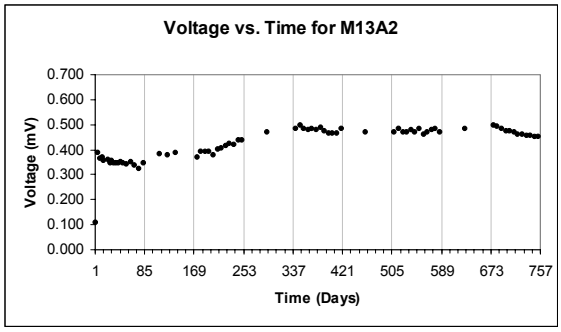



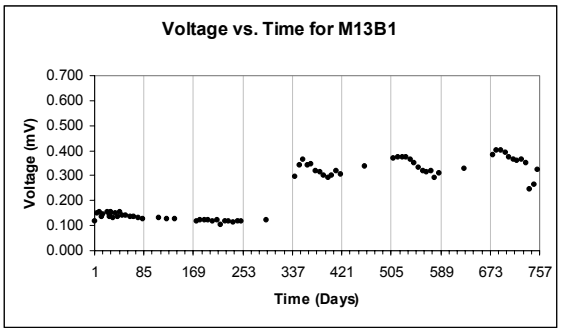



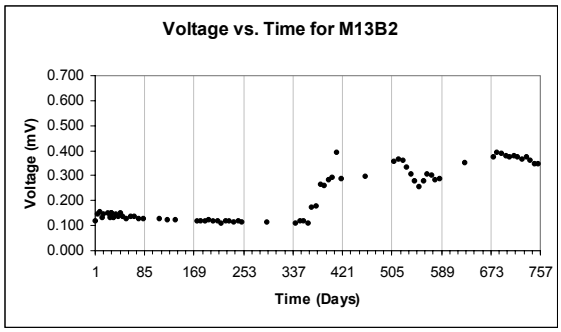



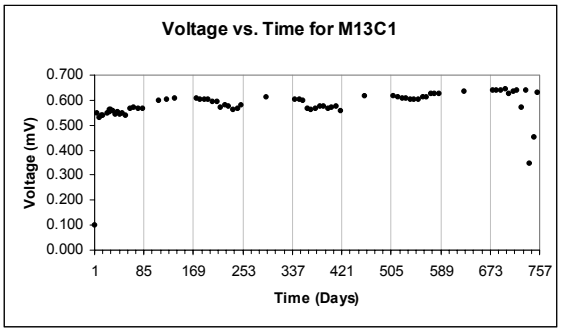
# MIX 13 Half-Cell Data

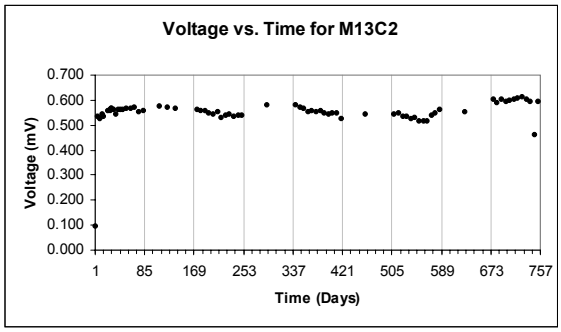


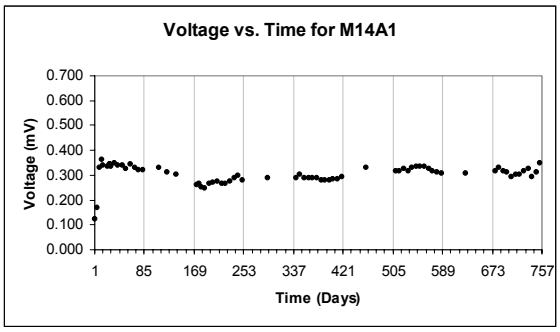



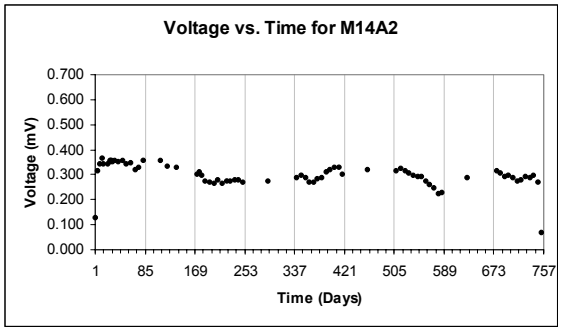



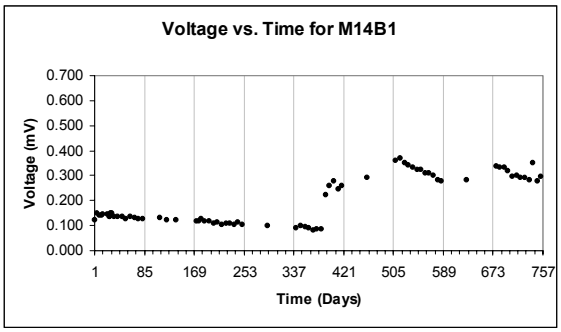



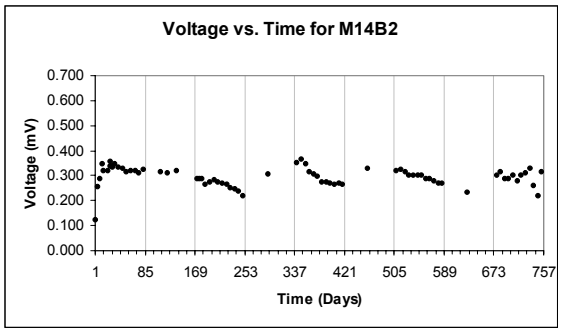



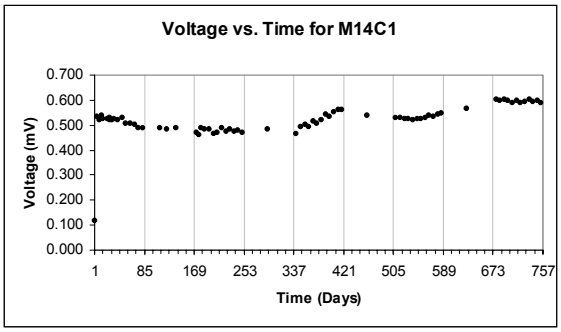
# MIX 14 Half-Cell Data

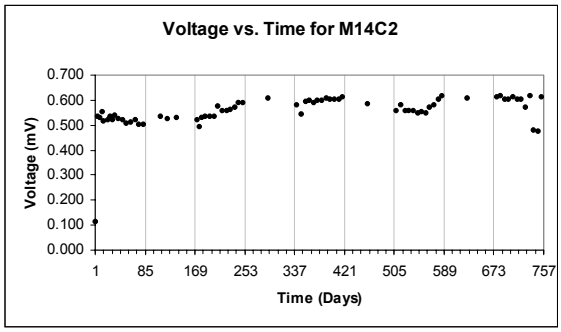
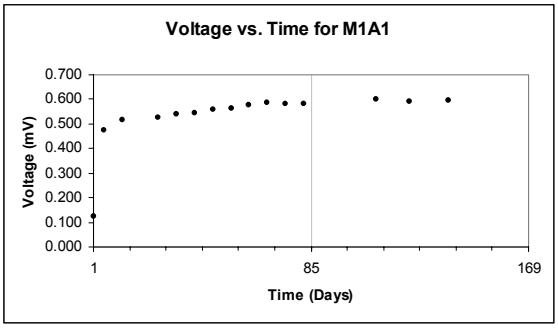
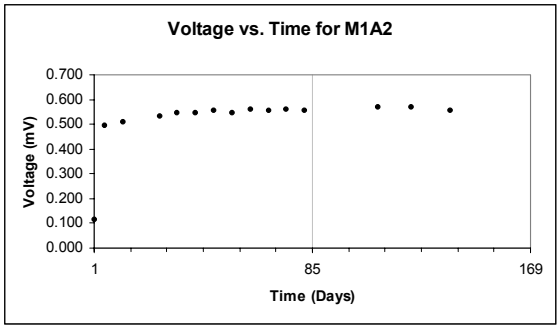
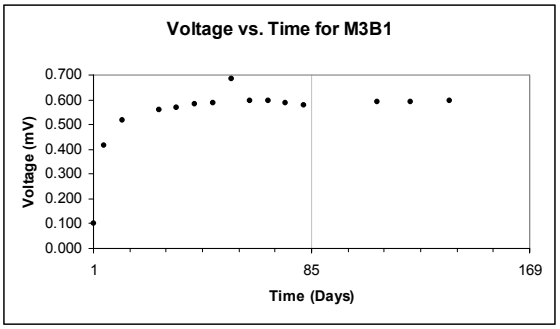
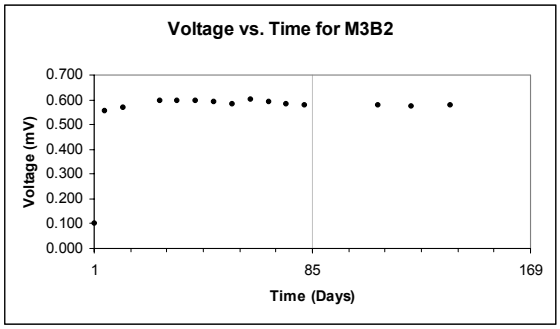
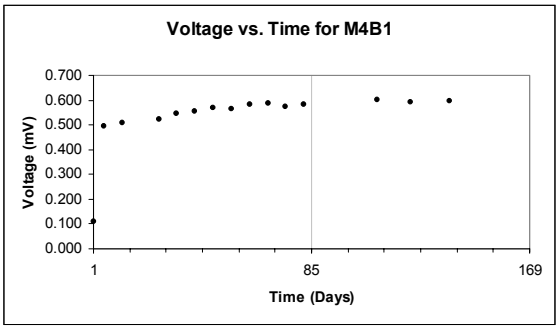
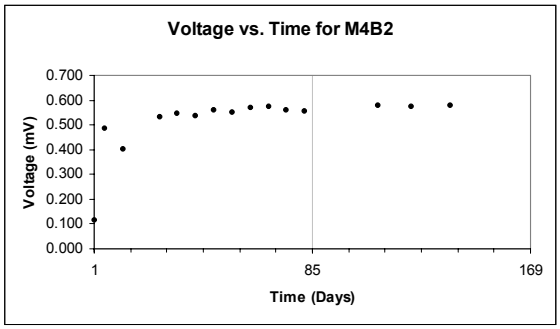





# Discontinued Specimen Half-Cell Data