

# **Protection of reinforced concrete using corrosion inhibitors and coatings**

**Abdul Nabi Lashari**

Civil Engineering

May 1996

## **Abstract**

The useful service-life of reinforced concrete structures in aggressive environments is less than that in normal conditions. In such environments, both concrete and reinforcing steel need to be protected. Among many alternatives, this protection can be achieved through the use of corrosion inhibitors and surface coatings. While several studies have been conducted on the effectiveness of such inhibitors in mitigating reinforcement corrosion, data are lacking on their performance in environments characterized by the concomitant presence of chloride and sulfate salts. Further, the effect of heat-cool cycling, typical of that prevailing in the Arabian Gulf, on the performance of concrete surface coatings is not fully elucidated.

In this study, four corrosion inhibitors and four concrete surface coatings were evaluated. The results indicated that calcium nitrite was efficient in delaying the initiation of reinforcement corrosion in the concrete specimens contaminated with chloride, chloride plus sulfate and those made with sea water. In the concrete specimens made with brackish water or unwashed aggregates, all the inhibitors were generally effective in reducing the rate of reinforcement corrosion. However, the type of inhibitor and its dosage was observed to be dependent on the type of contamination. Similarly, the depth of carbonation in the mortar specimens incorporating corrosion inhibitors was less than that in the control specimens. The combined effect of delayed reinforcement corrosion, decreased carbonation and lower water of reinforcement corrosion extended the useful service life of reinforced concrete structures. Among all the surface coatings used in this study, acrylic and siloxane coatings were the most effective in reducing the rate of reinforcement corrosion. The concrete specimens treated with these two coatings exhibited the least water absorption.

# Protection of Reinforced Concrete Using Corrosion Inhibitors and Coatings

by

Abdul Nabi Lashari

A Thesis Presented to the

FACULTY OF THE COLLEGE OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the  
Requirements for the Degree of

**MASTER OF SCIENCE**

In

**CIVIL ENGINEERING**

May, 1996

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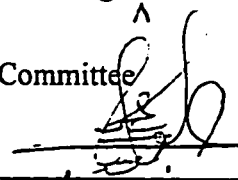
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**Master of Science in Civil Engineering**

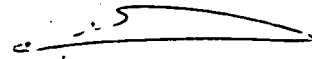
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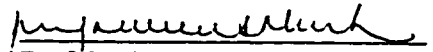
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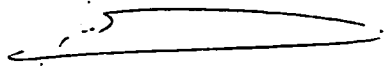
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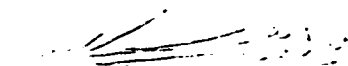


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**This work is  
dedicated to:**

**my parents,  
wife and children**

**for their love, sacrifices, prayers  
and overall understanding**



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# TABLE OF CONTENTS

ACKNOWLEDGMENTS .....	iv
LIST OF TABLES .....	ix
LIST OF FIGURES.....	xi
LIST OF PLATES.....	xv
THESIS ABSTRACT (ENGLISH).....	xvi
THESIS ABSTRACT (ARABIC).....	xvii
 <b>CHAPTER 1 INTRODUCTION.....</b>	 <b>1</b>
1.1 DURABILITY OF CONCRETE IN THE ARABIAN GULF .....	1
1.2 IMPROVEMENT OF CONCRETE DURABILITY .....	4
1.3 RESEARCH OBJECTIVES.....	5
1.4 EXPERIMENTAL PROGRAM.....	5
1.4.1 SERIES I: EFFECT OF CORROSION INHIBITORS ON REINFORCENT CORROSION.....	6
1.4.2 SERIES II: CARBONATION.....	7
1.4.3 SERIES III: EFFECT OF CONCRETE SURFACE COATINGS ON REINFORCEMENT CORROSION.....	8
 <b>CHAPTER 2 LITERATURE REVIEW.....</b>	 <b>11</b>
2.1 USE OF CORROSION INHIBITORS.....	11
2.1.1 EFFECT OF NITRITE ON THE CORROSION MECHANISM.....	14
2.1.2 TYPES OF CORROSION INHIBITORS .....	16
2.1.3 PREVIOUS STUDIES ON CORROSION INHIBITORS.....	21

2.2	USE OF SURFACE COATINGS .....	34
2.2.1	TYPES OF SURFACE COATINGS.....	36
2.2.1.1	PENETRANTS.....	36
2.2.1.2	SILANES AND SILOXANES .....	37
2.2.1.3	SILOCONE RESINS.....	38
2.2.1.4	SEALERS AND COATINGS .....	38
2.2.1.5	EPOXY COATINGS.....	39
2.2.2	PERFORMANCE OF SURFACE COATINGS .....	40
2.3	SIGNIFICANCE OF THIS RESEARCH.....	44
<b>CHAPTER 3 METHODOLOGY OF RESEARCH .....</b>		<b>46</b>
3.1	CONCRETE MIX DESIGN.....	46
3.2	MATERIALS .....	47
3.2.1	AGGREGATE.....	47
3.2.2	CEMENT .....	47
3.2.3	CORROSION INHIBITORS .....	48
3.2.4	CONCRETE SURFACE COATINGS.....	48
3.3	SPECIMENS PREPARATION.....	49
3.3.1	MIXING AND CASTING .....	49
3.3.2	CURING .....	50
3.3.3	EXPOSURE CONDITIONS .....	50
3.3.3.1	EXPOSURE SOLUTIONS .....	50
3.3.3.2	HEAT-COOL CYCLING.....	51

3.3.3.3	WET-DRY CYCLING .....	51
3.3.3.4	CARBONATION .....	52
3.4	TEST METHODS .....	52
3.4.1	COMPRESSIVE STRENGTH.....	52
3.4.2	PULSE VELOCITY .....	53
3.4.3	ABSORPTION .....	53
3.4.4	REINFORCEMENT CORROSION.....	54
3.4.4.1	CORROSION POTENTIALS.....	54
3.4.4.2	CORROSION CURRENT DENSITY .....	55
3.4.5	CARBONATION DEPTH .....	56
<b>CHAPTER 4 RESULTS AND DISCUSSIONS .....</b>		<b>74</b>
4.1	EFFECT OF INHIBITORS ON COMPRESSIVE STRENGTH.....	75
4.2	EFFECT OF INHIBITORS ON REINFORCEMENT CORROSION....	75
4.2.1	CORROSION POTENTIALS .....	76
4.2.1.1	EFFECT OF CALCIUM NITRITE.....	76
4.2.1.2	EFFECT OF CALCIUM NITRATE .....	79
4.2.1.3	EFFECT OF CI1 AND CI2 INHIBITORS .....	82
4.2.1.4	SUMMARY OF THE CORROSION POTENTIAL RESULTS .....	85
4.2.2	CORROSION CURRENT DENSITY .....	86
4.2.2.1	EFFECT OF CALCIUM NITRITE.....	87
4.2.2.2	EFFECT OF CALCIUM NITRATE .....	89
4.2.2.3	EFFECT OF CI1 AND CI2 INHIBITORS .....	92

4.2.2.4	SUMMARY OF THE CORROSION CURRENT DENSITY	
	RESULTS .....	95
4.3	EFFECT OF CORROSION INHIBITORS ON CARBONATION .....	98
4.4	SURFACE COATINGS .....	102
4.4.1	EFFECT OF WET-DRY CYCLING .....	102
4.4.2	EFFECT OF HEAT-COOL CYCLING .....	104
4.4.3	SUMMARY ON THE PERFORMANCE OF SURFACE	
	COATINGS .....	106
4.4.4	EFFECT OF COATINGS ON REINFORCEMENT CORROSION ....	109
4.4.4.1	CORROSION POTENTIALS .....	109
4.4.4.2	CORROSION CURRENT DENSITY .....	111
CHAPTER 5 CONCLUSIONS.....		166
CHAPTER 6 LIST OF REFERENCES .....		172
VITAE .....		180

## LIST OF TABLES

Table 1.1: Summary of Tests and Number of Specimens Used in Series I .....	10
Table 1.2: Summary of Test and Number of Specimens Used in Series II .....	10
Table 1.3: Summary of Tests and Number of Specimens Used in Series III.....	10
Table 3.1: Chemical Analysis of the Water-Soluble Species for the Coarse Aggregate.....	58
Table 3.2: Specific Gravity and Absorption of Coarse Aggregate .....	59
Table 3.3: Grading of Coarse Aggregate .....	59
Table 3.4: Chemical and Mineralogical Compositions of Cement .....	60
Table 3.5: Rate of Application of the Concrete Surface Coatings .....	61
Table 3.6: Chemical Analysis of the Sea Water in mg/l (ppm) .....	62
Table 3.7: Chemical Analysis of the Brackish Water in mg/l (ppm).....	63
Table 3.8: Typical Weighs of Concrete Constituents Used in Casting.....	64
Table 4.1: Summary of the Time to Initiation of Reinforcement Corrosion in Concrete Specimens incorporating Corrosion Inhibitors.....	113
Table 4.2: Summary of the Corrosion Current Density on Steel in Concrete Specimens incorporating Corrosion Inhibitors after 122 Days of Exposure.....	114
Table 4.3: Summary of the Time to Initiation of Reinforcement Corrosion as Determined from the Corrosion Current Density Results in Concrete Specimens incorporating Corrosion Inhibitors .....	115
Table 4.4: Preferred Corrosion Inhibitors for Different Environments .....	116
Table 4.5: Cost Analysis of the Preferred Dosages of Corrosion Inhibitors.....	117
Table 4.6: Summary of the Depth of Carbonation for Various Mortar Specimens after One Month of Exposure .....	118
Table 4.7: Summary of the Depth of Carbonation for Various Mortar Specimens after Three Months of Exposure .....	119

Table 4.8: Summary of the Initial and Final Water Absorption in the Coated and Uncoated Concrete Specimens.....	120
Table 4.9: Summary of the Initial and Final Compressive Strength in the Coated and Uncoated Concrete Specimens.....	121
Table 4.10: Summary of the Initial and Final Pulse Velocity in the Coated and Uncoated Concrete Specimens.....	122
Table 4.11: Summary of the Time to Initiation of Reinforcement Corrosion in the Coated and Uncoated Concrete Specimens.....	123
Table 4.12: Summary of the Corrosion Current Density in Coated and Uncoated Concrete Specimens, after 122 Days of Exposure.....	124

## **LIST OF FIGURES**

Figure 4.1: Compressive Strength of Concrete Specimens Incorporating Corrosion Inhibitors (after 28 Days of Curing) .....	125
Figure 4.2: Corrosion Potentials on Steel in the Concrete Specimens Contaminated with 0.8% Chloride and Incorporating Calcium Nitrite. ....	126
Figure 4.3: Corrosion Potentials on Steel in the Concrete Specimens Contaminated with 0.8% Chloride plus 1.5% Sulfate and Incorporating Calcium Nitrite .....	127
Figure 4.4: Corrosion Potentials on Steel in the Concrete Specimens made with Sea Water and Incorporating Calcium Nitrite .....	128
Figure 4.5: Corrosion Potentials on Steel in the Concrete Specimens made with Brackish Water and Incorporating Calcium Nitrite.....	129
Figure 4.6: Corrosion Potentials on Steel in the Concrete Specimens made with Unwashed Aggregate and Incorporating Calcium Nitrite.....	130
Figure 4.7: Corrosion Potentials on Steel in the Concrete Specimens Contaminated with 0.8% Chloride and Incorporating Calcium Nitrate.....	131
Figure 4.8: Corrosion Potentials on Steel in the Concrete Specimens Contaminated with 0.8% Chloride plus 1.5% Sulfate and Incorporating Calcium Nitrate.....	132
Figure 4.9: Corrosion Potentials on Steel in the Concrete Specimens made with Sea Water and Incorporating Calcium Nitrate .....	133
Figure 4.10: Corrosion Potentials on Steel in the Concrete Specimens made with Brackish Water and Incorporating Calcium Nitrate.....	134
Figure 4.11: Corrosion Potentials on Steel in the Concrete Specimens made with Unwashed Aggregate and Incorporating Calcium Nitrate .....	135



Figure 4.12: Corrosion Potentials on Steel in the Concrete Specimens Contaminated with 0.8% Chloride and Incorporating CI1 and CI2 Inhibitors.....	136
Figure 4.13: Corrosion Potentials on Steel in the Concrete Specimens Contaminated with 0.8% Chloride plus 1.5% Sulfate and Incorporating CI1 and CI2 Inhibitors .....	137
Figure 4.14: Corrosion Potentials on Steel in the Concrete Specimens made with Sea Water and Incorporating CI1 and CI2 Inhibitors .....	138
Figure 4.15: Corrosion Potentials on Steel in the Concrete Specimens made with Brackish Water and Incorporating CI1 and CI2 Inhibitors .....	139
Figure 4.16: Corrosion Potentials on Steel in the Concrete Specimens made with Unwashed Aggregate and Incorporating CI1 and CI2 Inhibitors.....	140
Figure 4.17: Corrosion Current Density in the Concrete Specimens Contaminated with 0.8% Chloride and Incorporating Calcium Nitrite .....	141
Figure 4.18: Corrosion Current Density in the Concrete Specimens Contaminated with 0.8% Chloride plus 1.5% Sulfate and Incorporating Calcium Nitrite .....	142
Figure 4.19: Corrosion Current Density in the Concrete Specimens made with Sea Water and Incorporating Calcium Nitrite .....	143
Figure 4.20: Corrosion Current Density in the Concrete Specimens made with Brackish Water and Incorporating Calcium Nitrite.....	144
Figure 4.21: Corrosion Current Density in the Concrete Specimens made with Unwashed Aggregate and Incorporating Calcium Nitrite.....	145
Figure 4.22: Corrosion Current Density in the Concrete Specimens Contaminated with 0.8% Chloride and Incorporating Calcium Nitrate .....	146

Figure 4.23: Corrosion Current Density in the Concrete Specimens Contaminated with 0.8% Chloride plus 1.5% Sulfate and Incorporating Calcium Nitrate.....	147
Figure 4.24: Corrosion Current Density in the Concrete Specimens made with Sea Water and Incorporating Calcium Nitrate .....	148
Figure 4.25: Corrosion Current Density in the Concrete Specimens made with Brackish Water and Incorporating Calcium Nitrate.....	149
Figure 4.26: Corrosion Current Density in the Concrete Specimens made with Unwashed Aggregate and Incorporating Calcium Nitrate .....	150
Figure 4.27: Corrosion Current Density in the Concrete Specimens Contaminated with 0.8% Chloride and Incorporating CI1 and CI2 Inhibitors.....	151
Figure 4.28: Corrosion Current Density in the Concrete Specimens Contaminated with 0.8% Chloride plus 1.5% Sulfate and Incorporating CI1 and CI2 Inhibitors.....	152
Figure 4.29: Corrosion Current Density in the Concrete Specimens made with Sea Water and Incorporating CI1 and CI2 Inhibitors .....	153
Figure 4.30: Corrosion Current Density in the Concrete Specimens made with Brackish Water and Incorporating CI1 and CI2 Inhibitors .....	154
Figure 4.31: Corrosion Current Density in the Concrete Specimens made with Unwashed Aggregate and Incorporating CI1 and CI2 Inhibitors.....	155
Figure 4.32: Water Absorption of the Coated and Uncoated Concrete Specimens Subjected to Wet-Dry Cycling.....	156
Figure 4.33: Compressive Strength of the Coated and Uncoated Concrete Specimens Subjected to Wet-Dry Cycling .....	157
Figure 4.34: Pulse Velocity of the Coated and Uncoated Concrete Specimens Subjected to Wet-Dry Cycling.....	158

Figure 4.35: Water Absorption of the Coated and Uncoated Concrete Specimens Subjected to Heat-Cool Cycling .....	159
Figure 4.36: Compressive Strength of the Coated and Uncoated Concrete Specimens Subjected to Heat-Cool Cycling .....	160
Figure 4.37: Pulse Velocity of the Coated and Uncoated Concrete Specimens Subjected to Heat-Cool Cycling .....	161
Figure 4.38: Corrosion Potentials on Steel in the Coated and Uncoated Concrete Specimens Exposed to 5% Sodium Chloride Solution .....	162
Figure 4.39: Corrosion Potentials on Steel in the Coated and Uncoated Concrete Specimens Exposed to 5% Sodium Chloride plus 3% Sodium Sulfate Solution .....	163
Figure 4.40: Corrosion Current Density on Steel in the Coated and Uncoated Concrete Specimens Exposed to 5% Sodium Chloride Solution .....	164
Figure 4.41: Corrosion Current Density on Steel in the Coated and Uncoated Concrete Specimens Exposed to 5% Sodium Chloride plus 3% Sodium Sulfate Solution.....	165

## **LIST OF PLATES**

Plate 3.1: Molds Filled with Concrete.....	65
Plate 3.2: Reinforced Concrete Specimens under Wet Burlap Curing .....	66
Plate 3.3: Reinforced Concrete Specimens in an Exposure Solution.....	67
Plate 3.4: Concrete Specimens under Heat-Cool environment.....	68
Plate 3.5: Concrete Specimens under Wet-Dry environment .....	69
Plate 3.6: Mortar Specimens in the Carbonation Chamber.....	70
Plate 3.7: Pulse Velocity Apparatus.....	71
Plate 3.8: Typical Coated and Uncoated Reinforced Concrete Specimens .....	72
Plate 3.9: Experimental Set-up for Corrosion Current Density Measurement.....	73

## **THESIS ABSTRACT**

NAME : ABDUL NABI LASHARI

TITLE : PROTECTION OF REINFORCED  
CONCRETE USING CORROSION  
INHIBITORS AND COATINGS

MAJOR FIELD : CIVIL ENGINEERING (STRUCTURES)

DATE OF DEGREE : MAY, 1996

The useful service-life of reinforced concrete structures in aggressive environments is less than that in normal conditions. In such environments, both concrete and reinforcing steel need to be protected. Among many alternatives, this protection can be achieved through the use of corrosion inhibitors and surface coatings. While several studies have been conducted on the effectiveness of such inhibitors in mitigating reinforcement corrosion, data are lacking on their performance in environments characterized by the concomitant presence of chloride and sulfate salts. Further, the effect of heat-cool cycling, typical of that prevailing in the Arabian Gulf, on the performance of concrete surface coatings is not fully elucidated.

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**MASTER OF SCIENCE**

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## خلاصة الرسالة

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تاريخ الشهادة : مايو ١٩٩٦ م (محرم ١٤١٧ هـ)

إن العمر الافتراضي للمنشآت الخرسانية المسلحة في البيئات العدوانية أقل منه في البيئات الطبيعية والعادية . ولذلك ، فإن كلاً من الخرسانة وحديد التسليح يحتاجان إلى حماية . ومن الطرق العديدة للحماية : استخدام موانع الصدأ وطلاء الأسطح الخارجية للخرسانة . ولقد أجريت عدة دراسات سابقة على فعالية هذه الموانع لإنقاذ صدأ حديد التسليح ، ولكن لا يوجد دراسات على أداء هذه الموانع في البيئات المحتوية على أملاح الكلور والكبريتات معاً . أيضاً لا توجد دراسات سابقة على فعالية طلاء أسطح الخرسانة في البيئات المتعرضة للحرارة والبرودة والمائلة للبيئة السائدة في الخليج العربي .

تم في هذا البحث دراسة أربعة أنواع من موانع الصدأ وأربعة أنواع من الطلاء . ودلت نتائج البحث أن نيتريت الكالسيوم كان فعالاً في تأخير الوقت الأولي لظهور الصدأ في العينات الخرسانية الملوثة بأملاح الكلور والكبريتات وماء البحر . أما في العينات المصبوبة بالماء الضارب للملوحة أو بالخصي غير المفسول ، فإن كل موانع الصدأ كانت فعالة في إنقاذ معدل الصدأ . ولذلك ، فإن فعالية نوع مانع الصدأ وكميته يعتمد على نوع التلوث في الخرسانة . أما عمق الكربة فكان قليلاً في العينات الملائية المحتوية على موانع الصدأ مقاومة بعينات الملاط العادية . ودلت الدراسة على أن العمر الافتراضي للمنشآت يمكن زيادته باستخدام موانع الصدأ نظراً لتأخير الوقت الأولي لظهور الصدأ وخفض معدل الصدأ وإنقاذ عمق الكربة . وأثبتت الدراسة أن الطلاءات المصنوعة من مواد الأكرليك والسايلاكسين كانت الأكثر فعالية في إنقاذ معدل صدأ حديد التسليح ، لأن العينات الخرسانية الملائية بهاذين النوعين كانا الأقل إمتصاصاً للماء .

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# **CHAPTER 1**

## **INTRODUCTION**

### **1.1 DURABILITY OF CONCRETE IN THE ARABIAN GULF**

Portland cement concrete is the best and most widely used construction material in the world. Its annual consumption was 3 billion cubic meters in 1964 and is expected to increase to 6 billion cubic meters in 1995 [1]. This wide spread use of concrete is attributed, among other factors, to its economic superiority over other construction materials and the availability of its constituent materials during both the manufacturing stage of cement and the mixing period of concrete. Added to these advantages is the low maintenance requirement of reinforced concrete structures which is the other predominant criterion for the selection of this material. The potential of using this material has been fully exploited by the construction industry, and research has been conducted to make concrete stronger and economical.

While the cement industry's research and development efforts have been totally diverted towards the production of energy-efficient and high-strength cement

concrete, the durability performance of such cements, due to the resulting changes in their physico-chemical characteristics, has not been well investigated. It was assumed that concrete produced by mixing of cement, aggregate and water can withstand all the weather and exposure conditions. Concrete was once thought to be a maintenance-free material, until durability problems have been reported from different parts around the world.

Notable among the case histories, where concrete was blamed for poor durability, are the deterioration of the bridge decks in the USA and Europe and of the reinforced concrete structures in the Arabian Gulf. Considerable resources have to be diverted towards the repair and rehabilitation of these structures. In the USA, more than \$ 50 billions were spent on the repair of inter-state highway systems [2]. In the UK, £ 20 billions were spent on building repair and maintenance, out of which £ 500 millions were totally utilized for concrete repairs [3]. While the deterioration of highway structures in the temperate climatic conditions of North America and Europe is attributed to the use of deicer salts, the poor durability of concrete structures in the Arabian Gulf is caused by: (1) severe climatic and geomorphic conditions, (2) lack of appreciation of the problem, (3) incorrect materials specifications, and (4) inadequate construction practices.



In the aggressive environmental conditions of the Arabian Gulf, the predominant modes of concrete deterioration are : (1) corrosion of reinforcing steel, (2) sulfate attack, (3) salt weathering, (4) cracking due to thermal gradients, and (5) cracking due to plastic and drying shrinkage. However, the wide occurrence of concrete deterioration due to reinforcement corrosion overshadows its failures due to all the other causes [4].

Corrosion of reinforcing steel in concrete is brought about mainly by two factors. **Firstly**, it is due to the ingress of atmospheric carbon dioxide to the steel-concrete interface, and **secondly**, and more importantly, due to the diffusion of the chloride ions. Field studies conducted at King Fahd University of Petroleum and Minerals [5] indicated that the presence of excessive chloride concentrations in the deteriorated concrete structures is the main cause of reinforcement corrosion. The chloride ions were reported to be contributed by either the mix constituents or those entering the concrete from the external environments. The concomitant presence of sulfate salts with the chloride ions are known to aggravate the corrosive attack on reinforcing steel [6,7].

## 1.2 IMPROVEMENT OF CONCRETE DURABILITY

As the environmental conditions of the Arabian Gulf constitute a very aggressive environment for concrete structures, the construction practices need to be modified to be compatible with the exposure conditions. The concrete construction in such environments should be designed for durability rather than for strength only [8,9]. The concrete quality should be specified in terms of diffusion and permeability indices. In order to produce a durable concrete, a four-step approach is often recommended. **Firstly**, the concrete should be designed to be dense and impermeable. **Secondly**, improved construction practices with proper consolidation and curing should be utilized. **Thirdly**, the concrete should be further protected through the application of surface coatings. **Fourthly**, the reinforcing steel should be protected by the use of corrosion inhibitors and/or coating it with an impermeable coating [10]

While the first two aspects have been considerably investigated [8,11-13], this research is mainly concerned with evaluating the effectiveness of corrosion inhibitors and concrete surface coatings in inhibiting the corrosion of reinforcing steel in the environment of the Arabian Gulf.

### **1.3 RESEARCH OBJECTIVES**

The primary objective of this research program was to assess the performance of corrosion inhibitors and concrete surface coatings in retarding reinforcement corrosion. The specific objectives were:

1. to evaluate the performance of selected corrosion inhibitors in retarding chloride-induced reinforcement corrosion;
2. to assess the carbonation behavior of concrete specimens containing corrosion inhibitors; and
3. to investigate the performance of concrete surface coatings under thermal variations and wet-dry cycles.

### **1.4 EXPERIMENTAL PROGRAM**

To achieve the objectives of this study, plain and reinforced concrete specimens were prepared using ASTM C 150 Type V cement. A coarse-to-fine aggregate ratio of 1.63 by weight was kept invariant in all the mixtures. All the concrete mixtures were proportioned for an effective water-cement ratio of 0.45 and a

cement content of  $350 \text{ kg/m}^3$ . For the mortar specimens, a sand-to-cement ratio of 2 was used.

The experimental program was broadly divided into three series. In **Series I**, the effect of corrosion inhibitors on corrosion of reinforcing steel in concrete was studied. In **Series II**, the effect of these inhibitors on the carbonation of mortar specimens was evaluated. In **Series III**, the effect of concrete surface coatings in inhibiting reinforcement corrosion was evaluated. The details of experimental variables in these three series are detailed below.

#### **1.4.1 Series I: Effect of Corrosion Inhibitors on Reinforcement Corrosion**

The following corrosion inhibitors (i.e. type and dosage) were used in this part of the study:

- |                                |                                    |
|--------------------------------|------------------------------------|
| 1. Calcium nitrite:            | 2 and 4% by weight of cement       |
| 2. Calcium nitrate:            | 2, 3, and 4% by weight of cement   |
| 3. CI1 (Commercial Inhibitor): | 5 liters/ $\text{m}^3$ of concrete |
| 4. CI2 (Commercial Inhibitor): | 1.2 $\text{kg/m}^3$ of concrete    |

The last two are organic-based inhibitors and available in the Saudi market and their dosages were specified by the manufacturer. The following five

contamination levels were used in the reinforced concrete specimens made with the above inhibitors:

1. 0.8% chloride;
2. 0.8% chloride + 1.5%  $\text{SO}_3$ ;
3. Sea water;
4. Brackish water; and
5. Unwashed Aggregate

The tests conducted and the number of concrete specimens prepared in this series are detailed in Table 1.1. Concrete cylinders of 75 mm (3 inch) diameter and 150 mm (6 inch) height were cast for all the tests.

#### **1.4.2 Series II: Carbonation**

In the specimens of this series, the following three contamination levels were used:

1. Control;
2. 0.8% chloride;
3. 0.8% chloride + 1.5%  $\text{SO}_3$ ; and
4. Sea water.

For evaluating the depth of carbonation, 49x75 mm (2x3 inch) mortar specimens were exposed to a carbonation chamber where the concentration of carbon dioxide was maintained at 3%. The test conducted and the number of mortar specimens prepared in this series are detailed in Table 1.2.

#### **1.4.3 Series III: Effect of Concrete Surface Coatings on Reinforcement Corrosion**

The following four types of concrete surface coatings were used in this part of the study:

1. Sodium Silicate: Sodium silicate-based compound for surface application to harden, seal and dust proof concrete.
2. Siloxane: Siloxane-based, deep penetrating sealer.
3. Silicone: Silicone-based coating.
4. Acrylic: Cement-based, acrylic-modified water proofing coating.

The tests conducted and the number of concrete specimens prepared in this series are detailed in Table 1.3.

For evaluating the effectiveness of surface coatings under heat-cool and wet-dry cycles, the following three tests were conducted after one, two, four, and six months of exposure:

1. Pulse velocity;
2. Compressive strength; and
3. Absorption.

For evaluating the effectiveness of surface coatings in inhibiting reinforcement corrosion, the coated reinforced concrete specimens were exposed to a 5% sodium chloride solution and 5% sodium chloride plus 3% sodium sulfate solution. In this series, concrete cylinders of 75 mm diameter and 150 mm height were used.

Table 1.1: Summary of Tests and Number of Specimens Used in Series I

Test	Number of Specimens
Compressive strength	24
Corrosion potential	120
Corrosion current density	120

Table 1.2: Summary of Test and Number of Specimens Used in Series II

Test	Number of Specimens
Carbonation	50

Table 1.3: Summary of Tests and Number of Specimens Used in Series III

Test	Number of Specimens
Corrosion potential	30
Corrosion current density	30
Wet-dry cycling	75
Heat-cool cycling	75



## **CHAPTER 2**

### **LITERATURE REVIEW**

In this Chapter, a review of the recently published literature, pertinent to both corrosion inhibitors and surface coatings, is presented.

#### **2.1 USE OF CORROSION INHIBITORS**

Reinforced concrete is extensively used in the Arabian Gulf region, due to its durability and cost advantages over other structural materials. However, due to the severe exposure conditions and chloride-contaminated concrete ingredients, premature deterioration of concrete, mainly due to reinforcement corrosion, is inevitable if additional corrosion protection measures, as discussed in the earlier chapter, are not implemented [14].

The main factors that can affect the ability of concrete to protect reinforcing steel against corrosion are concrete quality, thickness of concrete cover, and the chloride contamination of the constituent materials. Almost all the codes of practice suggest the need for a maximum water-to-cementitious materials (w/c)

ratio, minimum cover to the steel, minimum cement content and tolerable chloride and sulfate contamination contributed by the mixture ingredients [15]. However, in situations where chloride and sulfate contamination is inevitable, one of the means of protecting reinforcing steel from corrosion is to add a corrosion inhibitor to the concrete. While numerous inhibitors have been suggested, only a small group have been critically studied, and only a few are used commercially [15].

ACI 116R-85 defines a corrosion inhibitor as “*a chemical compound, either liquid or powder, that effectively decreases corrosion of steel reinforcement before being embedded in concrete, or in hardened concrete if introduced, usually in very small concentrations, as an admixture*” [16]. The National Association of Corrosion Engineers (NACE) defines corrosion inhibitors as “*substances which, when added to an environment, decrease the rate of attack of the metal*” [16].

Steel in portland cement concrete is protected by a passive iron oxide layer that forms on it because of the high pH of the concrete. As long as this protective layer is intact, corrosion will not occur. Thus, most corrosion inhibitors work by maintaining or providing an additional passive layer or preventing the penetrating deleterious species from reacting with it [16].

During the past fifteen years, corrosion inhibitors have been increasingly used for long-term protection of reinforced concrete structures in many applications, such as parking garages, highway bridges, and marine structures, etc. In the Arabian Gulf, corrosion inhibitors have also been used successfully. In the UAE, according to Matta and Berke [17], more than 100,000 m<sup>3</sup> of concrete containing calcium nitrite have been used to build sea walls, swimming pools, power stations and other residential structures.

It is well documented that the function of a concrete admixture is not to make a good concrete out of a poor quality concrete. It is to improve the quality and performance of good concrete, either in the plastic or hardened state or both. The function of a corrosion inhibiting admixture by definition is to reduce the risk of corrosion of embedded metallic elements by chemical action [18].

For proper evaluation of a corrosion inhibiting admixture and its performance in concrete, both in the laboratory and in the field, it is essential to relate it to the performance of a similar concrete containing no admixture. Both concretes should be exposed to similar environmental and aging conditions. All conclusions derived on any admixture, both in the short and in the long term, should be based on the relative values of such comparative evaluation [18].

The corrosion inhibiting admixtures are mainly used in concrete exposed to sea water or to varying degrees of exposure to aggressive chemical environments. They should not be viewed as an alternative to the design specifications for durable concrete but as an addition to it as these specifications are fundamental. They are also essential for superior performance or when corrosion inhibiting admixtures or any other type of corrosion protection system are demanded [18].

The advantages of using inhibitors to provide corrosion protection are that they are distributed throughout the concrete matrix, protecting all the steel; and that the concrete's low permeability prevents the inhibitor from leaching out. An ideal corrosion inhibitor is a chemical compound that, when added in adequate amounts to concrete, can prevent corrosion of embedded steel and at the same time has no adverse effect on the properties of fresh and hardened concrete.

### **2.1.1 Effect of Nitrite on the Corrosion Mechanism**

To understand the mechanisms of corrosion inhibition by calcium nitrite, the process of corrosion of reinforcing steel will be outlined first in the following paragraphs.

The first reaction that occurs when steel is placed in an alkaline environment, such as concrete, is :



Later reactions will convert the  $\text{Fe}^{++}$  to  $\text{Fe}(\text{OH})_2$  or  $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$  or  $\gamma\text{-FeOOH}$  at the steel surface. In the absence of chlorides, all the phases are stable in an alkaline environment.  $\gamma\text{-FeOOH}$  is the most unstable in the presence of chloride or other depassivating ions [18].

On a microscopic scale, there will be regions where the protective oxide is not present due to mechanical damage and/or reaction with acids, etc. At these locations, chloride ions can form a complex with  $\text{Fe}^{++}$  [18].

The nitrite ions prevent the continuation of the corrosion reaction at the anode by reacting with the ferrous ions,  $\text{Fe}^{++}$ , as follows:



or



If the corrosion reaction (Eqn. 1) occurs, the ferrous ions produced are changed, through calcium nitrite to a stable passive layer. Thus, the passivating reaction of nitrite with ferrous ions is to block the active corrosion centers by producing a passive ferric oxide protective film. The iron in the ferric state is not complexed by chloride and therefore corrosion is reduced [18].

It is worth noting here that the nitrite does not enter into reactions involved in producing the anode, but reacts with the resulting products of the anode. Consequently, it cannot affect the size of the anode. Further, only monolayers of oxides are involved, and essentially no nitrite or hydroxide are consumed in forming the initial protective oxides or hydroxide [18].

Note that all  $\text{Cl}^-$  (or other aggressive anions),  $\text{NO}_2^-$ , and  $\text{OH}^-$  are competing at the “flaws” in the oxide layers for  $\text{Fe}^{++}$ . Over time, a nitrite and/or an alkaline environment free of chloride will reduce the number of sites where  $\text{Fe}^{++}$  ions are formed through the formation of a protective coating, i.e.  $\gamma\text{-FeOOH}$  or  $\text{Fe}_2\text{O}_3$ , [18].

### **2.1.2 Types of Corrosion Inhibitors**

Corrosion inhibitors can be divided into three types: anodic, cathodic, and mixed,

depending on whether they interfere with the corrosion reaction preferentially at the anodic or cathodic sites or whether both are involved [19].

**Anodic types** of corrosion inhibitors are materials which function as inhibitors due to their ability to accept electrons. They exert their action by stifling the reaction at the anode. Most of the admixtures in this group are effective only when present in sufficiently high concentrations. The concentration required is often determined by the level of chlorides to which the steel will be exposed. When insufficient quantities are used, corrosion occurs, intensity being localized thereby causing severe pitting. The most widely used materials belonging to the group of anodic inhibitors are calcium and sodium nitrite, sodium benzoate and sodium chromate. Other chemicals which have shown promise in various studies are sodium salts as silicates and phosphates, stannous chloride and hydrazine hydrate [19]. One of the serious drawbacks in the use of anodic inhibitors is that the admixtures are effective in maintaining passivity only if present in sufficiently high concentrations. If inadequate quantities are used or if the ratio of the inhibitor to the chloride level is small, corrosion becomes intensely localized and the attack is significant.

The mechanism of reactions involving most anodic inhibitors is essentially that of oxidizing the dissolving ferrous oxide to form a protective film of hydrated ferric

oxide on the steel surface. Gradually no new surface of the steel is exposed and the corrosion process ceases. Effective inhibition is provided only if the admixture is present in sufficient quantities to meet the ratio of inhibitor:chloride required by the system. If this ratio is small, the competing reactions of protective film repaired by the nitrite ion and breakdown by chloride attack occur simultaneously with the latter exerting greater control. Corrosion becomes intensely localized and dangerous pitting type of corrosion occurs. Sodium benzoate behaves differently in that general corrosion attack, rather than localized corrosion, occurs if low levels of inhibitor addition are used. They are therefore generally considered as safe inhibitors [19].

The efficiency of anodic inhibitors is directly dependent on the amount of chloride present in concrete. Higher chloride contents drastically reduce their effectiveness and larger amounts of the inhibitor are required to prevent chloride attack and corrosion. Each inhibitor has a critical chloride concentration below which corrosion is arrested [19].

**Cathodic inhibitors** act either by slowing the cathodic reaction or by selectively precipitating at the cathodic sites. Materials in this group are strong proton acceptors and their action, in contrast to anodic inhibitors, is usually indirect. Some of the commonly used cathodic inhibitors are bases, such as NaOH,  $\text{Na}_2\text{CO}_3$ ,



or  $\text{NH}_4\text{OH}$ , which increase the pH of the concrete medium and thereby also decrease the solubility of the ferrous ions. Most of the work done, chiefly on a laboratory scale, has centered around aniline and its chloro-, alkyl- and nitro-substituted forms and mercaptobenzothiazole. In general, the molecular structure of these types of inhibitors plays a significant role in the effectiveness of these admixtures. An increase in the overall electron density and spatial distribution of the branch groups determines the extent of chemisorption on the metal and therefore their effectiveness [19].

Cathodic inhibitors consisting of aniline and its chloroalkyl- and nitro-substituted forms, as well as the aminoethanol group are used at 1 to 2% dosage levels by cement weight in the presence of 1 to 2%  $\text{CaCl}_2$ . Inorganic salts, such as  $\text{NaOH}$ ,  $\text{Na}_2\text{CO}_3$  and  $\text{NH}_4\text{OH}$ , are generally used at a dosage of 2 to 4% [19].

As was mentioned previously, cathodic inhibitors act by either slowing the cathodic reaction or selectively precipitating at the cathodic sites to increase the electrolytic resistance and restrict the diffusion of reducible species to the cathode. The reactive products of such inhibitors do not bond to the metal as rigidly as those of anodic inhibitors. Inorganic materials which are strong bases usually increase the pH of the medium causing a decrease in the solubility of ferrous ions [19].

**Mixed inhibitors** may simultaneously affect both the anodic and cathodic processes. A mixed inhibitor is usually more desirable because its effect is all encompassing, covering corrosion resulting from chloride attack as well as that due to microcells on the metal surface [19].

Mixed inhibitors contain molecules in which the electron density distribution causes the inhibitor to be attracted to both the anodic and cathodic sites. The molecules may have more than one orienting group attached.

Each group may include materials which function by one of the following mechanisms: (a) formation of barrier layers; (b) oxidation by passivation of the surface; and (c) influencing the environment in contact with the metal. To be an effective corrosion inhibitor, the selected chemical or mixture of chemicals should meet the following requirements [19]:

1. The molecules should possess strong electron acceptor or donor properties or both.
2. The solubility should be such that rapid saturation of the corroding surface occurs without being readily leached out.
3. Induce polarization of the respective electrodes at relatively low current values.

4. Be compatible with the intended system so that adverse side effects are not produced.
5. Be effective at the pH and temperature of the environment in which it was used.

Normal, untreated concrete forms a protective oxide layer around the reinforcing steel due to the high pH of concrete pore solution. This layer provides protection against up to 2.4 kg/m<sup>3</sup> of chlorides (1.5 lb/ft<sup>3</sup>) at the vicinity of the rebars. Anodic corrosion inhibitors improve this naturally-occurring oxide layer by further protecting the rebar [20].

### **2.1.3 Previous Studies on Corrosion Inhibitors**

The use of corrosion inhibitors in concrete has been reviewed by Treadaway and Russell [21], Craig and Wood [22], Griffin [23], Slater [24], and most recently by Berke [25]. Early studies looked at numerous inhibitors with the most attention focused on sodium nitrite, potassium chromate, sodium benzoate and stannous chloride [18].

Craig and Wood [22] examined the mechanical properties of mortars produced with sodium nitrite, potassium chromate, sodium benzoate and calcium chloride.

They found a marked decrease (as high as 20 to 40%) in the compressive strength when the inhibitors were added to mortars. In contrast, calcium chloride increased the compressive strength. The tensile strength was adversely affected by sodium nitrite and sodium benzoate, but not by potassium chromate. Corrosion testing indicated that the inhibitors were not detrimental in the absence of chlorides, however, only sodium nitrite inhibited corrosion in the presence of chloride ions.

Treadaway [26] and Treadaway and Russell [21] conducted tests using sodium nitrite and sodium benzoate. They also showed a decrease in compressive strength when these chemicals were added to concrete. Corrosion tests were conducted in alkaline solutions and in cement extracts. They found that sodium nitrite inhibited steel corrosion in the presence of chlorides in cement extracts, whereas sodium benzoate did not. In the solution testing, they emphasized that corrosion was uniform with sodium benzoate and pitting occurred with sodium nitrite. The lack of pitting in the sodium benzoate solutions might suggest that the solutions carbonated over time, thus reducing the pH and changing the mode of corrosion from pitting to uniform. Initiation of reinforcement corrosion was delayed due to the addition of sodium nitrite.

Evans [27] and Short et al. [28], based on theoretical interpretation, and Nurenberger [29], based on experimental work on concrete, cautioned of the

possibility of accelerated pitting of steel reinforcement in the presence of chloride ions due to insufficient calcium nitrite.

Nurenberger [29] used concrete of high water-to-cement ratio ( $w/c = 0.9$ ), low concrete cover, less than 25 mm, and low nitrite dosage, 1% by weight of cement, to accelerate the reinforcement corrosion. His results indicated that the addition of sufficient amounts of inhibitor (especially nitrites) to concrete would seem to be an effective and economic protection against corrosion of reinforcement. He, however, expressed reservation with regard to the possible migration and leaching out of nitrite from concrete [29]. It was noted that a decrease in general corrosion occurred after 2.5 years, but an increased tendency of pitting was observed. Similar concrete exposed for 2.5 years to sea water and alternating freezing and thawing indicated that the protective effect of nitrite was particularly negligible. These results are not surprising considering the low concrete cover and ultra high  $w/c$  ratio which would provide essentially a porous system, much different from field design criteria.

Brieseman [30] investigated different types of corrosion inhibitors. In his work, low strength concrete was used to enhance the rate of corrosion. He reported no marked effect of the inhibitor in concrete made with a  $w/c = 0.7$ . However, in prestressed crack-induced concrete, of  $w/c = 0.6$ , it was found that sodium nitrite

displayed the best performance, the corroded steel surface was about 50% lower than that in the uninhibited concrete [30]. Furthermore, pitting corrosion could not be found on steel in concrete as a result of under-dosage of inhibitors such as that observed in media other than concrete.

Chen et al. [31] reported results of ten year field exposure tests of reinforced concrete to sea water and fresh water. They determined periodically the weight loss of steel, depth of pits, area of corrosion and chloride content of concrete around the reinforcement. It was found that the area above high tide level suffered the highest rate of corrosion. It was observed that the increased cover of plain and air-entrained concrete from 15 to 30 mm reduced corrosion by about 60 and 58%, respectively, and reducing the w/c ratio was also beneficial. After ten years of exposure, it was reported [31] that for concrete of 0.65 w/c, cover of 15 mm, mixed with beach sand containing chloride ion concentration of 0.1%, and without sodium nitrite had an area ratio of corrosion to reinforcement of 8.95 as against 3.5 in similar concrete having 2% sodium nitrite by weight of cement [31]. They concluded that the inhibiting effect of nitrite on the long period of the steel bars in portland cement concrete, whose w/c ratio is 0.65 and coverage in 15 mm, is significant even after 10 years.

23

Sodium nitrite, however, suffers two disadvantages, one pertinent to reduction in strength [21,22] and the other being the risk of the alkali-aggregate reaction which is to be aggravated by the addition of sodium salts [32].

The use of calcium salt of nitrite eliminated the disadvantages of sodium nitrite with regard to the risk of alkali-silica reaction [32] as well as the reduction in strength. Calcium nitrite also meets the ASTM C 494 specifications as a concrete accelerator and has no detrimental effect on durability. Further, since cracking is frequently due to localized corrosion, the increased time to cracking due to the use of calcium nitrite is a manifestation of the decrease in localized corrosion[32].

In the 1970's, numerous corrosion studies were performed documenting the corrosion inhibiting properties of calcium nitrite. It was determined that the mechanism of corrosion protection was that of anodic inhibition and that the steel in chloride-containing concrete may fail by pitting [33].

El-Jazairi et al. [18], from their work on calcium nitrite, concluded that, for effective performance of calcium nitrite exposed to aggressive environments, it is essential for long-term durability to use good quality concrete with the following limits:

1. Water-to-cement ratio should not be more than 0.5, preferably 0.4.
2. Minimum cement content should be 300 kg/m<sup>3</sup>, preferably 350 kg/m<sup>3</sup>.
3. Minimum cover to reinforcement should be 30 mm, preferably 38 or greater than maximum aggregate size plus 18 mm.

They indicated that the use of adequate dosage of the corrosion inhibiting admixture based on calcium nitrite in good quality concrete provides additional safeguard and protection to reinforcement in concrete exposed to aggressive environments [18]. According to them, calcium nitrite based admixture has no detrimental effect on the durability of reinforced concrete even at reduced levels. It enhances the early strength development of concrete and provides long-term protection to reinforcement [18].

Gaidis and Rosenberg [34] reported that corrosion-inhibiting admixture based on calcium nitrite inhibits reinforcement corrosion if the chloride to nitrite weight ratio does not exceed 1.5. Visual observations made on rebars in lime water solutions containing chloride and nitrite ions, and corrosion current and potential measurements on concrete cylinders with embedded reinforcing steel bars, and potential measurements on simulated concrete bridge decks, were in substantial agreement.



Andrade et al. [35], based on the results of several years of research about the inhibiting effect of sodium nitrite on corrosion of reinforcement in concrete, reported that nitrite in concrete, if used in sufficient proportions, is a complete inhibitor when chloride is added during mixing. According to them, insufficient amounts of nitrites have never provoked more corrosion in their experiments in concrete. The presence of nitrite always produced a beneficial effect. The nitrites are also beneficial in carbonated concrete, suppressing or, at least, reducing the attacked area and the corrosion rate of steel.

Alonso and Andrade [36] studied the effect of sodium nitrite as a corrosion inhibitor in contaminated and chloride-free carbonated mortars. They found that sodium nitrite reduces and even completely avoids the aggressive effect of concrete carbonation and this protective character, however, was not effective enough when both carbonation and chlorides acted together in the mix.

Hope and Ip [37] studied the effect of calcium nitrite and sodium molybdate on the corrosion inhibition of steel in simulated concrete environments. They found that the combination of calcium nitrite (4.5 parts) and sodium molybdate (1 part) effectively protected steel specimens in oxygenated lime water when the ratio of the combined inhibitor to chloride ions was about 1:11. The combined inhibitor appeared to be more effective than calcium nitrite in corrosion protection.

They also found in another research work [38] that calcium nitrite exhibits promising corrosion inhibiting properties. The corrosion threshold level, in terms of the ratio of nitrite to chloride ions, was probably between 0.07 and 0.09. Stannous chloride, however, did not appear to be a promising corrosion inhibitor.

Collepari et al. [39] studied the use of nitrite salt as a corrosion inhibitor in reinforced concrete structures immersed in sea-water. They concluded that in cracked concrete specimens immersed in sea-water, the presence of sodium nitrite, supposed to be a corrosion inhibitor, makes reinforcement corrosion more severe.

Berke [40] found out that calcium nitrite significantly improves the corrosion resistance of steel in concrete made with w/c values under 0.50 and the chloride levels were significantly reduced by lowering the w/c ratio. Even after the corrosion begins due to high chloride levels, steel in calcium nitrite concrete corrodes at a lower rate than that in concrete without nitrite.

Berke et al. [41] recommended the use of calcium nitrite corrosion inhibitor to improve the durability of reinforced concrete in the Arabian Gulf. According to them, calcium nitrite is a well tested and proven corrosion inhibitor that can provide significant improvement in corrosion resistance when used with good quality concrete. They stated that good quality concrete alone is not enough to

provide a maintenance-free service-life of structures in the severe Gulf environment. Calcium nitrite corrosion inhibitor, in combination with good quality concrete, is a viable means to achieving long-term durability.

Alonso et al. [42] conducted research on the inhibiting effect of nitrites on the corrosion of rebars embedded in carbonated concrete and concluded that nitrites added in the mix (3% by weight of cement) protects reinforcement from further corrosion due to concrete carbonation and their inhibiting action is enhanced in wet concrete. When the proportion of nitrites was not high enough to completely avoid rebar corrosion, an increase in the attack was not found. Further, the presence of nitrites reduced the attacked area of the rebars (weight loss) [42].

Berke and Rosenberg [43] stated that nitrites have been used in concrete for more than 30 years in Europe and calcium nitrite has been available in the United States as a concrete admixture for more than 8 years. Extensive testing shows that:

- a) it protects steel against chloride-induced corrosion;
- b) efficiency increases as concrete quality improves;
- c) it improves the compressive strength;
- d) it lowers corrosion rate once corrosion begins; and

50

e) it works in the presence of cracks.

Andrade et al. [44] tested sodium fluoro-phosphite ( $\text{Na}_2\text{PO}_3\text{F}$ ) as a curative corrosion inhibitor for steel in concrete. They concluded that this chemical acts as an anodic inhibitor of reinforcement corrosion promoted by NaCl when added in alkaline solutions or added to mortar at the mixing stage.

Rosenberg et al. [33] worked on a corrosion inhibitor formulated with calcium nitrite for use in reinforced concrete and concluded that calcium nitrite can be used as an effective means of combating corrosion, that it passes the requirements of ASTM C 494, and that it improves the strength of the resulting concrete.

Berke et al. [45], in their work on a corrosion inhibitor, concluded that calcium nitrite delays the initiation time to corrosion of reinforcing steel and lowers the corrosion rate after the onset of corrosion.

Corbo and Farazam [46] studied the effect of calcium chloride, calcium nitrate and sodium nitrite on the pore solution chemistry of hardened cement and corrosion of steel in concrete. The possibility of an ion-exchange mechanism between ingressed chloride ions and complex admixed chloride ions was also evaluated. The results indicated that the majority of admixed chloride ions are removed from the pore

solution and incorporated in the cement after 14 days of curing. No ion exchange between the ingressed chloride ions and admixed ones was observed. The calcium ion concentration in the pore solution was noted to decrease drastically with time and was negligible after 14 days of curing. Therefore, the authors believe that it is inappropriate to utilize saturated  $\text{Ca(OH)}_2$  solution to simulate pore solution for corrosion testing.

Tomosawa et al. [47] conducted an experimental study on the effectiveness of a corrosion inhibitor in reinforced concrete. They conducted two experiments to examine the relationship between the quantity of calcium nitrite and the inhibition effect on corrosion. In experiment 1, the test specimens of concrete to which chloride and calcium nitrite had been added, were subjected to accelerated corrosion by means of repeated drying and wetting. In experiment 2, the reinforced concrete specimens containing calcium nitrite were repeatedly immersed in a chloride solution and dried. This procedure accelerated the penetration of chlorides and the corrosion of embedded steels. From the results, it was confirmed that the occurrence of corrosion can be prevented and the corrosion rate can be suppressed, if more chlorides are penetrated, depending on the amount of nitrite ions.

Cigna et al. [48] studied the influence of calcium nitrite on reinforcement corrosion in concrete mixtures containing different cements. They concluded, on

the basis of the results of two years experimentation, that the presence of the inhibitor hinders the corrosion initiation process. Moreover, in some cases, when probably chlorides entered the concrete through existing cracks, also the corrosion propagation process seems to be stopped.

Justnes and Nygaard [49] used calcium nitrate as a corrosion inhibitor in their research work. The scope of their work was to find the effect of calcium nitrate (CN) on both the chloride binding and the chloride-induced reinforcement corrosion. They concluded that the addition of 3.85% CN to 1:3 mortars, with and without 5% condensed silica fume (CSF) replacement, tend to reduce the 1 day strength, but increases the compressive strength from 8 until 56 days of curing. The strength improving effect of 3.85% CN is reduced when 5% of the cement is replaced by CSF. The corrosion rate of steel embedded in a mortar with 3.85% CN was 5 times lower than that in an identical mortar excluding CN, when the pores were repeatedly filled with a 5% NaCl solution in order to initiate reinforcement corrosion and after a total of 14 month curing.

Maeder [50] investigated the effectiveness of some mixed type of organic inhibitors in retarding corrosion of reinforcing steel. These inhibitors were amines and alkanolamines and their salts with organic and inorganic acids. These types of inhibitors have been patented for different applications, including the protection of

reinforcing steel in cementitious matrices. According to the author [50], the unique feature of these inhibitors is their ability to diffuse a considerable distance through concrete because of their high vapor pressure. When these inhibitors are added to concrete, they do not delay the time of set. They diffuse to both anodic and cathodic sites and provide protection to reinforced steel. The author cites various examples where these inhibitors have been successfully used because [50]:

1. They provided corrosion inhibition in the presence of varying amounts of chlorides;
2. they can diffuse through concrete thereby providing both cathodic and anodic protection;
3. they are organic in nature and environmentally sound; and
4. they are not detrimental to other concrete properties.

Furthermore, the author indicates that these inhibitors are preferable over nitrites as they are non-toxic.

Hope and Thompson [51] have recently studied the damaging effect of calcium nitrite on concrete. In their study of corrosion inhibitors, all samples of mortar containing sodium chloride that were soaked in a calcium nitrite solution, underwent severe deterioration. The mortar specimens cracked and bulged without

corrosion of reinforcing steel. Although a definite cause was not determined, deterioration occurred only in mortar specimens soaked in a solution containing a high concentration of calcium nitrite. The findings of their experiments indicated that mortar deterioration occurred only in the presence of calcium nitrite and in samples that had not been initially air-dried for two months prior to immersion in solutions containing calcium nitrite. This indicates that there is a potential problem when concrete is soaked in a high concentration of calcium nitrite, however, curing prior to exposure to calcium nitrite may be an important factor. Furthermore, the results of this study may not be of practical significance, as the calcium nitrite is used in practice in small dosages as an admixture, and situations where a concrete component comes into contact with such a high concentration of calcium nitrite solution is rare.

## **2.2 USE OF SURFACE COATINGS**

Durability of concrete structures depends on the quality of concrete. One of the most important properties of concrete that governs its durability performance is its permeability. Permeability of concrete is controlled by a number of variables from physical and chemical properties of cement, aggregate, additives and mixing water used, to procedures followed during proportioning, mixing, casting and curing of the concrete [52]. Further, the movement of aggressive solutions and water



charged with chlorides, sulfates, dissolved carbon dioxide and oxygen and other corrosive agents into concrete, and soluble reaction products out of the concrete, depends on the permeability of concrete. Therefore, permeability is a very important property of concrete which determines the extent of its susceptibility to corrosive attack and the effectiveness of its corrosion protection for reinforcing steel bars in aggressive solutions, water and corrosive gases.

Of all the methods of protecting and preserving existing structures into serviceable and useable conditions, the use of surface coatings has the unique advantage that it can be applied to protect both existing and new structures, or as part of a program of refurbishment of damaged and deteriorating structures. Surface or barrier coatings have also a long history of application to concrete to protect it and the embedded steel from various aggressive agents and external environments. A wide range of vapor barriers, vapor permeable coatings and surface penetrating sealers and sealants have also been reported in the literature [53], and some of these products are available in the Saudi market.

The nature and severity of exposure, i.e. environmental conditions, is the major factor determining the performance characteristics of barrier coatings. Vapor barrier coatings, for example, do not always exclude passage of oxygen; on the other hand, coatings based on silane/siloxane are known to have poor resistance to

carbon dioxide penetration, although they may have good resistance to water absorption and chloride penetration. Similarly, a coating with variable water diffusion resistance may be required for different exposure conditions. The surface coatings should, therefore, be used with considerable engineering judgment and knowledge of the short and long-term performance characteristics of the coating, and the exposure regime of the structure to which the coating is applied [53].

### **2.2.1 Types of Surface Coating**

In the following paragraphs, the types of concrete surface coatings and their physical and chemical properties are discussed.

#### **2.2.1.1 Penetrants**

These materials are low viscosity liquids that penetrate into the concrete and line the pores. They are colorless and therefore have little effect on the appearance of the structure. The systems are hydrophobic and thus repel water and water-containing chloride salts. They do not block the pores of the concrete and so allow the passage of potentially harmful water vapor and other gases which may otherwise remain trapped within the structure. The majority of commercially available penetrants are based on either silane, siloxane or silicone resins [54].

### 2.2.1.2 Silanes and Siloxanes

Silanes are more correctly described as alkylalkoxysilanes. The most widely used “monomeric silane” for the protection of concrete is iso-butyl trimethoxysilane. Silanes become reactive in the presence of moisture with the speed of reaction being governed by the surrounding pH. Thus, in normal alkaline concrete, the silane will react with the pore lining quite rapidly, but if the substrate is neutral, e.g. brick, stone, etc., or there is no moisture, no reaction can take place. Since much of the concrete requiring treatment has lost its alkalinity due to the action of acidic gases, the reaction time is frequently slow. While the reaction takes place, the volatile silane will continually evaporate and to maximize the chances of success, it is therefore necessary to use very high concentrations of silane (up to 100%) [54].

Siloxanes are more correctly described as oligomeric alkylalkoxysiloxanes. They have virtually all the advantages of silanes with respect to reactivity and water repellency but, in addition, have low vapor pressure. They may, however, under very dry substrate conditions, exhibit slightly less penetrability than silanes due to their relatively large molecules [54].

### **2.2.1.3 Silicone Resins**

These materials are much higher in molecular weight than silanes or siloxanes and thus are not penetrative. They are not normally reactive materials and dry by solvent evaporation to leave a surface film of resin. The substrate has to be air-dry before application of the product and the systems can be susceptible to dirt pick up and weathering. Their use has declined in recent years [54].

### **2.2.1.4 Sealers and Coatings**

Sealers are intermediate between penetrants and coatings and work by blocking the pores of the substrate. They are more viscous than penetrants and generally form a film on the surface of the concrete. This group includes silicates, silica fluorides and linseed oils, and their effectiveness as a barrier against environmental attack has been shown to be limited [54].

Coatings are more viscous than sealers and provide protection to the structure by forming a relatively thick film on the concrete surface (up to 1 mm). These materials generally consist of binder, pigments, fillers and a carrier. The binder is the polymer which can be of various types. It imparts the majority of the properties of the system including anti-carbonation resistance and, in some cases, flexibility. It is generally acknowledged that a degree of flexibility is needed in coating systems so that the anti-carbonation properties are not reduced in areas of the

structures which are subjected to movement. The pigments provide color, while the fillers provide thickness and surface texture. The carrier is either water or solvent and is incorporated into the system to reduce the viscosity and aid application. Solvents generally have a much greater effect at reducing the viscosity and improving early age washout resistance as well as improving low temperature application and drying properties. However, concern is increasing about the long-term health risks associated with using solvents with the inevitable increase in interest in water-based systems. A large number of polymer types have been used in coatings including chlorinated rubbers, urethanes, epoxies and acrylics [54].

#### **2.2.1.5 Epoxy Coatings**

Epoxy coatings can be either in emulsion form, solution form or solvent free. They are almost always made up of two components and based on liquid resins and hardeners. The solution epoxy systems are generally of lower viscosity than the solvent free and can therefore penetrate more effectively into the substrate. Water-borne systems are available but these are not as penetrative. As class paints, the epoxies have excellent chemical and abrasion resistance as well as good anti-carbonation properties. The major disadvantages of these systems is their tendency to chalk out when subjected to ultra-violet (UV) light in external situations. Recent improvements in formulation technology have reduced the chalking significantly but still the problem remains. Epoxies have limited breathability and are not

generally as flexible as polyurethanes [54].

### **2.2.2 Performance of Surface Coatings**

Swamy and Tanikawa [53] studied the effect of surface coatings to preserve concrete durability and reported that the application of impervious surface coatings to concrete surfaces to prevent the ingress of potentially harmful agents, such as water, air and chloride ions, is a very attractive solution to protect new and existing concrete structures. They concluded that the “Aron Wall” coating has an excellent performance characteristics in resisting the penetration of a wide range of aggressive agents into concrete.

Sergi et al. [55] studied the influence of surface coating treatments on the corrosion rate of steel in carbonated concrete and concluded that the water-repellent surface treatments, which line the pores of concrete with hydrophobic layers, proved effective in resisting water penetration and limiting the corrosion rate of steel in carbonated regions of the specimens, during exposure to cycles of wetting and drying.

Fluckiger et al. [56] investigated the effects of organic coatings on water and chloride transport in reinforced concrete. They concluded that the surface coatings

strongly reduce the water and chloride uptake of concrete. Coatings do not affect the transport of water and chlorides in concrete, the exposure conditions (humidity gradient), however, determine the transport direction. The magnitude of this transport zone is determined by the porosity of concrete, i.e. in a high porosity (or high permeability) concrete the transport zone is high. If the rebars are located in the transport zone with inhomogeneous oxygen and moisture content, high corrosion risk should be expected [56].

Cabrera and Hassan [57] studied the effectiveness of surface coating treatment against the ingress of chlorides into mortar and concrete and they concluded that the Leeds chloride permeability test is reliable and using this test it is possible to obtain quantitative data to assess the chloride protection resistance of surface treatment compounds. One of the materials tested, silane, showed signs of deterioration within the period of the chloride permeability test. This feature of the test is very useful to assess whether the effectiveness of a treatment is short lived.

Tanikawa and Swamy [58] investigated the effectiveness of an acrylic rubber surface coating in protecting reinforcing steel and reported that the coating totally prevented the penetration of chlorides into concrete, whereas substantial amounts of chlorides penetrated the unprotected concrete. The coating also totally prevented the penetration of  $\text{CO}_2$ , while the depth of carbonation was 2 to 3 mm in

the unprotected concrete.

Tanikawa and Swamy [59] further studied the penetration of chloride in unprotected and protected concretes. They concluded that the chlorides permeate from a very early age into unprotected concrete exposed to a salt-laden environment and this salt penetration increases progressively with time. The acrylic rubber coating has two important roles in protecting concrete and the embedded steel. It provides a total barrier to water and chloride ions, and it also permits a steady mobility of the chlorides within the body of the concrete thus preventing any build of chloride concentration in the vicinity of the reinforcing bars.

Yasui and Fukushima [60] worked on the performance of high build coating materials for concrete structures for preventing corrosion damage and they used new types of high build materials, soft type epoxy, polymer rich cement and others as coatings for concrete structures in their research work. They concluded that the concrete surface coating was effective as a counter-measure against the salt damage to concrete structures because coatings can shield the movement of corrosive factors such as moisture, salt and oxygen from the outside, reducing the corrosion of reinforcing steel in concrete.



Kamal and Salama [61] worked on the protection of reinforced concrete elements against corrosion by polymer coatings and concluded that the exposure of reinforced concrete structures in agricultural areas or chemical factories and to the ammonium nitrate solutions causes deterioration of concrete and corrosion of steel. The reduction in the concrete compressive strength and the bond between steel and concrete is higher for higher solution concentrations and lower concrete cover. Solvent-free epoxy resin coating showed high protection for concrete structures exposed to ammonium nitrate solutions.

Marusin [61] stated, based on her research, that certain chemical materials used as sealers over the concrete exposed surfaces can enhance the concrete durability and limit the corrosion of embedded steel by reducing the intrusion of chloride-laden water into the concrete. Among the most successful materials were epoxies, urethanes, latexes, silanes, and silane/siloxanes. However, the performance of all these materials varies from excellent through unsatisfactory. The effectiveness of all these sealers is greatly influenced by their chemical formulations, concrete quality, surface preparation, and application conditions. Generally, epoxies exhibited glossy surface, while urethanes and latexes varied in color, and penetrating silanes or silane/siloxanes did not change the appearance of concrete. Choosing the proper sealer for a specific structure should be based on the results of experimental testing and trial applications. Further, a periodic testing program

should be designed to provide proper maintenance of each structure protected by sealers. Although some sealers can significantly reduce the permeability of a concrete surface, a properly consolidated and properly cured low water to cement ratio concrete and deep cover over the embedded reinforcing steel is still needed for a long-term durable concrete.

## **2.3 SIGNIFICANCE OF THIS RESEARCH**

The present review of the literature, mostly cited in this Chapter, indicates that several chemical admixtures and surface coatings have been used in concrete construction to inhibit or retard reinforcement corrosion. However, data is lacking on the performance of corrosion inhibitors in concrete contaminated with both chloride and sulfate salts. Further, the usefulness of these chemical admixtures in inhibiting reinforcement corrosion in concrete made with brackish water, sea water and unwashed aggregates, as frequently used in Saudi Arabia, was not fully elucidated. Such a study is essential for the Arabian Gulf countries, since potable water is scarce. Similarly, the performance of concrete surface coatings exposed to temperature variation, representative of the environmental conditions of the Arabian Gulf, and the wetting and drying cycles, commonly observed in the marine environments, was not adequately studied.

The development of data on the performance of corrosion inhibitors and concrete surface coatings in the environments characterized by the presence of chloride and sulfate salts is certainly useful in improving the durability performance of concrete thereby leading to economic benefits by increasing the useful service-life and delaying the repair and rehabilitation of reinforced concrete structures.

## **CHAPTER 3**

### **METHODOLOGY OF RESEARCH**

This Chapter outlines the materials and the test methods utilized to fulfill the objectives of this investigation. Wherever applicable, ASTM or BS test methods were adopted.

#### **3.1 CONCRETE MIX DESIGN**

The absolute volume method was used to proportion concrete. The following parameters were kept invariant in all the concrete mixes.

Cement content:	350 kg/m <sup>3</sup>
Coarse to fine aggregate ratio:	1.63
Effective water to cement ratio:	0.45

In the mortar specimens used in the carbonation studies, an effective w/c ratio of 0.45 was used, while the sand to cement ratio was maintained at 2.

## **3.2 MATERIALS**

### **3.2.1 Aggregates**

Crushed limestone from Abu-Hadriyah with a maximum size of 12.5 mm was used as coarse aggregate. It was first sieved into different sizes and then washed with potable water to remove dust and salt contamination. It was thereafter air-dried for 48 hours and stored till used. The concentration of water soluble ingredients in the aggregate are shown in Table 3.1. The bulk specific gravity and absorption of the coarse aggregate were determined as per ASTM C 127 and were found to be 2.46 and 2.9%, respectively. The data is shown in Table 3.2. Dune sand with a specific gravity of 2.64 and an average absorption of 0.57% was used as fine aggregate.

The coarse aggregate was proportioned to conform to ASTM C 33 grading limits of size # 7. Table 3.3 shows the grading of the coarse aggregate.

### **3.2.2 Cement**

ASTM C 150 Type V sulfate resisting portland cement was used in all the mortar and concrete mixes. The chemical composition of this cement is shown in Table 3.4.

### **3.2.3 Corrosion Inhibitors**

The following four types of chemical corrosion inhibitors were used in this study:

1. Calcium nitrite
2. Calcium nitrate
3. CI1 (Commercial Inhibitor)
4. CI2 (Commercial Inhibitor)

Calcium nitrite was in a liquid form and the solid content was not less than 30% by weight and it was used in the mixing water at two dosages of 2% and 4% (by weight of cement), as per the data sheet of the manufacturer. Analar type calcium nitrate, which was in the form of powder, was used in the mixing water at a dosages of 2%, 3% and 4% by weight of cement. While the commercially available organic inhibitors CI1 and CI2 were also used in the mixing water at a dosage of 5 l/m<sup>3</sup> and 1.2 kg/m<sup>3</sup> of concrete, respectively, as prescribed by the manufacturers.

### **3.2.4 Concrete Surface Coatings**

The following four types of concrete surface coatings were used in this study:

1. Sodium Silicate: Sodium silicate-based compound for surface application to harden, seal and dust proof concrete.
2. Siloxane: Siloxane based, deep penetrating sealer.
3. Silicone: Silicone based coating.
4. Acrylic: Cement based, acrylic-modified water proofing coating.

After 14 days of wet burlap curing, the concrete specimens were retrieved from the curing tank and allowed to dry for 48 hours in the laboratory environment ( $25 \pm 3$  °C). Thereafter, the concrete specimens were cleaned with a brush in order to remove the dust and debris, and the coatings were applied with brush thereafter. The rate of application of the concrete surface coatings was prescribed by the manufacturer as shown in Table 3.5.

### **3.3 SPECIMENS PREPARATION**

#### **3.3.1 Mixing and Casting**

The concrete constituents were mixed in a revolving drum type mixer for approximately 3 to 5 minutes till a uniform mixture was achieved. The molds were filled with concrete in approximately three equal layers and vibrated for consolidation using a small vibrating table (Plate 3.1). The constituents for the

mortar specimens were mixed in a mortar blender. The molds were filled with mortar in approximately two equal layers and vibrated for consolidation using a small vibrating table. The inhibitors and contaminants were added to the mixes by dissolving them in the mixing water.

### **3.3.2 Curing**

After casting, the specimens were covered with wet burlap for 24 hours. Thereafter, they were cured by covering them with wet burlap and plastic sheets for two weeks. The burlaps were wetted twice daily (Plate 3.2). Following the curing period, the specimens were exposed to different exposure conditions.

### **3.3.3 Exposure Conditions**

#### **3.3.3.1 Exposure Solutions**

The specimens contaminated with 0.8% chloride and sea water were partially immersed in 5% sodium chloride solution, while the specimens contaminated with 0.8% chloride plus 1.5%  $\text{SO}_3$  were immersed in 5% sodium chloride plus 3.11% sodium sulfate solution. The specimens contaminated with brackish water and unwashed aggregates were immersed in brackish water. On the other hand, the reinforced concrete specimens coated with the various surface coatings were divided into two groups. The specimens in the first group were placed in a 5%



sodium chloride solution, while the second group of the specimens were placed in a 5% sodium chloride plus 3.11% sodium sulfate solution (Plate 3.3). The chemical analysis of the sea water and brackish water are shown in Tables 3.6 and 3.7, respectively.

#### **3.3.3.2 Heat-Cool Cycling**

To evaluate the performance of coatings under the hot weather conditions, 75 concrete specimens were placed in an oven, maintained at 70 °C for 8 hours (Plate 3.4). The temperature was gradually increased till it reached a maximum temperature of 70 °C (158 °F). It took about 4 hours for the oven to attain this temperature. The oven was maintained at 70 °C for eight hours, and then the temperature was gradually decreased to room temperature ( $23 \pm 3$  °C) for 12 hours to complete one heat-cool cycle. At the end of 30, 60, 120, and 180 cycles, the effectiveness of each coating was evaluated by measuring the water absorption, pulse velocity, and compressive strength of the concrete specimens.

#### **3.3.3.3 Wet-Dry Cycling**

To simulate the effect of the splash zone of a marine environment, the coated and the uncoated concrete specimens were exposed to wet-dry environment. The wet-dry cycles were achieved by wetting the samples for one day in the water tank and drying them in the laboratory environment ( $23 \pm 3$  °C) for two days (Plate 3.5). The

effect of wet-dry cycling on the performance of coated concrete specimens was evaluated after 10, 20, 40, and 60 cycles by measuring the water absorption, pulse velocity, and compressive strength of concrete specimens.

#### **3.3.3.4 Carbonation**

The experimental set-up used in the carbonation studies is shown in Plate 3.6. To ensure uniform distribution, the carbon dioxide (CO<sub>2</sub>) gas was passed through 3 inch (75 mm) deep water and the concrete specimens were kept 1 inch (25 mm) above the water level in a special chamber. The concentration of the carbon dioxide was maintained at 3%.

### **3.4 TEST METHODS**

#### **3.4.1 Compressive Strength**

The compressive strength of 75 mm Ø and 150 mm high cylinders was determined according to ASTM C 39, using a hydraulically-operated digital compression machine of  $\pm 0.1$  kN accuracy. Three cylinders, of similar exposure period and test conditions, were tested and the average values were reported throughout this research program.

### **3.4.2 Pulse Velocity**

The pulse-velocity of the concrete specimens was determined according to ASTM C 597 using Pulse Velocity Ultrasonic Non-destructive Indicating Tester (PUNDIT) equipment, as shown in Plate 3.7. In this technique, a transducer is affixed on one face of the specimen which propagates ultrasonic pulses through the concrete to be received by a second transducer affixed on the opposite face of the specimen. The time taken by the ultrasonic wave to travel the measured path of concrete is indicated on a digital display. The path length divided by this time gives the pulse velocity, which measures the general quality and the relative denseness of concrete. Transducers of 82 kHz frequency were used for measuring the pulse velocity. Lubricating grease was applied to the junction of the sample and the transducers to ensure good coupling of the transducers with the concrete surface.

### **3.4.3 Absorption**

In order to quantify the damage to coatings due to thermal and moisture variations, the absorption of concrete specimens was determined as per ASTM C 642. The specimens were placed in water for 48 hours and then weighed in saturated surface dry condition ( $w_I$ ). The samples were thereafter placed in an oven at 110 °C for 24

hours and allowed to cool down for 24 hours and re-weighed ( $w_2$ ). Absorption (%) was calculated using the following relationship:

$$Absorption(\%) = \frac{w_1 - w_2}{w_2} \times 100$$

### 3.4.4 Reinforcement Corrosion

Concrete specimens, 75 mm  $\varnothing$  and 150 mm high, reinforced with a 12 mm diameter steel bar embedded at the center, were used for the corrosion studies (Plate 3.8). They had an effective cover of 25 mm at the bottom. A total of 150 specimens were cast to assess the effectiveness of inhibitors and surface coatings in retarding reinforcement corrosion. Reinforcement corrosion was monitored by measuring the corrosion potentials and corrosion current density at periodic intervals.

#### 3.4.4.1 Corrosion Potentials

The corrosion potentials were measured using a saturated calomel electrode (SCE) and a high impedance voltmeter. These measurements provide qualitative information on the state of passivity of reinforcing steel [63]. According to ASTM C 876 [64], potentials more negative than -270 mV, with respect to SCE, indicate

greater than 95% probability of active reinforcement corrosion. Values less negative than -120 mV, indicate a probability of corrosion below 5%, while those falling between -270 and -120 mV are not easily interpreted, and the probability of corrosion is uncertain.

#### 3.4.4.2 Corrosion Current Density

The corrosion current density was measured using the linear polarization resistance method (LPRM). This is a traditional DC technique for measuring the corrosion rate of reinforcing steel. In this technique, the polarization resistance ( $R_p$ ) is determined by conducting a linear polarization scan in the range of  $\pm 10$  mV of the corrosion potential. The corrosion current density is then calculated using the Stern-Geary formula [65]:

$$I_{\text{corr}} = B/R_p \quad (3.1)$$

where:

$I_{\text{corr}}$  = corrosion current density,  $\mu\text{A}/\text{cm}^2$ ;

$R_p$  = polarization resistance,  $\text{k}\Omega\text{-cm}^2$ ;

$B = (\beta_a \beta_c) / (2.3(\beta_a + \beta_c))$ ; and

$\beta_a$  and  $\beta_c$  are the anodic and cathodic Tafel constants, respectively.

For steel in aqueous media, values of  $\beta_a$  and  $\beta_c$  of 100 mV are normally used. However, in the absence of sufficient data on  $\beta_a$  and  $\beta_c$  for steel in concrete,

values of  $B$  equal to 52 mV for steel in passive condition and equal to 26 mV in active condition are frequently used [63]. Andrade et al. [66] indicated a good correlation between the weight loss determined using gravimetric and electrochemical methods when these values were used. Lambert et al. [67] indicated a good correlation between the corrosion current density determined by the linear polarization resistance method and gravimetric weight loss using these values. Therefore, the above two values of  $\beta$  were consistently used in this investigation.

The experimental set-up used in the determination of corrosion current density is shown in Plate 3.9. A Potentiostat/Galvanostat was used to polarize the steel at a rate of 0.1 mV/sec. The Ohmic drop between the working and reference electrodes was compensated for using a positive feed back technique.

### **3.4.5 Carbonation Depth**

After continual storage in the carbonation chamber for one and three months, the 49x75 mm mortar specimens were retrieved and dry cut at three levels. The levels of cutting were at the middle as well as at 12 mm (0.5 inch) from both the top and bottom of the mortar specimens. The carbonation depth was measured by spraying phenolphthalein on the freshly cut six surface levels. The phenolphthalein

indicator gradually changes from colorless to pink at the broken surfaces with a pH greater than 9.5 for the non-carbonated regions, while the carbonated surface remains colorless. At least 5 readings were taken on each surface and a total number of 30 readings for each mortar specimen were taken to determine the average depth of carbonation.

Table 3.1: Chemical Analysis of the Water-Soluble Species for the Coarse Aggregate

Ions	Concentration, % by Weight of Aggregate
Chloride ( $\text{Cl}^-$ )	0.424
Sulfate ( $\text{SO}_4^{2-}$ )	0.110
Alkalinity as $\text{CaCO}_3$	0.018
Sodium ( $\text{Na}^+$ )	0.112
Calcium ( $\text{Ca}^{2+}$ )	0.072
Magnesium ( $\text{Mg}^{2+}$ )	0.008
Potassium ( $\text{K}^+$ )	0.006
pH	7.87



Table 3.2: Specific Gravity and Absorption of Coarse Aggregate

A	B	C	$G_s = A/(B-C)$	Absorption %= $(B-A)/A \times 100$
1989.2	2046	1239	2.46	2.90

where:

A = weight of oven-dry test sample in air in grams;

B = weight of saturated surface dry test sample in air in grams;

C = weight of saturated test sample in water in grams; and,

$G_s$  = specific gravity of the sample.

Table 3.3: Grading of Coarse Aggregate

Sieve Opening (mm)	Percentage Retained	Cumulative Percentage Retained	Percentage Passing	ASTM C 33 (Number 7 Limits)
19.0	0	0	100	100
12.5	10	10	90	90 to 100
9.5	45	55	45	40 to 70
4.75 (No. 4)	40	95	5	0 to 15
2.36 (No. 8)	5	100	0	0 to 5

Table 3.4: Chemical and Mineralogical Compositions of Cement

Chemical Compound	% by Weight
Silicone dioxide ( $\text{SiO}_2$ )	22.3
Aluminum oxide ( $\text{Al}_2\text{O}_3$ )	3.55
Ferric oxide ( $\text{Fe}_2\text{O}_3$ )	3.63
Magnesium oxide ( $\text{MgO}$ )	2.10
Sulfur trioxide ( $\text{SO}_3$ )	1.93
Calcium oxide ( $\text{CaO}$ )	64.6
Sodium oxide ( $\text{Na}_2\text{O}$ )	0.10
Potassium oxide ( $\text{K}_2\text{O}$ )	0.21
Titanium dioxide ( $\text{TiO}_2$ )	0.29
Loss on ignition	1.22
Insoluble residue	0.59
Mineralogical Composition	
Tricalcium aluminate ( $\text{C}_3\text{A}$ )	3.27
Tetracalcium aluminoferrite ( $\text{C}_4\text{AF}$ )	11.04
Tricalcium silicate ( $\text{C}_3\text{S}$ )	58.97

Table 3.5: Rate of Application of the Concrete Surface Coatings

Coating	Coverage Rate*
Sodium Silicate	0.204 L/m <sup>2</sup>
Siloxane	0.544 L/m <sup>2</sup>
Silicone	0.544 L/m <sup>2</sup>
Acrylic	1.80 kg/m <sup>2</sup>

\*Specified by the manufacturers

Table 3.6: Chemical Analysis of the Sea Water in mg/l (ppm)

Ions	Al-Khobar Beach Sea Water
Chloride ( $\text{Cl}^-$ )	24,408
Sulfate ( $\text{SO}_4^{2-}$ )	4,211
Bicarbonate ( $\text{HCO}_3^-$ )	114
Alkalinity as $\text{CaCO}_3$	128
Sodium ( $\text{Na}^+$ )	14,400
Calcium ( $\text{Ca}^{2+}$ )	642
Magnesium ( $\text{Mg}^{2+}$ )	1570
Potassium ( $\text{K}^+$ )	937
Iron ( $\text{Fe}^{2+}$ )	60
Total Dissolved Solids	46,324
pH	7.6

Table 3.7: Chemical Analysis of the Brackish Water in mg/l (ppm)

Ions	KFUPM Brackish Water
Chloride ( $\text{Cl}^-$ )	893
Sulfate ( $\text{SO}_4^{2-}$ )	630
Alkalinity as $\text{CaCO}_3$	216
Sodium ( $\text{Na}^+$ )	459
Total Dissolved Solids	3,270
Turbidity as NTU	1.5
Total Hardness as $\text{CaCO}_3$	1,155
pH	7.78

Table 3.8: Typical Weights of Concrete Constituents Used in Casting

Constituent	Weight
Cement	15.65 kg
Water	8.75 kg
Coarse Aggregate	51.20 kg
Fine Aggregate	31.50 kg
Superplasticizer	113.5 ml

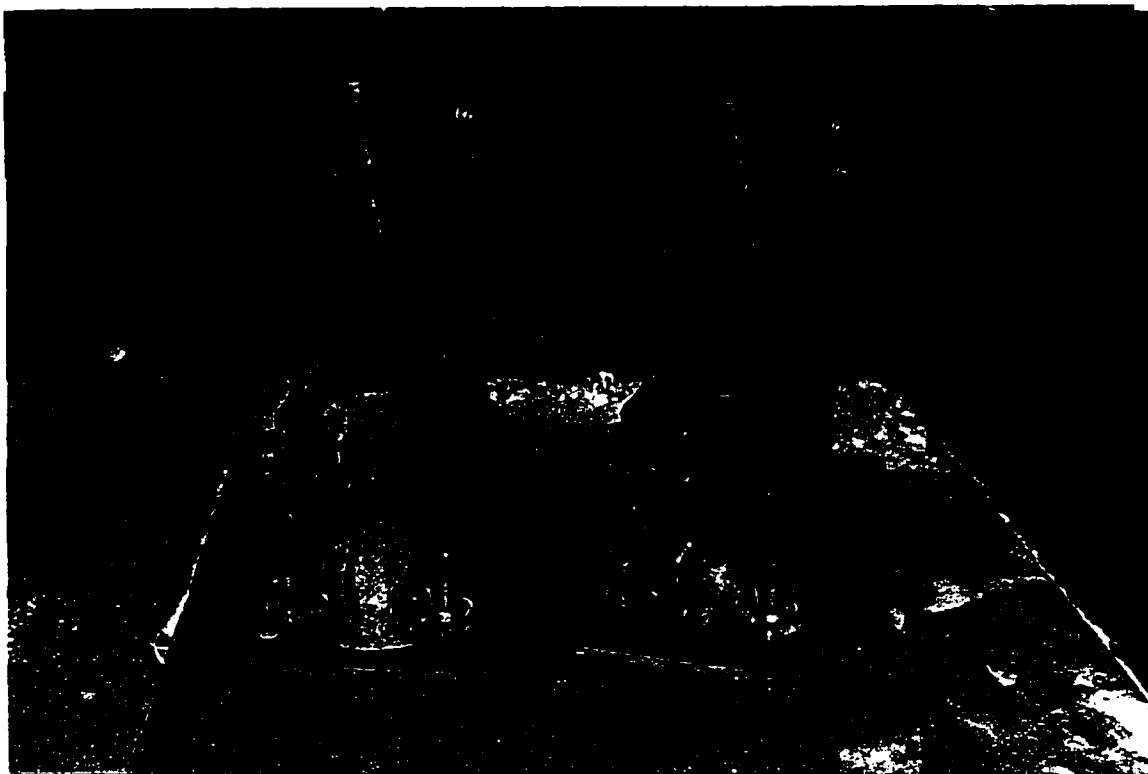


Plate 3.1: Molds Filled with Concrete

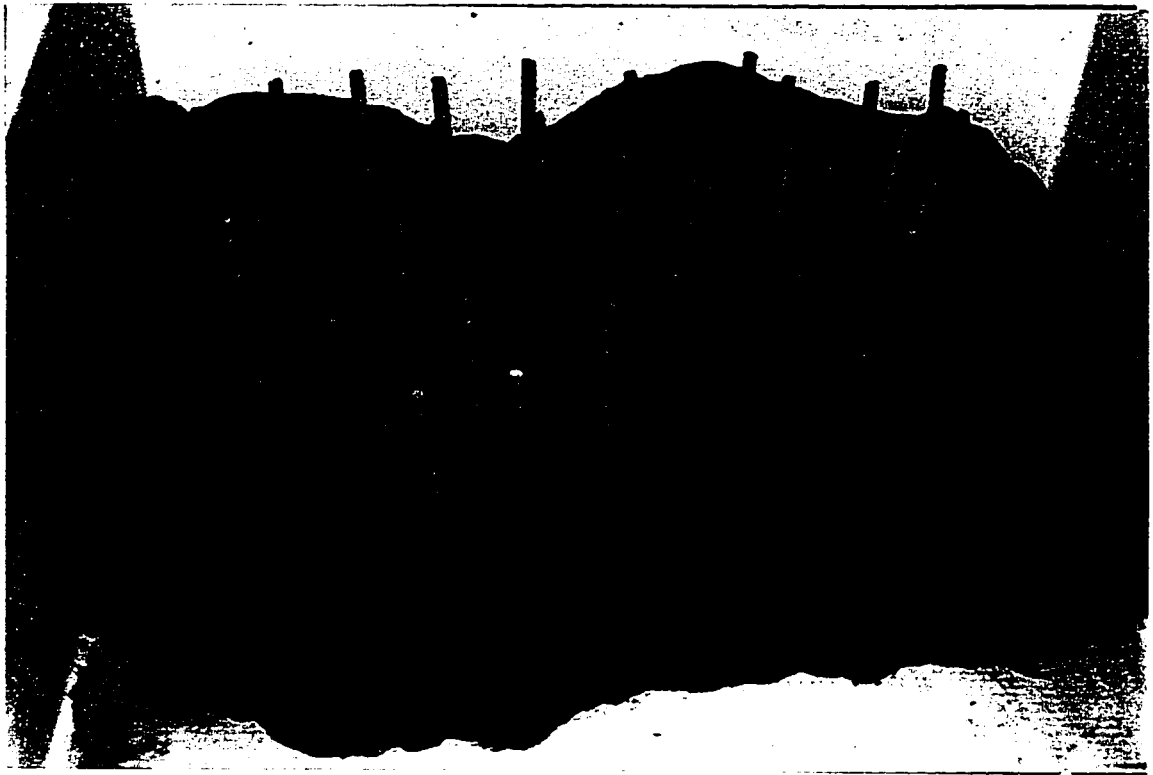


Plate 3.2: Reinforced Concrete Specimens under Wet Burlap Curing



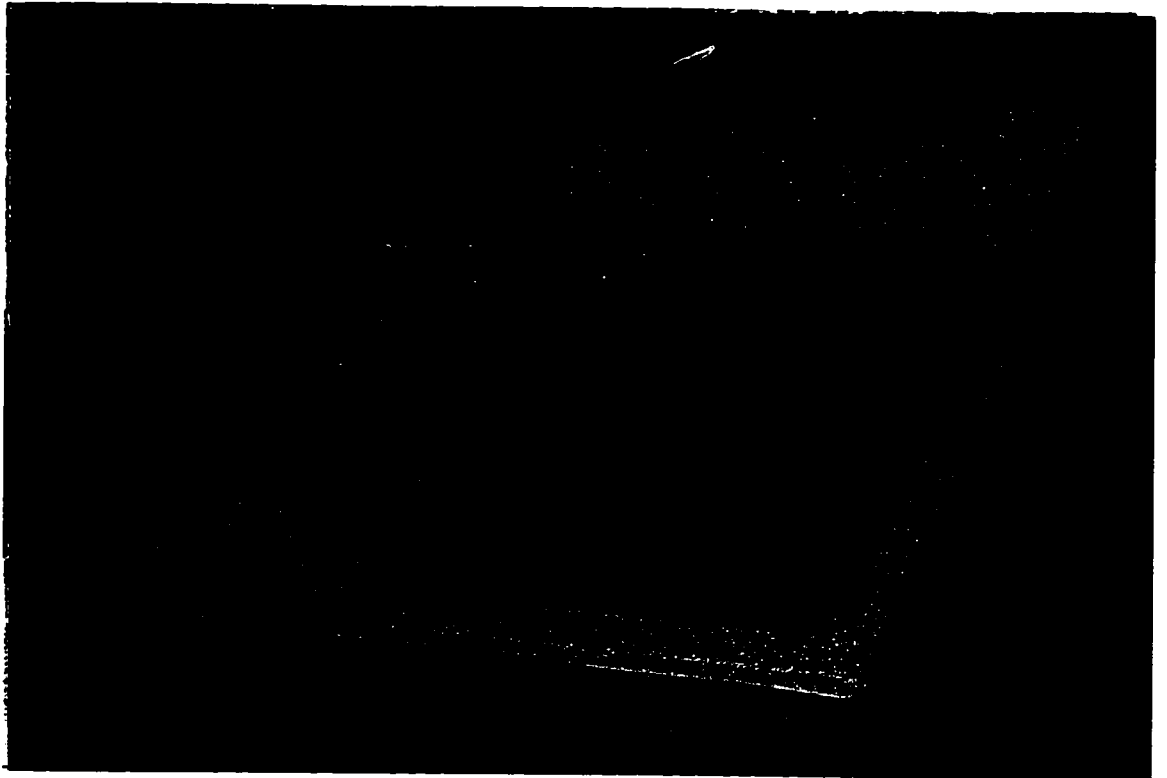


Plate 3.3: Reinforced Concrete Specimens in an Exposure Solution

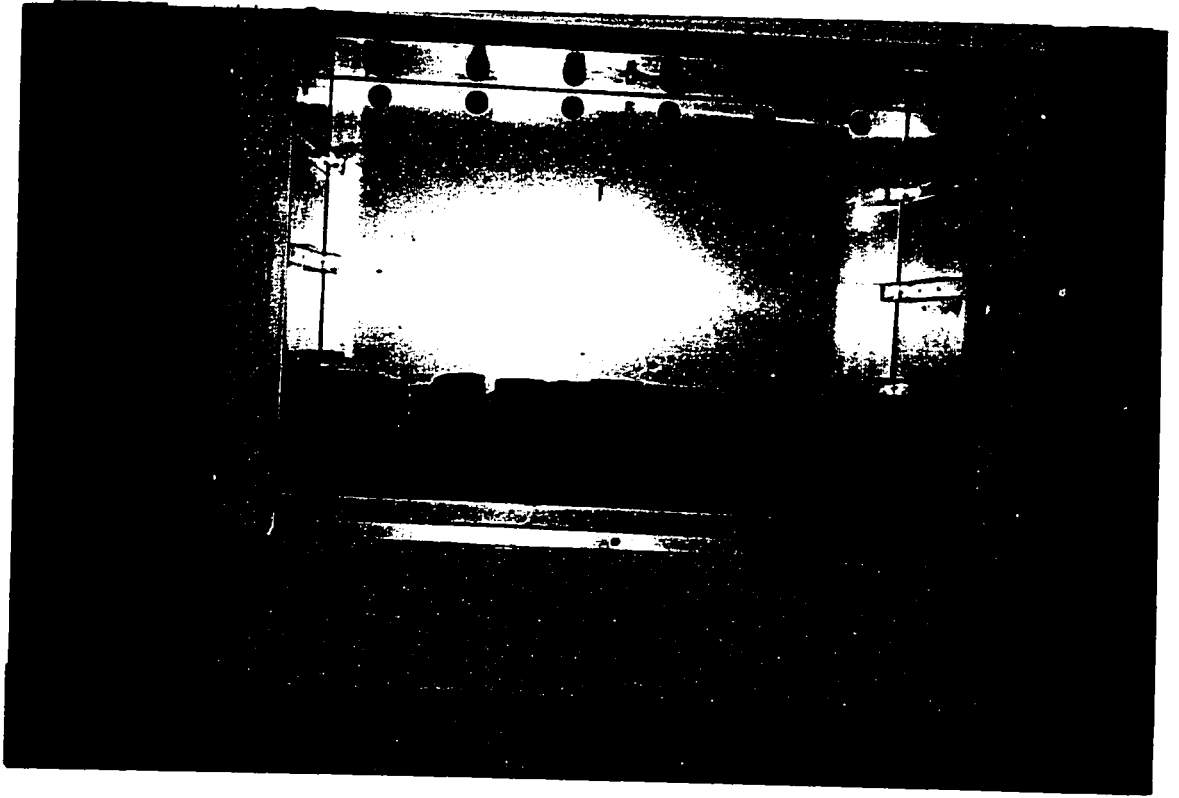


Plate 3.4: Concrete Specimens under Heat-Cool environment



Plate 3.5: Concrete Specimens under Wet-Dry environment

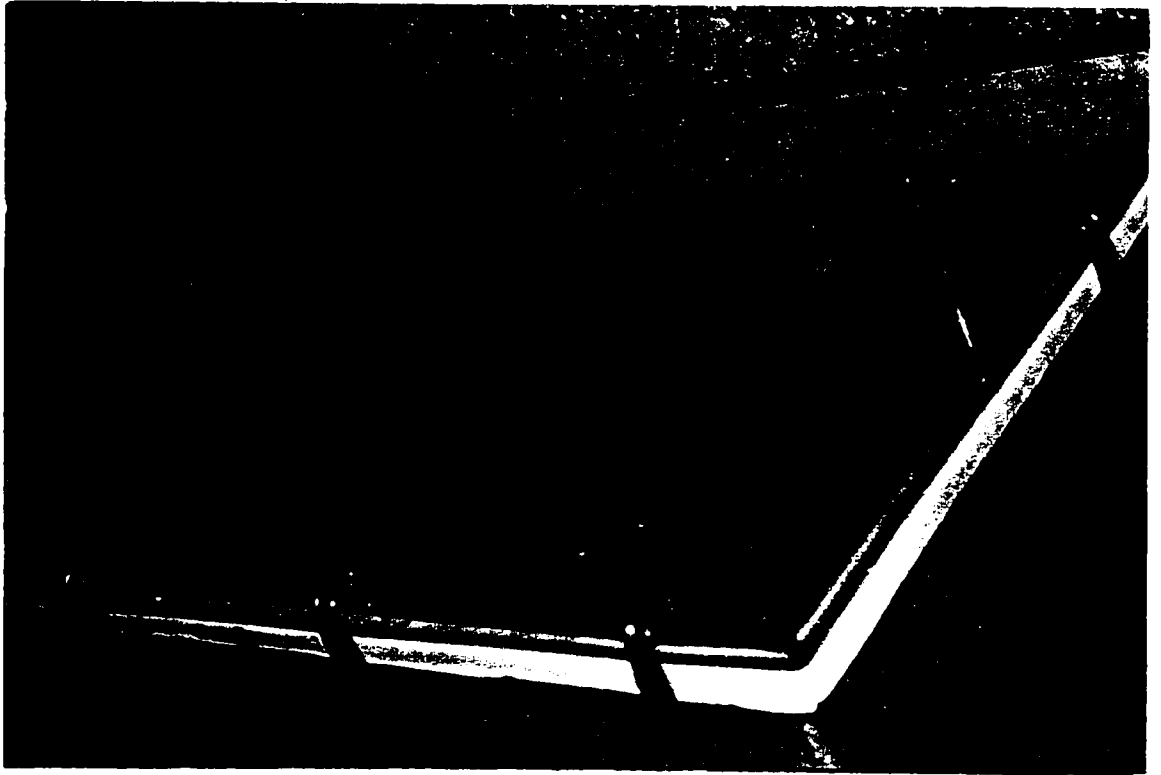


Plate 3.6: Mortar Specimens in the Carbonation Chamber

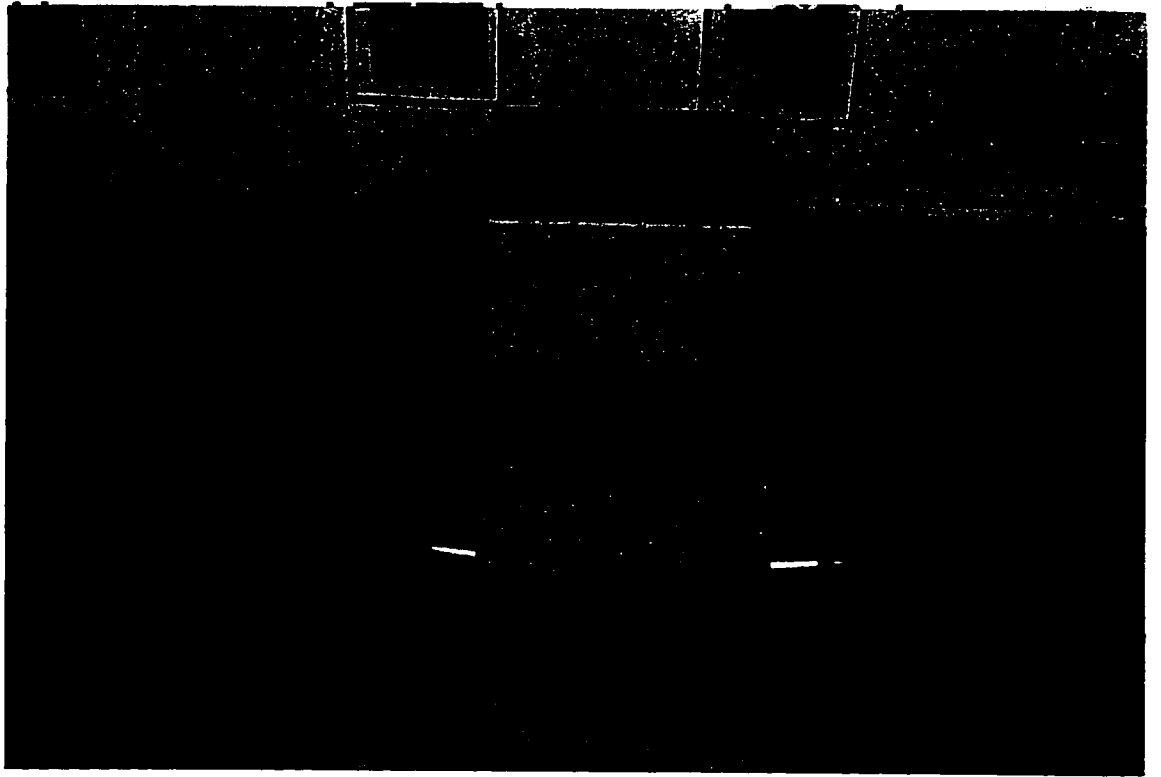


Plate 3.7: Pulse Velocity Apparatus

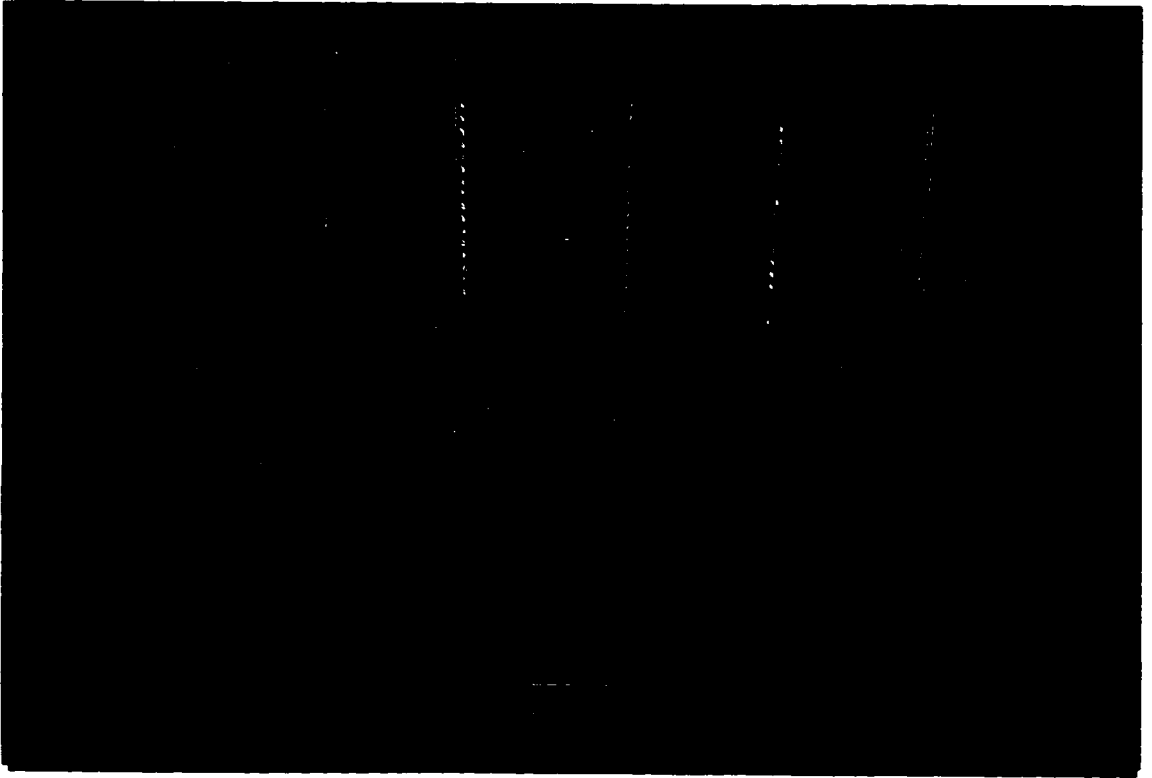


Plate 3.8: Typical Coated and Uncoated Reinforced Concrete Specimens

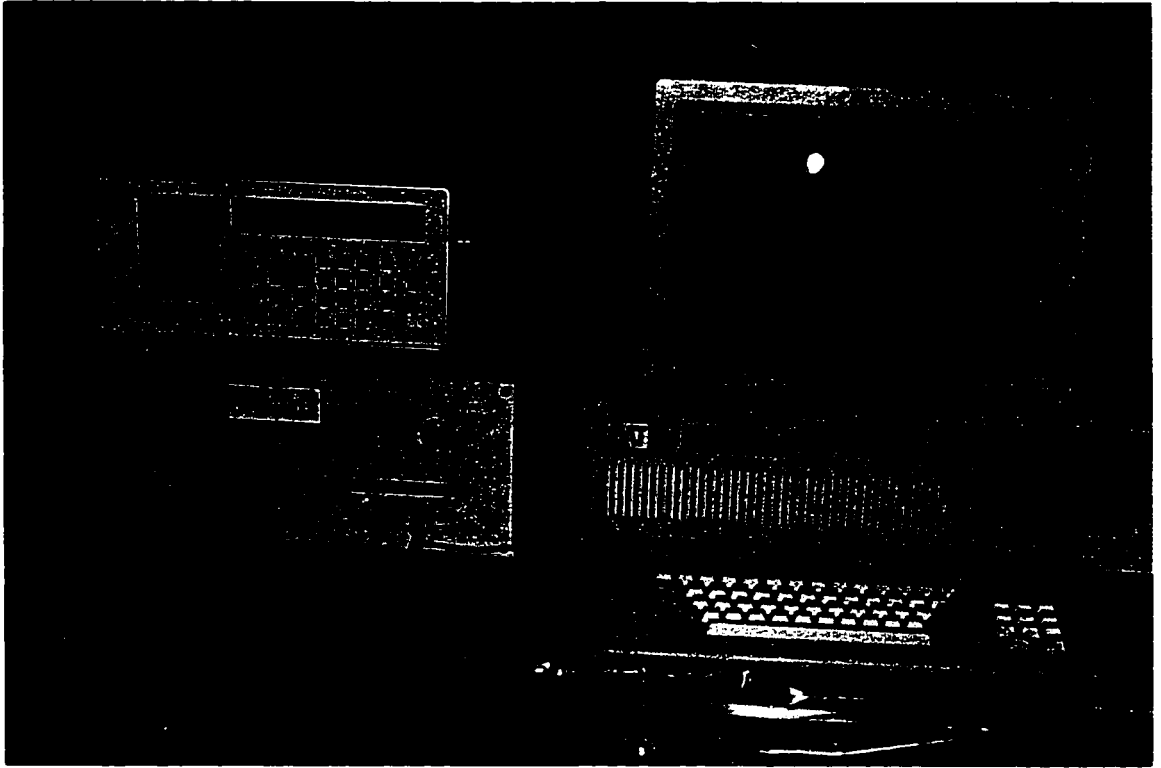


Plate 3.9: Experimental Set-up for Corrosion Current Density Measurement

## **CHAPTER 4**

### **RESULTS AND DISCUSSION**

This Chapter is devoted to present the results obtained in this investigation and their possible interpretation. These results are shown in Figures 4.1 through 4.41 and Tables 4.1 through 4.12. Broadly speaking, the data developed fall in the following categories:

1. Reinforcement corrosion in the reinforced concrete specimens incorporating corrosion inhibitors;
2. carbonation depth in the mortar specimens containing corrosion inhibitors;
3. reinforcement corrosion in the coated and uncoated reinforced concrete specimens; and
4. effect of wet-dry and heat-cool cycling on the performance of coated and uncoated concrete specimens.



## **4.1 EFFECT OF INHIBITORS ON COMPRESSIVE STRENGTH**

Figure 4.1 summarizes the results of the compressive strength of concrete specimens incorporating corrosion inhibitors and that of the control specimens. The compressive strength was determined after 28 days of burlap curing. As could be observed from the figure, the compressive strength of all the specimens incorporating the inhibitors was more than that of the control specimens. The compressive strength of concrete specimens made with 4% calcium nitrite was 10% more than that of the control specimens, while the compressive strength of concrete specimens made with 4% calcium nitrate was 14.5% more. Similarly, the compressive strength of concrete specimens made with CI1 and CI2 inhibitors was 4 and 11%, respectively, more than that of the control specimens. This indicates that all the corrosion inhibitors investigated in this study do not affect the compressive strength of concrete, as is normally reported in the literature, in the concrete made with sodium nitrite and sodium nitrate [21,22].

## **4.2 EFFECT OF INHIBITORS ON REINFORCEMENT CORROSION**

The effect of inhibitors on reinforcement corrosion was evaluated by measuring the corrosion potentials and corrosion current density at regular intervals. The corrosion potentials were monitored using a high impedance voltmeter in

conjunction with a saturated calomel reference electrode, while the corrosion current density was measured using the linear polarization resistance technique. The details of these two test methods have been discussed in Chapter 3.

## **4.2.1 Corrosion Potentials**

### **4.2.1.1 Effect of Calcium Nitrite**

The time-corrosion potential curves for steel in the concrete specimens contaminated with 0.8% chloride and incorporating calcium nitrite are shown in Figure 4.2. The data therein indicate that the corrosion potentials on steel in the concrete specimens without inhibitor were more negative than those dosed with calcium nitrite. Further, the corrosion potentials on steel in the concrete specimens prepared with 2% calcium nitrite were relatively more negative than those in the concrete specimens dosed with 4% calcium nitrite. The corrosion potentials on steel in the concrete specimens made with 2 and 4% calcium nitrite were more negative than the ASTM C 876 threshold value of -270 mV SCE, after 28 days of exposure. In the concrete specimens without inhibitor, the corrosion potentials were more negative than -270 mV SCE right from the initial stages of exposure. The corrosion potentials on steel in the concrete specimens without inhibitor and those made with 2 and 4% calcium nitrite were -691, -583 and -580 mV SCE, respectively, after 166 days of exposure.

Figure 4.3 depicts the time-corrosion potential curves for steel in the concrete specimens contaminated with 0.8% chloride plus 1.5% sulfate and incorporating calcium nitrite. The corrosion potentials on steel in the concrete specimens without inhibitor were more negative than those dosed with calcium nitrite. Moreover, the corrosion potentials on steel in the concrete specimens prepared with 2 and 4% calcium nitrite were more or less similar. The corrosion potentials on steel in the concrete specimens containing 2 and 4% calcium nitrite crossed the ASTM C 876 threshold value of -270 mV SCE, after 35 to 40 days of exposure, respectively. In the specimens with no inhibitor, the potentials were less than -270 mV right from the beginning of the test. The corrosion potentials on steel in the concrete specimens without inhibitor and those made with 2 and 4% calcium nitrite were -673, -481 and -510 mV SCE, respectively, after 166 days of exposure.

The corrosion potential curves for steel in the concrete specimens made with sea water and incorporating calcium nitrite are presented in Figure 4.4. The corrosion potentials on steel in the concrete specimens without inhibitor were more negative than those dosed with calcium nitrite. Further, the corrosion potentials on steel in the specimens prepared with 2 and 4% calcium nitrite were more or less similar and they were more negative than the ASTM C 876 threshold value of -270 mV SCE, after about 35 days of exposure. In the concrete specimens without inhibitor, the corrosion potentials were less than -270 mV SCE from the initial stages. After

166 days of exposure, the corrosion potentials on steel in the concrete specimens without inhibitor and those made with 2 and 4% calcium nitrite were -715, -563 and -572 mV SCE, respectively.

Figure 4.5 shows the time-corrosion potential curves for steel in the concrete specimens made with brackish water (chloride = 893 mg/l and sulfate = 630 mg/l) and incorporating calcium nitrite. The corrosion potentials on steel in the concrete specimens prepared without inhibitor were more negative than those dosed with calcium nitrite. Moreover, the corrosion potentials on steel in the concrete specimens incorporating 4% calcium nitrite were unexpectedly more negative than those incorporating 2% calcium nitrite. The corrosion potentials on steel in the concrete specimens made with 4% calcium nitrite became more negative than the ASTM C 876 threshold value of -270 mV SCE, after 52 days of exposure. In the concrete specimens without inhibitor, the values were less than -270 mV right from the beginning. The corrosion potentials on steel in the specimens incorporating 2% calcium nitrite were more than -270 mV SCE, indicating the passivity of reinforcing steel even after 166 days of exposure. The corrosion potentials on steel in the concrete specimens without any inhibitor and those made with 2 and 4% calcium nitrite were -604, -205 and -340 mV SCE, respectively, after 166 days of exposure.

The time-corrosion potential curves for steel in the concrete specimens made with unwashed aggregate and incorporating calcium nitrite are shown in Figure 4.6. The corrosion potentials on steel in the concrete specimens without inhibitor were more negative than those dosed with calcium nitrite. Further, the corrosion potentials on steel in the concrete specimens dosed with 2 and 4% calcium nitrite were more or less similar. The corrosion potentials on steel in the concrete specimens without inhibitor were more negative than the ASTM C 876 threshold value of -270 mV SCE, after 32 days of exposure, while in the specimens made with 2 and 4% calcium nitrite, the rebars are in a passive state of corrosion because the corrosion potentials were numerically more than -270 mV SCE. The corrosion potentials on steel in the concrete specimens without inhibitor and those made with 2 and 4% calcium nitrite were -606, -227 and -268 mV SCE, respectively, after 166 days of exposure.

#### **4.2.1.2 Effect of Calcium Nitrate**

Figure 4.7 depicts the time-corrosion potential curves for steel in the concrete specimens contaminated with 0.8% chloride and incorporating calcium nitrate. In these specimens, the corrosion potentials on steel in the concrete specimens without inhibitor were more negative than those dosed with calcium nitrate. Further, the corrosion potentials on steel in the specimens prepared with 2, 3 and 4% calcium nitrate were more or less similar. The corrosion potentials on steel in

all the specimens were more negative than the ASTM C 876 threshold value of -270 mV SCE, right from the beginning of the test. The corrosion potentials on steel in the concrete specimens without inhibitor and those dosed with 2, 3 and 4% calcium nitrate were -691, -598, -575 and -580 mV SCE, respectively, after 166 days of exposure.

The time-corrosion potential curves for steel in the concrete specimens contaminated with 0.8% chloride plus 1.5% sulfate and incorporating calcium nitrate are presented in Figure 4.8. The corrosion potentials on steel in the concrete specimens without inhibitor were more negative than those dosed with calcium nitrate. The corrosion potentials on steel in all the concrete specimens were less than the ASTM C 876 threshold value of -270 mV SCE, right from the beginning. The corrosion potentials on steel in the concrete specimens without inhibitor and those made with 2, 3 and 4% calcium nitrate were -673, -523, -564 and -505 mV SCE, respectively, after 166 days of exposure.

Figure 4.9 shows the time-corrosion potential curves for steel in the concrete specimens made with sea water and incorporating calcium nitrate. The corrosion potentials on steel in the concrete specimens without inhibitor were less than those dosed with calcium nitrate. Further, the corrosion potentials on steel in the concrete specimens prepared with 2% calcium nitrate were less than those in the

concrete specimens dosed with 3 and 4% calcium nitrate. The corrosion potentials on steel in all the concrete specimens were less than the ASTM C 876 threshold value of -270 mV SCE, right from the initial stages of exposure. The corrosion potentials on steel in the concrete specimens without inhibitor and those made with 2, 3 and 4% calcium nitrate were -715, -601, -548 and -568 mV SCE, respectively, after 166 days of exposure.

The time-corrosion potential curves for steel in the concrete specimens made with brackish water and dosed with calcium nitrate are shown in Figure 4.10. The corrosion potentials on steel in the concrete specimens without inhibitor were much more negative than those dosed with calcium nitrate. Further, the corrosion potentials on steel in the concrete specimens prepared with 2, 3 and 4% calcium nitrate were more or less similar. The corrosion potentials on steel in the concrete specimens without inhibitor were more negative than the ASTM C 876 threshold value of -270 mV SCE, right from the beginning. The corrosion potentials on steel in the concrete specimens without inhibitor and those made with 2, 3 and 4% calcium nitrate were -604, -260, -228 and -253 mV SCE, respectively, after 166 days of exposure.

Figure 4.11 depicts the time-corrosion potential curves for steel in the concrete specimens made with unwashed aggregate and incorporating calcium nitrate. The

corrosion potentials on steel in the concrete specimens without inhibitor were more negative than those dosed with calcium nitrate. Moreover, the corrosion potentials on steel in the specimens incorporating 4% calcium nitrate were more negative than in the concrete specimens dosed with 2 and 3% calcium nitrate, however, the difference is small. The corrosion potentials on the steel in the concrete specimens without inhibitor were more negative than the ASTM C 876 threshold value of -270 mV SCE, after 32 days. The corrosion potentials on steel in the concrete specimens incorporating 3 and 4% calcium nitrate crossed the -270 mV SCE threshold value after 150 and 134 days, respectively. The steel in the concrete specimens dosed with 2% calcium nitrate is passive even after 166 days of exposure. The corrosion potentials on steel in the concrete specimens without inhibitor and those made with 2, 3 and 4% calcium nitrate were -606, -261, 313 and -361 mV SCE, respectively, after 166 days of exposure.

#### **4.2.1.3 Effect of CI2 and CI1 Inhibitors**

The time-corrosion potential curves for steel in the concrete specimens contaminated with 0.8% chloride and incorporating CI1 and CI2 corrosion inhibitors are shown in Figure 4.12. The corrosion potentials on steel in the concrete specimens without any inhibitor and those made with CI2 were more or less similar and more negative than those made with CI1. It is observed that the corrosion potentials on steel in all the concrete specimens were more negative than



the ASTM C 876 threshold value of -270 mV SCE, right from the beginning. The corrosion potentials on steel in the concrete specimens without inhibitor and those dosed with CI1 and CI2 were -691, -542 and -655 mV SCE, respectively, after 166 days of exposure.

The time-corrosion potential curves for steel in the concrete specimens contaminated with 0.8% chloride plus 1.5% sulfate and incorporating CI1 and CI2 corrosion inhibitors are presented in Figure 4.13. The corrosion potentials on steel in the concrete specimens without inhibitor and those made with CI2 were more negative than those made with CI1. The corrosion potentials on steel in all the concrete specimens were more negative than the ASTM C 876 threshold value of -270 mV SCE, right from the initial stages of exposure. The corrosion potentials on steel in the concrete specimens without inhibitor and those made with CI1 and CI2 were -673, -523 and -614 mV SCE, respectively, after 166 days of exposure.

The time-corrosion potential curves for steel in the concrete specimens made with sea water and incorporating CI1 and CI2 corrosion inhibitors are shown in Figure 4.14. The corrosion potentials on steel in the concrete specimens with no inhibitor and those made with CI2 were relatively more negative than those made with CI1. The corrosion potentials on steel in the concrete specimens incorporating CI2 were less negative than those made without inhibitor. Further, the corrosion potentials

on steel in all the concrete specimens were more negative than the ASTM C 876 threshold value of -270 mV SCE, right from the beginning. The corrosion potentials on steel in the concrete specimens without inhibitor and those made with CI1 and CI2 were -715, -566 and -653 mV SCE, respectively, after 166 days of exposure.

Figure 4.15 shows the time-corrosion potential curves for steel in the concrete specimens made with brackish water and incorporating CI1 and CI2 corrosion inhibitors. The corrosion potentials on steel in the concrete specimens without any inhibitor were more negative than those made with CI1 and CI2. Further, the corrosion potentials on steel in the concrete specimens incorporating CI1 and CI2 were more or less similar and are in a passive corrosion state. On the contrary, the corrosion potentials on steel in the concrete specimens without inhibitor were more negative than the ASTM C 876 threshold value of -270 mV SCE, right from the beginning. The corrosion potentials on steel in the concrete specimens without inhibitor and those made with CI1 and CI2 were -604, -250 and -201 mV SCE, respectively, after 166 days of exposure.

The time-corrosion potential curves for steel in the concrete specimens made with unwashed aggregate and incorporating CI1 and CI2 corrosion inhibitors are depicted in Figure 4.16. The corrosion potentials on steel in the concrete

specimens without inhibitor were much more negative than those dosed with CI1 and CI2. Further, the corrosion potentials on steel in the specimens incorporating CI1 and CI2 were more or less similar and on the verge of crossing the threshold potential. The corrosion potentials on steel in the concrete specimens without inhibitor were more negative than the ASTM C 876 threshold value of -270 mV SCE, after 32 days of exposure. The corrosion potentials on steel in the specimens made with CI1 were less than -270 mV SCE after 152 days. The corrosion potentials on steel in the control concrete specimens and those made with CI1 and CI2 were -606, -267 and -259 mV SCE, respectively, after 166 days of exposure.

#### **4.2.1.4 Summary of the Corrosion Potential Results**

A summary of the time to initiation of reinforcement corrosion in the concrete specimens incorporating corrosion inhibitors and five contaminations is presented in Table 4.1.

These data indicate that the calcium nitrite inhibitor was efficient in delaying the reinforcement corrosion in the concrete specimens contaminated with chloride, chloride plus sulfate and sea water. In the specimens made with brackish water or unwashed aggregate, all the inhibitors were generally effective in delaying reinforcement corrosion within the 170 day duration of this investigation. This indicates that the former three exposure, namely chloride, chloride plus sulfate and

sea water, are relatively more aggressive to reinforcing steel than the latter two, namely brackish water and unwashed aggregate.

The mechanism by which corrosion inhibitors prevent corrosion of reinforcing steel is ascribable to the creation and maintenance of a fortified, flawless and stable passive film around the steel, even in the presence of chloride levels that are much higher than the critical chloride concentrations for corrosion initiation in concrete [19]. When chloride is present at extremely high chloride to nitrite ion ratio and/or chloride to hydroxyl ion ratios the probability of chloride ions reacting with a  $\text{Fe}^{++}$  is increased. The chloride to nitrite ion ratio is typically stated to be between 1 to 1.5 [18].

#### **4.2.2 CORROSION CURRENT DENSITY**

The linear polarization resistance test has been considered as a relatively simple and reliable to assess the corrosion state of rebars in concrete [63]. As was mentioned in the Experimental Program in Chapter 3, this test is used to evaluate the corrosion current density ( $I_{\text{corr}}$ ), the later being related to the corrosion rate in concrete [35]. An  $I_{\text{corr}}$  value less than 0.1 to 0.2  $\mu\text{A}/\text{cm}^2$  indicates negligible corrosion, while values greater than 0.1  $\mu\text{A}/\text{cm}^2$  mean active corrosion. In terms of service life, an  $I_{\text{corr}}$  value more than 1  $\mu\text{A}/\text{cm}^2$  indicates important corrosion,

while an  $I_{\text{corr}}$  value more than  $10 \mu\text{A}/\text{cm}^2$  is a severe corrosion [35]. Therefore, in this investigation, an  $I_{\text{corr}}$  value of  $0.1 \mu\text{A}/\text{cm}^2$  is considered as a threshold criterion for corrosion initiation.

#### **4.2.2.1 Effect of Calcium Nitrite**

The  $I_{\text{corr}}$  on steel in the concrete specimens contaminated with 0.8% chloride and incorporating calcium nitrite as a corrosion inhibitor is plotted against exposure period in Figure 4.17. The data of  $I_{\text{corr}}$  on steel in the concrete specimens with calcium nitrite was much less than those in the concrete specimens without any inhibitor. The  $I_{\text{corr}}$  on steel in the concrete specimens without inhibitor was more than the threshold value of  $0.1 \mu\text{A}/\text{cm}^2$  [68] right from the beginning, whereas the  $I_{\text{corr}}$  on steel in the concrete specimens with 2 and 4% calcium nitrite was much less than the above threshold value. After 122 days of exposure, the  $I_{\text{corr}}$  on steel in the concrete specimens without any inhibitor and those made with 2 and 4% calcium nitrite was 0.52, 0.061 and  $0.057 \mu\text{A}/\text{cm}^2$ , respectively.

Figure 4.18 depicts the  $I_{\text{corr}}$  on steel in the concrete specimens contaminated with 0.8% chloride plus 1.5% sulfate and incorporating calcium nitrite. The  $I_{\text{corr}}$  on steel in the concrete specimens without inhibitor was more than the threshold value of  $0.1 \mu\text{A}/\text{cm}^2$  from the beginning, whereas the  $I_{\text{corr}}$  in the specimens with calcium nitrite was less than the threshold value. The  $I_{\text{corr}}$  on steel in the concrete

specimens without inhibitor and those made with 2 and 4% calcium nitrite was 0.55, 0.095 and 0.062  $\mu\text{A}/\text{cm}^2$ , respectively, after 122 days of exposure.

The  $I_{\text{corr}}$  on steel in the concrete specimens made with sea water and incorporating calcium nitrite is plotted against the period of exposure in Figure 4.19. The  $I_{\text{corr}}$  on steel in the specimens with calcium nitrite was much less than that in the concrete specimens without inhibitor. Moreover, the  $I_{\text{corr}}$  in the specimens made with 2 and 4% calcium nitrite was more or less similar. The  $I_{\text{corr}}$  on steel in the concrete specimens without inhibitor was more than the threshold value of 0.1  $\mu\text{A}/\text{cm}^2$  right from the beginning, whereas these values in the specimens incorporating calcium nitrite were much less than the threshold value. The  $I_{\text{corr}}$  on steel in the concrete specimens without inhibitor and those made with 2 and 4% calcium nitrite was 0.54, 0.044 and 0.051  $\mu\text{A}/\text{cm}^2$ , respectively, after 122 days of exposure.

Figure 4.20 shows the variation of  $I_{\text{corr}}$  on steel in the concrete specimens made with brackish water and incorporating calcium nitrite. The  $I_{\text{corr}}$  on steel in the concrete specimens without inhibitor was much more than that in the specimens made with calcium nitrite. Further, the  $I_{\text{corr}}$  on steel in the concrete specimens made with 2 and 4% calcium nitrite was more or less similar. The  $I_{\text{corr}}$  on steel in the concrete specimens without inhibitor was more than the threshold value of 0.1

$\mu\text{A}/\text{cm}^2$  right from the initial stages, whereas these values in the specimens with calcium nitrite were less than the above threshold value, even after 122 days of exposure. The  $I_{\text{corr}}$  on steel in the concrete specimens without inhibitor and those made with 2 and 4% calcium nitrite was 0.395, 0.061 and 0.033  $\mu\text{A}/\text{cm}^2$ , respectively, after 122 days of exposure.

The  $I_{\text{corr}}$  on steel in the concrete specimens made with unwashed aggregates and incorporating calcium nitrite is plotted against time in Figure 4.21. The  $I_{\text{corr}}$  on steel in the specimens with calcium nitrite was much less than that in the concrete specimens without calcium nitrite. Further, the  $I_{\text{corr}}$  on steel in the concrete specimens made with 2 and 4% calcium nitrite was more or less the same. The  $I_{\text{corr}}$  on steel in the concrete specimens without inhibitor was more than the threshold value of 0.1  $\mu\text{A}/\text{cm}^2$  right from the beginning, whereas these values in the specimens incorporating calcium nitrite was much less than the above threshold value. The  $I_{\text{corr}}$  on steel in the concrete specimens without inhibitor and those made with 2 and 4% calcium nitrite was 0.24, 0.079 and 0.084  $\mu\text{A}/\text{cm}^2$ , respectively, after 122 days of exposure.

#### **4.2.2.2 Effect of Calcium Nitrate**

Figure 4.22 depicts the  $I_{\text{corr}}$  on steel in the concrete specimens contaminated with 0.8% chloride and incorporating 2, 3 and 4% calcium nitrate corrosion inhibitor.

The  $I_{\text{corr}}$  on steel in the concrete specimens without inhibitor was more than the threshold value right from the initial stages, whereas the  $I_{\text{corr}}$  on steel in the concrete specimens incorporating the different dosages of calcium nitrate was less than the above threshold value, even after 122 days of exposure. The  $I_{\text{corr}}$  on steel in the concrete specimens without inhibitor and those made with 2, 3 and 4% calcium nitrate was 0.52, 0.064, 0.087 and 0.061  $\mu\text{A}/\text{cm}^2$ , respectively, after 122 days of exposure.

The  $I_{\text{corr}}$  on steel in the concrete specimens contaminated with 0.8% chloride plus 1.5% sulfate and incorporating calcium nitrate is plotted against time in Figure 4.23. The  $I_{\text{corr}}$  on steel in the concrete specimens with calcium nitrate was less than that in the concrete specimens without inhibitor. Further, the  $I_{\text{corr}}$  on steel in the concrete specimens made with 2, 3 and 4% calcium nitrate was more or less similar. The  $I_{\text{corr}}$  on steel in the concrete specimens without inhibitor was more than the threshold value of 0.1  $\mu\text{A}/\text{cm}^2$  right from the beginning, whereas these values in the specimens with calcium nitrate were less than the above threshold value. After 122 days of exposure, the  $I_{\text{corr}}$  on steel in the concrete specimens without inhibitor and those made with 2, 3 and 4% calcium nitrate was 0.55, 0.072, 0.063 and 0.068  $\mu\text{A}/\text{cm}^2$ , respectively.

Figure 4.24 shows the variation of  $I_{\text{corr}}$  on steel, with time, in the concrete



specimens prepared with sea water and incorporating the various proportions of calcium nitrate. The  $I_{\text{corr}}$  on steel in the specimens dosed with 2, 3 and 4% calcium nitrate was more or less similar. The  $I_{\text{corr}}$  on steel in the concrete specimens without inhibitor was more than the threshold value right from the initial stages, whereas the  $I_{\text{corr}}$  on steel in the concrete specimens made with calcium nitrate was much less than the above threshold value. The  $I_{\text{corr}}$  on steel in the control concrete specimens and those made with 2, 3 and 4% calcium nitrate was 0.54, 0.059, 0.073 and 0.090  $\mu\text{A}/\text{cm}^2$ , respectively, after 122 days of exposure.

The  $I_{\text{corr}}$  on steel in the concrete specimens made with brackish water and incorporating calcium nitrate is plotted against time in Figure 4.25. The  $I_{\text{corr}}$  on steel in the concrete specimens made with calcium nitrate was much less than that in the concrete specimens without inhibitor. Further, the  $I_{\text{corr}}$  on steel in the concrete specimens made with 2, 3 and 4% calcium nitrate was more or less similar. The  $I_{\text{corr}}$  on steel in the concrete specimens without inhibitor was more than the threshold value right from the beginning, whereas the  $I_{\text{corr}}$  on steel in the concrete specimens incorporating calcium nitrate was much less than the above threshold value. The  $I_{\text{corr}}$  on steel in the concrete specimens without inhibitor and those made with 2, 3 and 4% calcium nitrate was 0.39, 0.064, 0.056 and 0.081  $\mu\text{A}/\text{cm}^2$ , respectively, after 122 days of exposure.

Figure 4.26 depicts the  $I_{\text{corr}}$  on steel in the concrete specimens made with unwashed aggregate and incorporating calcium nitrate. The  $I_{\text{corr}}$  on steel in the concrete specimens without inhibitor was more than that in the specimens made with calcium nitrate. However, the  $I_{\text{corr}}$  on steel in the concrete specimens made with various proportions of calcium nitrate was more or less similar. The  $I_{\text{corr}}$  on steel in the concrete specimens without inhibitor crossed the threshold value after 35 days of exposure, whereas the  $I_{\text{corr}}$  on steel in the specimens made with calcium nitrate was less than the above threshold value, even after 122 days of exposure. The  $I_{\text{corr}}$  on steel in the concrete specimens without inhibitor and those made with 2, 3 and 4% calcium nitrate was 0.24, 0.081, 0.074 and 0.087  $\mu\text{A}/\text{cm}^2$ , respectively, after 122 days of exposure.

#### 4.2.2.3 Effect of CI1 and CI2 Inhibitors

The  $I_{\text{corr}}$  on steel in the concrete specimens contaminated with 0.8% chloride and incorporating CI1 and CI2 corrosion inhibitors is plotted against the exposure period in Figure 4.27. The  $I_{\text{corr}}$  on steel in the specimens made with CI1 and CI2 was lower than that in the concrete specimens without any inhibitor. The  $I_{\text{corr}}$  on steel in the concrete specimens without inhibitor was more than the threshold value of 0.1  $\mu\text{A}/\text{cm}^2$  right from the beginning, whereas the  $I_{\text{corr}}$  on steel in the specimens made with CI1 and CI2 was less than the above threshold value. The  $I_{\text{corr}}$  on steel in the concrete specimens without inhibitors and those made with

CI1 and CI2 was 0.52, 0.073 and 0.082  $\mu\text{A}/\text{cm}^2$ , respectively, after 122 days of exposure.

Figure 4.28 shows the  $I_{\text{corr}}$  on steel in the concrete specimens contaminated with 0.8% chloride plus 1.5% sulfate and incorporating CI1 and CI2 corrosion inhibitors. The  $I_{\text{corr}}$  on steel in the concrete specimens without inhibitor was more than that in the specimens made with CI1 and CI2. Further, the  $I_{\text{corr}}$  on steel in the specimens made with CI1 and CI2 was more or less similar. The  $I_{\text{corr}}$  on steel in the concrete specimens without inhibitor was more than the threshold value of 0.1  $\mu\text{A}/\text{cm}^2$  right from the initial stages, whereas the  $I_{\text{corr}}$  on steel in the specimens made with CI1 and CI2 was less than the above threshold value. The  $I_{\text{corr}}$  on steel in the concrete specimens without inhibitor and those incorporating CI1 and CI2 was 0.55, 0.077, and 0.076  $\mu\text{A}/\text{cm}^2$ , respectively, after 122 days of exposure.

The  $I_{\text{corr}}$  on steel in the concrete specimens prepared with sea water and incorporating CI1 and CI2 corrosion inhibitors is plotted against time in Figure 4.29. The  $I_{\text{corr}}$  on steel in the specimens dosed with CI1 and CI2 was lower than that in the concrete specimens without any inhibitor. The  $I_{\text{corr}}$  on steel in the concrete specimens without inhibitor was more than the threshold value of 0.1  $\mu\text{A}/\text{cm}^2$  right from the beginning, whereas these values in the concrete specimens with CI1 were less than the above threshold value, even after 122 days of

exposure. The  $I_{\text{corr}}$  on steel in the concrete specimens without inhibitor and those made with CI1 and CI2 was 0.54, 0.087 and 0.11  $\mu\text{A}/\text{cm}^2$ , respectively, after 122 days of exposure.

Figure 4.30 shows the  $I_{\text{corr}}$  on steel in the concrete specimens made with brackish water and incorporating CI1 and CI2 corrosion inhibitors. The  $I_{\text{corr}}$  on steel in the concrete specimens without inhibitor was more than that in the specimens made with CI1 and CI2. Further, the  $I_{\text{corr}}$  on steel in the specimens made with CI2 was more than that in the specimens incorporating CI1. The  $I_{\text{corr}}$  on steel in the concrete specimens without inhibitor was more than the threshold value of 0.1  $\mu\text{A}/\text{cm}^2$  right from the initial stages, whereas the  $I_{\text{corr}}$  on steel in the concrete specimens made with and CI1 was less than 0.1  $\mu\text{A}/\text{cm}^2$ , even after 122 days of exposure. The  $I_{\text{corr}}$  on steel in the concrete specimens without inhibitor and those made with CI1 and CI2 was 0.39, 0.052, and 0.12  $\mu\text{A}/\text{cm}^2$ , respectively, after 122 days of exposure.

The  $I_{\text{corr}}$  on steel in the concrete specimens made with unwashed aggregate and incorporating CI1 and CI2 corrosion inhibitors is plotted against the exposure period in Figure 4.31. The  $I_{\text{corr}}$  on steel in the specimens made with CI1 and CI2 was less than that in the concrete specimens without any inhibitor. The  $I_{\text{corr}}$  on steel in the concrete specimens made with CI2 was more than that in the concrete

specimens incorporating CI1, after 40 days of exposure. The  $I_{\text{corr}}$  on steel in the concrete specimens without inhibitor and those incorporating CI2 and CI1 crossed the threshold value of  $0.1 \mu\text{A}/\text{cm}^2$  after about 10, 52 and 82 days of exposure, respectively. The  $I_{\text{corr}}$  on steel in the concrete specimens without inhibitor and those made with CI1 and CI2 was 0.24, 0.11 and  $0.14 \mu\text{A}/\text{cm}^2$ , respectively, after 122 days of exposure.

#### **4.2.2.4 Summary of the Corrosion Current Density Results**

A summary of the  $I_{\text{corr}}$  values on steel in the various concrete specimens with and without corrosion inhibitors, after an exposure period of 122 days, is presented in Table 4.2, whereas Table 4.3 shows the time to initiation of reinforcement corrosion as determined from the corrosion current density results. Based on the results presented in Table 4.3, it is vividly clear that the rebars in the control specimens were in an active state of corrosion for all contaminations. On the contrary, the rebars in the specimens incorporating calcium nitrite and calcium nitrate corrosion inhibitors, with all doses were in a passive state of corrosion. Based on the results of the control specimens, the data therein indicate that the aggressivity of the exposure environments is in the following order:

**Unwashed Aggregate < Brackish Water < Chloride < Sea Water < Chloride plus Sulfate**

It is evident from the above two Tables that almost all the reinforcing steel in the concrete specimens incorporating all the inhibitors used in this investigation are in a passive state of corrosion even after an exposure period of 122 days because the  $I_{\text{corr}}$  values are less than the threshold one, whereas the steel in the control concrete specimens is in active state of corrosion, since  $I_{\text{corr}}$  values are more than the threshold value right from the initial stages of exposure. This proves the efficiency of all inhibitors, however, different types of inhibitors exhibit different degrees of protection in terms of: (i) type of inhibitor and its content, and (ii) exposure aggressivity.

The lowest value of  $I_{\text{corr}}$  on steel in the concrete specimens contaminated with 0.8% chloride and incorporating 4% calcium nitrite was  $0.057 \mu\text{A}/\text{cm}^2$ , whereas the  $I_{\text{corr}}$  values in the specimens made with CI1 and CI2 were slightly more than the above value. This indicates that in the chloride-contaminated concrete almost all the inhibitors are suitable, however, the selection of these materials should be based on long-term performance as well as on economic bases.

In the concrete specimens contaminated with 0.8% chloride plus 1.5% sulfate, the lowest values of  $I_{\text{corr}}$  of 0.062 and 0.063 were indicated in the concrete specimens made with 4% calcium nitrite and 3% calcium nitrate, respectively. This indicates that in the chloride plus sulfate environment, 4% calcium nitrite and 3% calcium

nitrate are probably the most suitable.

In the concrete specimens made with sea water, the 2% calcium nitrite was more effective in minimizing reinforcement corrosion as compared to other inhibitors.

In the concrete specimens made with brackish water, all the inhibitors except the CI2 are efficient in minimizing reinforcement corrosion, while in the case of unwashed aggregate both CI1 and CI2 are not suitable.

In Table 4.1, active rebar corrosion was observed in all the inhibitors contaminated with chloride, chloride plus sulfate and sea water, based on measurement of corrosion potentials. However, based on the  $I_{\text{corr}}$  data in Table 4.2, this is not true. This indicates the unsoundness of the ASTM C 876 criterion, and several researchers have indicated the unsuitability of ASTM C 876 criterion, for quantitatively evaluating reinforcement corrosion [63,68,69]. Further, it may not be out of place to mention that, while the corrosion potentials provide a qualitative indication of reinforcement corrosion, quantitative and reliable information can only be obtained by measuring the corrosion current density. In the case when the  $I_{\text{corr}}$  is less than  $0.1 \mu\text{A}/\text{cm}^2$ , the inhibitor either forms a passive layer on the steel surface or inhibits the cathodic reactions. The mechanisms of such inhibition have been discussed in Chapter 2. However, once corrosion is started, inhibitors may also mitigate the rate of reinforcement corrosion by reducing the electrolytic

resistance [43].

Based on the corrosion current density measurements, the preferred corrosion inhibitors for the different exposure environments are outlined in Table 4.4. In order to facilitate the selection of an appropriate inhibitor for a particular environment, the cost analysis of these chemicals is detailed in Table 4.5, based on the current prices of these chemical products in the Saudi market (calcium nitrite = SR 12/litre and calcium nitrate = SR 160/kg). Economically speaking, 2% calcium nitrite and calcium nitrate can also be used for practical purposes, because, as evidenced from the data in Table 4.2, the rebars in the specimens incorporating these two inhibitors were in a passive state even after 122 days of exposure. The calcium nitrate corrosion inhibitor used in this investigation was analar type (i.e. laboratory grade), which is much expensive than the industrial grade. Therefore, for all practical purposes, industrial grade of calcium nitrate is recommended.

### **4.3 EFFECT OF CORROSION INHIBITORS ON CARBONATION**

The results on the depth of carbonation in the mortar specimens, with and without corrosion inhibitors, after 30 and 90 days of exposure to the CO<sub>2</sub> atmosphere is summarized in Tables 4.6 and 4.7, respectively. The various mortar specimens were contaminated with 0.8% chloride, 0.8% chloride plus 1.5% sulfate and sea



water.

The carbonation data presented in Tables 4.6 and 4.7 for the mortar specimens without inhibitor indicate that their depth of carbonation was relatively higher than that in the specimens incorporating corrosion inhibitors. Similar results have been reported by Alonso and Andrade [36]. As expected, these data indicate that the depth of carbonation increased with the exposure period. From the contamination point of view, the depth of carbonation in the mortar specimens with and without inhibitors is generally observed to be in the following manner:

**No Contamination < Chloride < Sea Water < Chloride plus Sulfate**

The data developed through measurement of the carbonation depth measurements indicated greater carbonation in the contaminated specimens than in the uncontaminated specimens. Macmillan and Treadaway [70] indicated that the inclusion of sodium chloride and sodium sulfate increased the depth of carbonation in both the plain and blended cement concrete specimens, though this difference was not consistent in all the specimens investigated. Kobayashi and Uno [71], investigating the effect of cement alkalinity on carbonation, reported that the rate of carbonation increases with the alkali content of cement. Two cements of  $\text{Na}_2\text{O}$  equivalent of 0.57% and 0.31% were used and NaOH was added to the former to

obtain  $\text{Na}_2\text{O}$  equivalent of 0.9, 1.2 and 1.5%. The specimens were exposed to 10%  $\text{CO}_2$  atmosphere and the depth of carbonation was measured up to 16 weeks of exposure. The depth of carbonation, which the authors represented as carbonation ratio, was observed to be strongly influenced by the  $\text{Na}_2\text{O}$  equivalent of the cement. In a later work, the same authors [72], investigated the effect of cement alkalinity on carbonation in concrete specimens, indicated that the depth of carbonation was dependent on the water-cement ratio as well as the alkalinity of the cement. For mixes with similar water-cement ratio, the depth of carbonation was observed to be higher in concrete made with higher  $\text{Na}_2\text{O}$  equivalent.

Bensted [73] indicated that the enhanced carbonation in the cements with a higher alkalinity can be related to the coarser pore structure formed in the presence of alkalis. He observed that the alkalis in concrete accelerate the hydration of portland cement. This results in greater quantities of hydrates, such as C-S-H and ettringite, being formed at earlier stages of the hydration process than under non-accelerated conditions. This results in relatively greater heterogeneities in the microstructure developed during hydration thereby accelerating the susceptibility to carbonation.

The increase in the depth of carbonation in the contaminated mortar specimens may be attributed to the coarsening of the pore structure of the hardened cement

matrix. In a recent study conducted at the King Fahd University of Petroleum and Minerals [74], the total pore volume in the contaminated plain and blended cement paste specimens was found to be more than that in the uncontaminated specimens. The pore volume in the contaminated specimens, contaminated with sodium chloride plus sodium sulfate, was 1.1 to 3.7 times that in the uncontaminated specimens.

The carbonation results indicate that all the mortar specimens prepared with corrosion inhibitors exhibited superior performance compared to those untreated ones. However, the depth carbonation is likely to be dependent upon the type of corrosion inhibitor. The depth of carbonation in the mortar specimens with corrosion inhibitors was generally observed to be in the following manner:

**No Inhibitor > CI2 > CI1 > Calcium Nitrate > Calcium Nitrite**

The reduction in the depth of carbonation in the concrete specimens incorporating inhibitors, particularly sodium nitrite, has been reported by Alonso and Andrade [36] and Andrade et al. [35]. However, the mechanisms of reduced carbonation in the concrete specimens incorporating this type of inhibitor have not been detailed [35,36].

## **4.4 SURFACE COATINGS**

The performance of concrete surface coatings was evaluated through wet-dry and heat-cool cycles by measuring the water absorption, compressive strength and pulse velocity over an exposure period of six months. The effect of coatings on reinforcement corrosion was evaluated by measuring the corrosion potentials and corrosion current density at regular intervals.

### **4.4.1 Effect of Wet-dry Cycling**

The effect of wet-dry cycling on the water absorption in the coated and uncoated concrete specimens is presented in Figure 4.32. The water absorption in the uncoated concrete specimens and those coated with sodium silicate was more than that in the specimens coated with other coatings. Further, the lowest water absorption was observed in the specimens coated with acrylic after the wet-dry cycles. A decrease in the water absorption was observed in the uncoated specimens and those coated with silicone and siloxane, after 10 wet-dry cycles. This reduction in the water absorption capacity can be attributed to the densification of concrete due to the hydration kinetics of cement. However, after 10 wet-dry cycles, there was a steady increase in the water absorption in all the coated and uncoated concrete specimens till the end of the 60 the wet-dry cycles. Compared with their

initial values, the absorption data in Figure 4.32 indicate that there was an increase of 23, 36, 34 and 29% in the water absorption in the concrete specimens coated with sodium silicate, siloxane, silicone and acrylic, respectively, after 60 wet-dry cycles. The water absorption in the specimens coated with sodium silicate was more or less similar to the uncoated specimens. The increase in the water absorption due to wet-dry cycling may be attributed to the micro-cracks created due to moisture variation. After 60 wet dry cycles, the minimum absorption was recorded by the specimens coated with acrylic followed by those coated with siloxane. This indicates the usefulness of these two types of coating compared with the other ones.

The effect of wet-dry cycling on the compressive strength in the coated and uncoated concrete specimens is summarized in Figure 4.33. An initial increase in the compressive strength of all the coated and uncoated concrete specimens was observed till 10 wet-dry cycles. This may be attributed to the initial curing of concrete. After 10 wet-dry cycles, there was a decrease in the compressive strength of the coated and uncoated concrete specimens. This reduction in compressive strength with wet-dry cycling may be attributed to the micro-cracks created by the moisture variation. After 60 wet-dry cycles and compared with the initial compressive strengths of all the coated specimens, there was an increase 31, 30, 21 and 18% in the specimens coated with sodium silicate, siloxane, silicone and

acrylic, respectively, whereas in the uncoated specimens the increase was only 7%.

The effect of wet-dry cycling on the pulse velocity in the coated and uncoated concrete specimens is reported in Figure 4.34. The pulse velocity in the uncoated concrete specimens was less than that in the coated specimens. The highest value of pulse velocity was observed in the concrete specimens coated with acrylic. An increase in the pulse velocity was noted in all the specimens till 10 wet-dry cycles. However, after this period, there was a steady decrease in the pulse velocity in all the specimens. This behavior is similar to that observed previously in the compressive strength (Figure 4.33) and is attributed to the densification of concrete due to the hydration kinetics of cement. The decrease in the pulse velocity in the specimens coated with sodium silicate, siloxane, silicone and acrylic, was 11, 4, 6 and 3%, respectively, after 60 wet-dry cycles, whereas, in the uncoated specimens the decrease was 11%.

#### **4.4.2 Effect of Heat-Cool Cycling**

The effect of heat-cool treatment on the performance of coatings was evaluated by measuring the water absorption, compressive strength and pulse velocity.

The effect of heat-cool cycling on the water absorption in the coated and uncoated concrete specimens is summarized in Figure 4.35. The water absorption in the uncoated specimens and those coated with sodium silicate was more or less similar, however, it is more than that in the specimens coated with the other coatings. Further, minimum water absorption was observed in the specimens coated with acrylic. A steady increase in water absorption was noted in all the coated and uncoated specimens, particularly after 30 heat-cool cycles. The increase in the water absorption in the concrete specimens coated with sodium silicate, siloxane, silicone and acrylic, was 29, 39, 19 and 33%, respectively, after 180 heat-cool cycles. The increase in water absorption due to heat-cool cycling may be attributed to the development of micro-cracks by the temperature variation in the concrete specimens.

The effect of heat-cool cycling on the compressive strength of the coated and uncoated concrete specimens is reported in Figure 4.36. The compressive strength of uncoated concrete specimens was less than that of all the coated specimens. An increase in the compressive strength in all the concrete specimens was observed till 30 heat-cool cycles. This may be attributed to the accelerated initial hydration of cement. After 30 heat-cool cycles, there was a consistent decrease in compressive strength in all the coated and uncoated concrete specimens. This may be attributed to the micro-cracks created due to temperature variation. The increase in the

compressive strength of the concrete specimens coated with sodium silicate, siloxane, silicone and acrylic, was 3, 0, 7 and 1% , respectively, after 180 heat-cool cycles, whereas in the uncoated specimens there was a decrease of 6%.

The effect of heat-cool cycling on the pulse velocity in the coated and uncoated concrete specimens is plotted against heat-cool cycles in Figure 4.37. The pulse velocity in the uncoated concrete specimens was less than that in the coated specimens. The highest pulse velocity was measured in the specimens coated with Acrylic. A steady decrease in the pulse velocity in all uncoated and coated specimens was observed with the heat-cool cycles. The decrease in the pulse velocity in the specimens coated with sodium silicate, siloxane, silicone and acrylic was 16, 11, 10 and 9%, respectively, after 180 heat-cool cycles, whereas, in the uncoated specimens the decrease was 15%.

#### **4.4.3 Summary on the Performance of Surface Coatings**

The effect of heat-cool and wet-dry cycling on the water absorption, compressive strength and pulse velocity in the uncoated and coated concrete specimens were evaluated over a period of six months. According to the data developed in this study, heat-cool treatment brought about a more severe deterioration in concrete than wet-dry exposure. This trend was observed in both the coated and uncoated



concrete specimens. At the end of 60 wet-dry cycles, the water absorption values in the uncoated concrete specimens and those coated with sodium silicate, siloxane, silicone and acrylic were 5.70, 5.80, 2.85, 3.78 and 1.70%, respectively, while at the end of 180 heat-cool cycles, these values were 5.80, 6.10, 2.93, 3.80 and 1.75% , respectively. At the end of 60 wet-dry cycles, the compressive strength values in the uncoated concrete specimens and those coated with sodium silicate, siloxane, silicone and acrylic were 18.6, 23.2, 22.6, 21.7 and 20.6 MPa. respectively, while at the end of 180 heat-cool cycles, these values were 16.3, 18.2, 17.4, 18.5, and 17.6 MPa, respectively. Similarly, the pulse velocity values at the end of 60 wet-dry cycles, in the uncoated concrete specimens and those coated with sodium silicate, siloxane, silicone and acrylic were 3.56, 3.81, 4.30, 4.13 and 4.44 km/sec, respectively, while at the end of 180 heat-cool cycles, these values were 3.41, 3.61, 4.05, 3.95 and 4.19 km/sec, respectively.

Among all the surface treatment systems used in this study, the siloxane, which is siloxane-based, and acrylic, which is a two-component cement-based acrylic-modified water proofing coating, were the most effective against concrete deterioration. This is evidenced by the summarized results delineated in Tables 4.8 through 4.10.

108

The improved performance of above two surface treatment systems may be attributed to the fact that these systems tend to eliminate the stresses and strains created by the continuous heat-cool and wet-dry cycles. However, the other two surface treatment systems, namely sodium silicate and silicone, which are based on sodium silicate and silicone resin, respectively, were relatively ineffective in retarding concrete deterioration due to thermal and moisture variations. The probable explanation for the early deterioration of concrete specimens coated with these two systems could be attributed to one or more of the following factors:

1. Insufficient penetration of the coating into the concrete matrix;
2. high solubility in water; and
3. inability to react with concrete.

Furthermore, silicone resin materials are much higher in molecular weight than silanes and siloxanes and normally these materials are not reactive and dry by solvent evaporation to leave a surface film of resin [54]. Therefore, it is not advisable to use sodium silicate and silicone resin solution to protect concrete in environments characterized by a large number of cycles of heat-cool and wet-dry.

#### **4.4.4 Effect of Coatings on Reinforcement Corrosion**

##### **4.4.4.1 Corrosion Potentials**

The time-corrosion potential curves for steel in the coated and uncoated concrete specimens exposed to the 5% NaCl solution are presented in Figure 4.38. The corrosion potentials on steel in the specimens coated with siloxane and acrylic were less than those in the uncoated specimens and those coated with other coatings. Further, the corrosion potentials on steel in the uncoated concrete specimens and those coated with sodium silicate and silicone were more or less similar. The corrosion potentials on steel in the uncoated concrete specimens and those coated with sodium silicate and silicone were more or less similar, however, they were more negative than the ASTM C 876 threshold value of -270 mV SCE, after about 20 days of exposure. On the contrary, the steel in the concrete specimens coated with siloxane and acrylic was in a passive state of corrosion even after 165 days of exposure. The corrosion potentials on steel in the uncoated concrete specimens and those coated with sodium silicate, siloxane, silicone and acrylic were -676, -623, -254, -619 and -258 mV SCE, respectively, after 165 days of exposure.

Figure 4.39 reports the time-corrosion potential curves for steel in the coated and uncoated concrete specimens exposed to the 5% sodium chloride plus 3% sodium sulfate solution. Again, the corrosion potentials on steel in the specimens coated

with siloxane and acrylic were less negative than those in the uncoated specimens and those coated with other coatings. Moreover, the corrosion potentials on steel in the uncoated concrete specimens and those coated with sodium silicate were more or less similar and crossed the ASTM C 876 threshold value of -270 mV SCE, after 20 days of exposure. The corrosion potentials on steel in the uncoated concrete specimens and those coated with Sodium silicate, siloxane, silicone and acrylic were -685, -631, -253, -514 and -304 mV SCE, respectively, after 165 days of exposure.

Table 4.11 summarizes the time to initiation of reinforcement corrosion in the coated and uncoated concrete specimens. The corrosion potentials in the uncoated concrete specimens exposed to the 5% sodium chloride and 5% sodium chloride plus 3% sodium sulfate solutions was more negative than the ASTM C 876 threshold value of -270 mV SCE right from the initial stages of exposure. The corrosion potentials in the concrete specimens coated with siloxane and acrylic and exposed to both solutions were less negative than the threshold value, even after 165 days of exposure. This indicates the excellent performance of siloxane and acrylic as compared with the other coatings studied in this research program, in delaying the initiation of reinforcement corrosion.

#### 4.4.4.2 Corrosion Current Density

The  $I_{\text{corr}}$  on steel in the uncoated and coated concrete specimens and exposed to the 5% NaCl solution, is plotted against the exposure period in Figure 4.40. The  $I_{\text{corr}}$  values on steel in the uncoated concrete specimens were more than those in the coated specimens. Further, the lowest  $I_{\text{corr}}$  value was measured in the concrete specimens coated with acrylic. The  $I_{\text{corr}}$  on steel in the uncoated concrete specimens and those coated with Silicone was more than the threshold value of  $0.1 \mu\text{A}/\text{cm}^2$  after 70 and 118 days of exposure, respectively. The  $I_{\text{corr}}$  values on steel in the concrete specimens prepared with the other coatings were less than the threshold value. The  $I_{\text{corr}}$  values on steel in the uncoated specimens and those coated with sodium silicate, siloxane, silicone and acrylic were 0.17, 0.061, 0.042, 0.11 and  $0.035 \mu\text{A}/\text{cm}^2$ , respectively, after 125 days of exposure.

Figure 4.41 reports the variation of  $I_{\text{corr}}$  results on steel in the uncoated and coated concrete specimens exposed to the 5% sodium chloride plus 3% sodium sulfate solution. The  $I_{\text{corr}}$  values on steel in the uncoated concrete specimens were more than those in the coated specimens. Moreover, the lowest  $I_{\text{corr}}$  value was observed in the specimens coated with acrylic. The  $I_{\text{corr}}$  value on steel in the uncoated concrete specimens was more than the threshold value of  $0.1 \mu\text{A}/\text{cm}^2$ , from the initial stages, whereas the  $I_{\text{corr}}$  on steel in the coated specimens was much less than the above threshold value except for the specimens coated with sodium silicate and

silicone in which the  $I_{\text{corr}}$  exceeded the above threshold value after 71 and 81 days of exposure, respectively. The  $I_{\text{corr}}$  values on steel in the uncoated specimens and those coated with sodium silicate, siloxane, silicone and acrylic were 0.47, 0.14, 0.062, 0.19 and 0.026  $\mu\text{A}/\text{cm}^2$ , respectively, after 125 days of exposure.

Table 4.12 summarizes the  $I_{\text{corr}}$  on steel in the coated and uncoated concrete specimens, after an exposure period of 125 days. The  $I_{\text{corr}}$  values in the concrete specimens coated with acrylic and siloxane were less than those in the specimens coated with the other two coatings. Based on the results presented above and within the limitation of exposure period, the acrylic and siloxane are most effective in retarding concrete deterioration in both the pure chloride and the chloride-sulfate environments.

This best performance of acrylic and siloxane coats is not only evidenced by the corrosion results (Tables 4.11 and 4.12), but also it is corroborated by the data developed through the water absorption test whereby these two types of coating recorded the lowest initial and final absorption values (Table 4.8). These low absorption values mean that the diffusion of chloride ions through concretes coated with acrylic and siloxane will also be minimal. This clue vividly indicates that the rating of corrosion resisting performance of coatings can probably be based on the simple absorption test.

Table 4.1: Summary of the Time to Initiation of Reinforcement Corrosion in Concrete  
Specimens incorporating Corrosion Inhibitors

Contamination	Time to Initiation of Reinforcement Corrosion, Days							
	Control	Calcium Nitrite		Calcium Nitrate			CII	CI2
		2%	4%	2%	3%	4%		
Chloride	*	28	28	*	*	*	*	*
Chloride + Sulfate	*	34	38	*	*	*	*	*
Sea water	*	30	35	*	*	*	*	*
Brackish water	*	**	**	**	**	**	**	**
Unwashed Aggr.	*	**	**	**	**	**	**	**

\* Potentials were more negative than -270 mV SCE before exposure.

\*\* Potentials were less negative than -270 mV SCE, even after 165 days of exposure.

Table 4.2: Summary of the Corrosion Current Density on Steel in Concrete Specimens incorporating Corrosion Inhibitors after 122 Days of Exposure

Contamination	Corrosion Current Density, $\mu\text{A}/\text{cm}^2$							
	Control	Calcium Nitrite		Calcium Nitrate			CI1	CI2
		2%	4%	2%	3%	4%		
Chloride	0.52	0.060	0.057	0.064	0.061	0.060	0.073	0.082
Chloride + Sulfate	0.55	0.095	0.062	0.072	0.063	0.068	0.077	0.076
Sea Water	0.54	0.044	0.042	0.059	0.061	0.060	0.087	0.11
Brackish Water	0.39	0.033	0.033	0.064	0.056	0.047	0.052	0.12
Unwashed Aggr.	0.24	0.075	0.064	0.062	0.059	0.057	0.110	0.14



Table 4.3: Summary of the Time to Initiation of Reinforcement Corrosion as Determined from the Corrosion Current Density Results in Concrete Specimens incorporating Corrosion Inhibitors

Contamination	Time to Initiation of Reinforcement Corrosion, Days						
	Control	Calcium Nitrite		Calcium Nitrate			CI2
		2%	4%	2%	3%	4%	
Chloride	*	**	**	**	**	**	**
Chloride + Sulfate	*	**	**	**	**	**	**
Sea water	*	**	**	**	**	**	122
Brackish water	*	**	**	**	**	**	35
Unwashed Aggr.	*	**	**	**	**	**	50

\*  $I_{corr}$  on steel was more than the threshold value before exposure.

\*\*  $I_{corr}$  on steel was less than the threshold value, even after 122 days of exposure.

Table 4.4: Preferred Corrosion Inhibitors for Different Environments

<b>Environment</b>	<b>Preferred Inhibitors</b>
Chloride	4% calcium nitrite or 4% calcium nitrate
Chloride and Sulfate	4% calcium nitrite or 3% calcium nitrate
Sea Water	4% calcium nitrite
Brackish Water	2% calcium nitrite
Unwashed Aggregate	4% calcium nitrate

Table 4.5: Cost Analysis of the Preferred Dosages of Corrosion Inhibitors

Environment	Preferred Dosage of Inhibitor		Cost per m <sup>3</sup> of Concrete, SR	
	Calcium Nitrite, %	Calcium Nitrate, %	Calcium Nitrite	Calcium Nitrate
Chloride	4	4	444	320
Chloride + Sulfate	4	3	444	240
Sea Water	4	-	444	-
Brackish Water	2	-	222	-
Unwashed Aggr.	-	4	-	320

Table 4.6: Summary of the Depth of Carbonation for Various Mortar Specimens  
after One Month of Exposure

Contamination	Depth of Carbonation, mm							
	Control	Calcium Nitrite		Calcium Nitrate			CI1	CI2
		2%	4%	2%	3%	4%		
None	0	*	*	*	*	*	*	*
Chloride	2.00	1.00	0	1.15	0	0	0.60	1.00
Chloride + Sulfate	3.00	1.80	1.20	2.30	1.90	1.20	1.75	2.20
Sea Water	2.45	1.15	0	1.2	0.20	0	1.30	0

\* Not used

Table 4.7: Summary of the Depth of Carbonation for Various Mortar Specimens  
after Three Months of Exposure

Contamination	Depth of Carbonation, mm							
	Control	Calcium Nitrite		Calcium Nitrate			CI1	CI2
		2%	4%	2%	3%	4%		
None	1.00	*	*	*	*	*	*	*
Chloride	3.25	2.10	0	2.20	0.30	0	1.40	1.30
Chloride + Sulfate	5.00	2.40	2.10	3.00	2.00	1.30	3.40	2.70
Sea Water	3.65	2.35	0.20	2.25	0.35	0.20	2.10	0.70

\* Not used

Table 4.8: Summary of the Initial and Final Water Absorption in the Coated and Uncoated Concrete Specimens

Exposure Environment	Water Absorption, %									
	Control		Sodium S.		Siloxane		Silicone		Acrylic	
	Initial	Final*	Initial	Final*	Initial	Final*	Initial	Final*	Initial	Final*
Wet-Dry	5.10	5.70	4.72	5.80	2.10	2.85	3.20	3.78	1.32	1.70
Heat-Cool	5.10	5.80	4.72	6.10	2.10	2.93	3.20	3.80	1.32	1.75

\* At the end of six month exposure period

Table 4.9: Summary of the Initial and Final Compressive Strength in the Coated and Uncoated Concrete Specimens

Exposure Environment	Compressive Strength, MPa									
	Control		Sodium S.		Siloxane		Silicone		Acrylic	
	Initial	Final*	Initial	Final*	Initial	Final*	Initial	Final*	Initial	Final*
Wet-Dry	17.37	18.6	17.75	23.2	17.40	22.60	18.00	21.70	17.45	20.60
Heat-Cool	17.37	16.3	17.75	18.20	17.40	17.40	18.00	18.50	17.45	17.60

\* At the end of six month exposure period

Table 4.10: Summary of the Initial and Final Pulse Velocity in the Coated and Uncoated Concrete Specimens

Exposure Environment	Pulse Velocity, km/sec									
	Control		Sodium S.		Siloxane		Silicone		Acrylic	
	Initial	Final*	Initial	Final*	Initial	Final*	Initial	Final*	Initial	Final*
Wet-Dry	4.00	3.56	4.30	3.81	4.50	4.30	4.40	4.13	4.60	4.44
Heat-Cool	4.00	3.41	4.30	3.61	4.50	4.05	4.40	4.10	4.60	4.19

\* At the end of six month exposure period



Table 4.1.1: Summary of the Time to Initiation of Reinforcement Corrosion in the Coated and Uncoated Concrete Specimens

Exposure Environment	Time to Initiation of Reinforcement Corrosion, Days				
	Control	Sodium Silicate	Siloxane	Silicone	Acrylic
5% NaCl	18	18	**	46	**
5%NaCl + 3% Na <sub>2</sub> SO <sub>4</sub>	18	18	**	32	**

\*\* Potentials were less negative than -270 mV SCE, even after 165 days exposure

Table 4.12: Summary of the Corrosion Current Density in Coated and Uncoated Concrete Specimens, after 122 Days of Exposure

Exposure Environment	Corrosion Current Density, $\mu\text{A}/\text{cm}^2$				
	Control	Sodium Silicate	Siloxane	Silicone	Acrylic
5% NaCl	0.17	0.060	0.042	0.11	0.025
5%NaCl + 3% $\text{Na}_2\text{SO}_4$	0.47	0.14	0.062	0.19	0.026

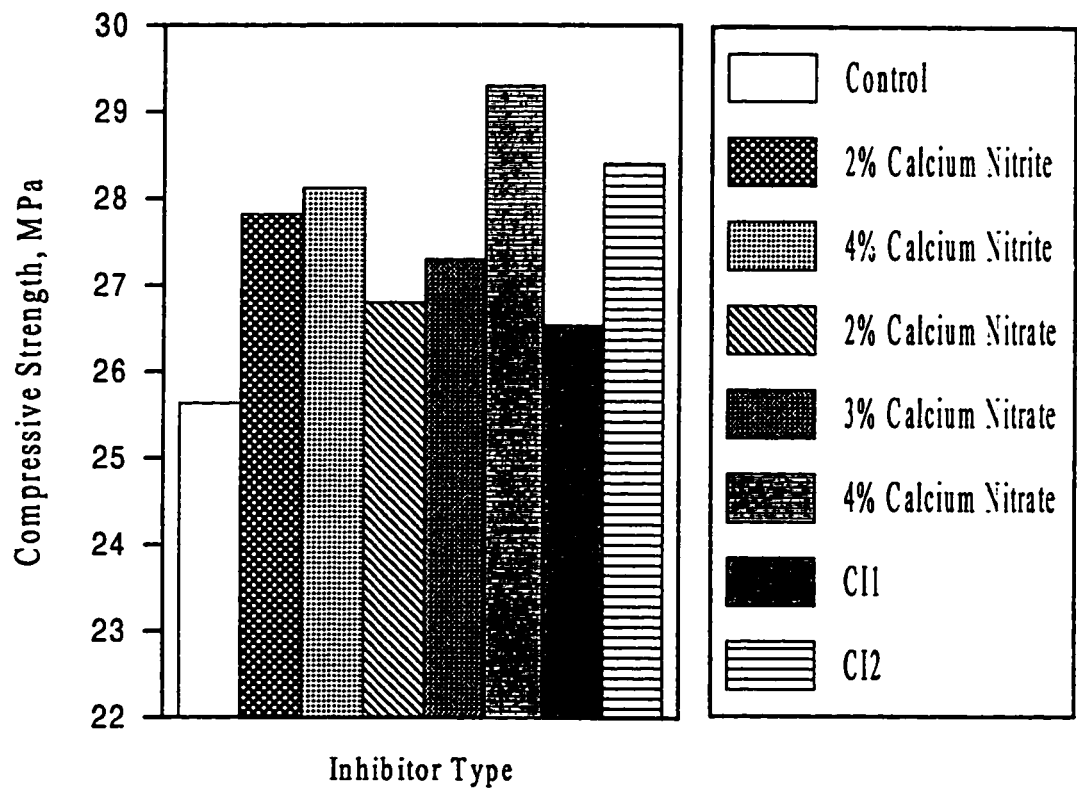


Figure 4.1: Compressive Strength of Concrete Specimens Incorporating Corrosion Inhibitors (after 28 Days of Curing)

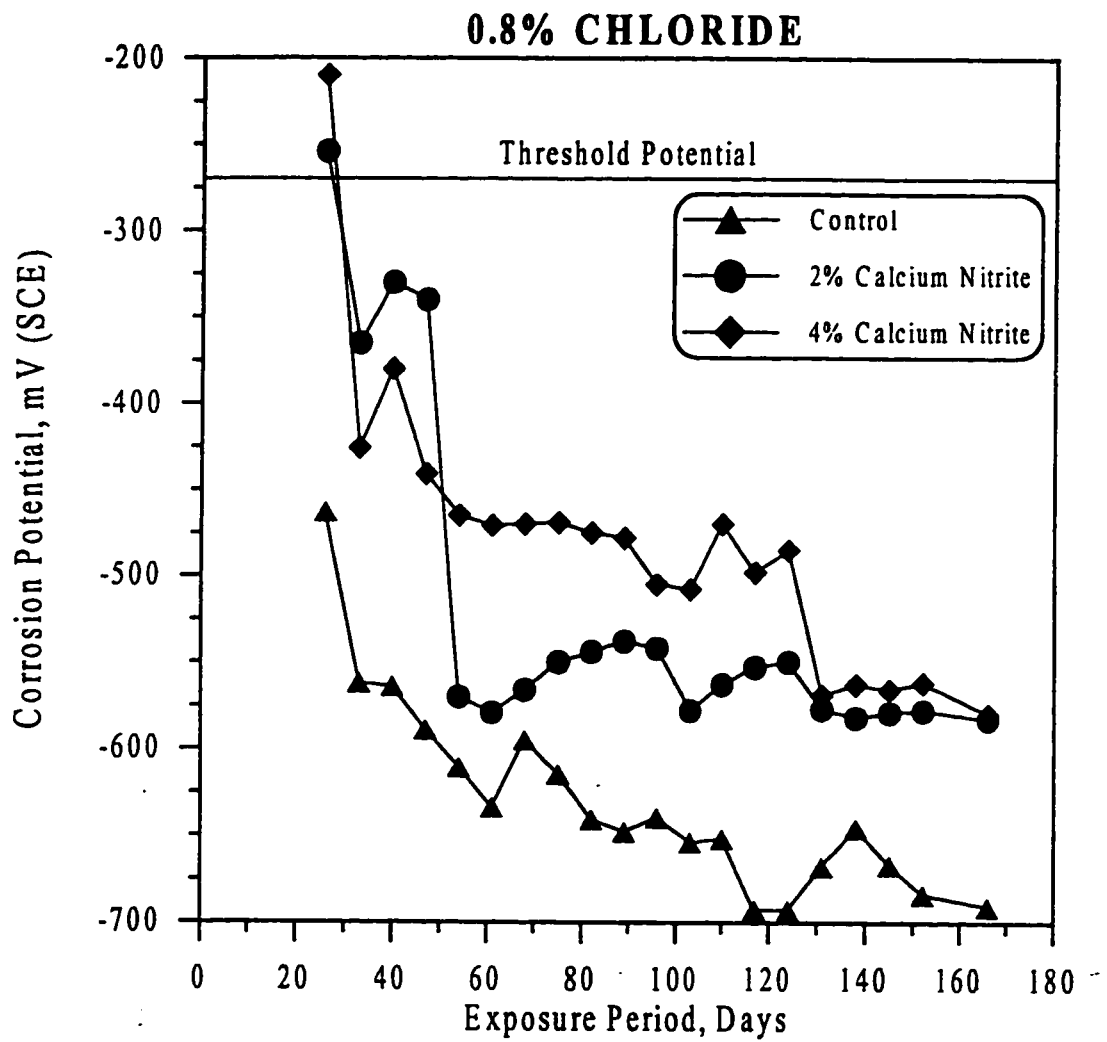


Figure 4.2: Corrosion Potentials on Steel in the Concrete Specimens Contaminated with 0.8% Chloride and Incorporating Calcium Nitrite.

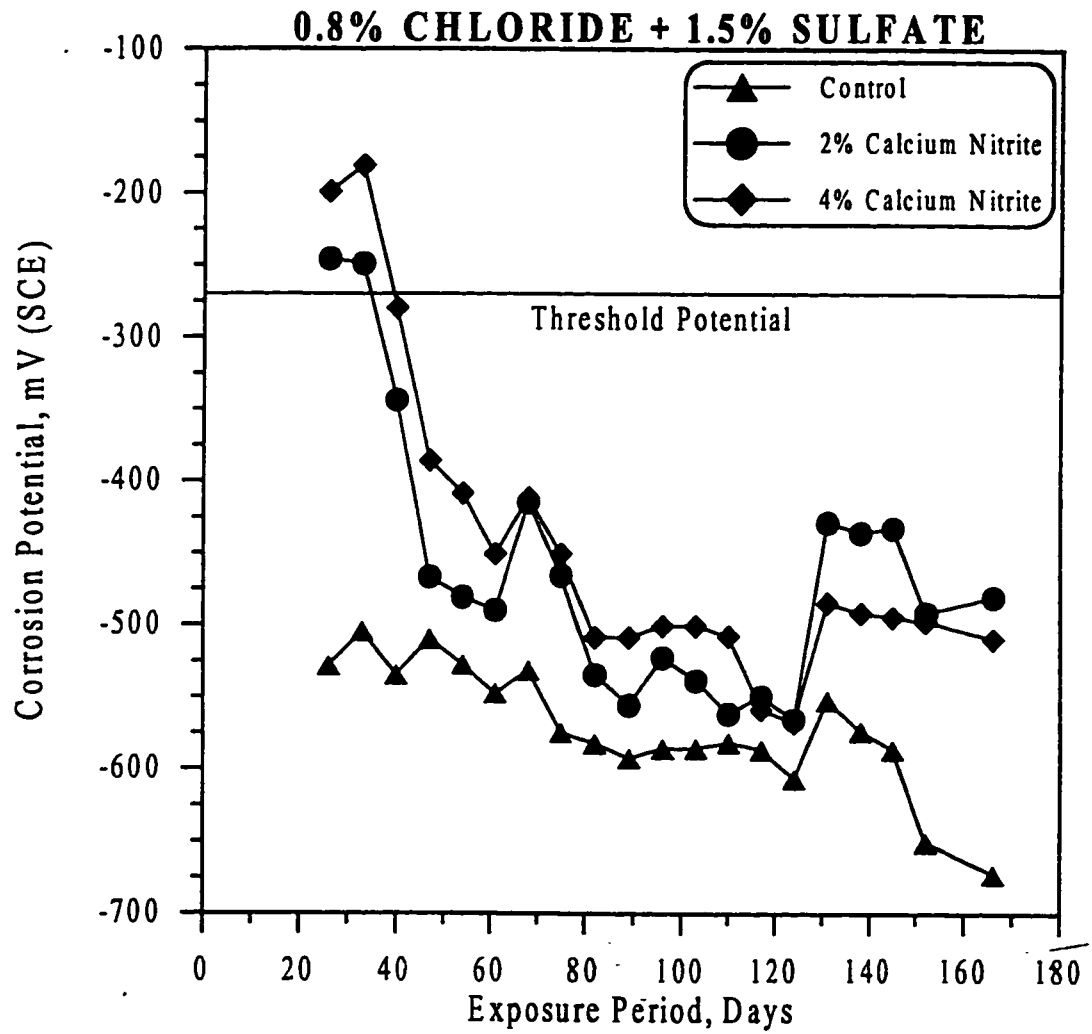


Figure 4.3: Corrosion Potentials on Steel in the Concrete Specimens Contaminated with 0.8% Chloride plus 1.5% Sulfate and Incorporating Calcium Nitrite

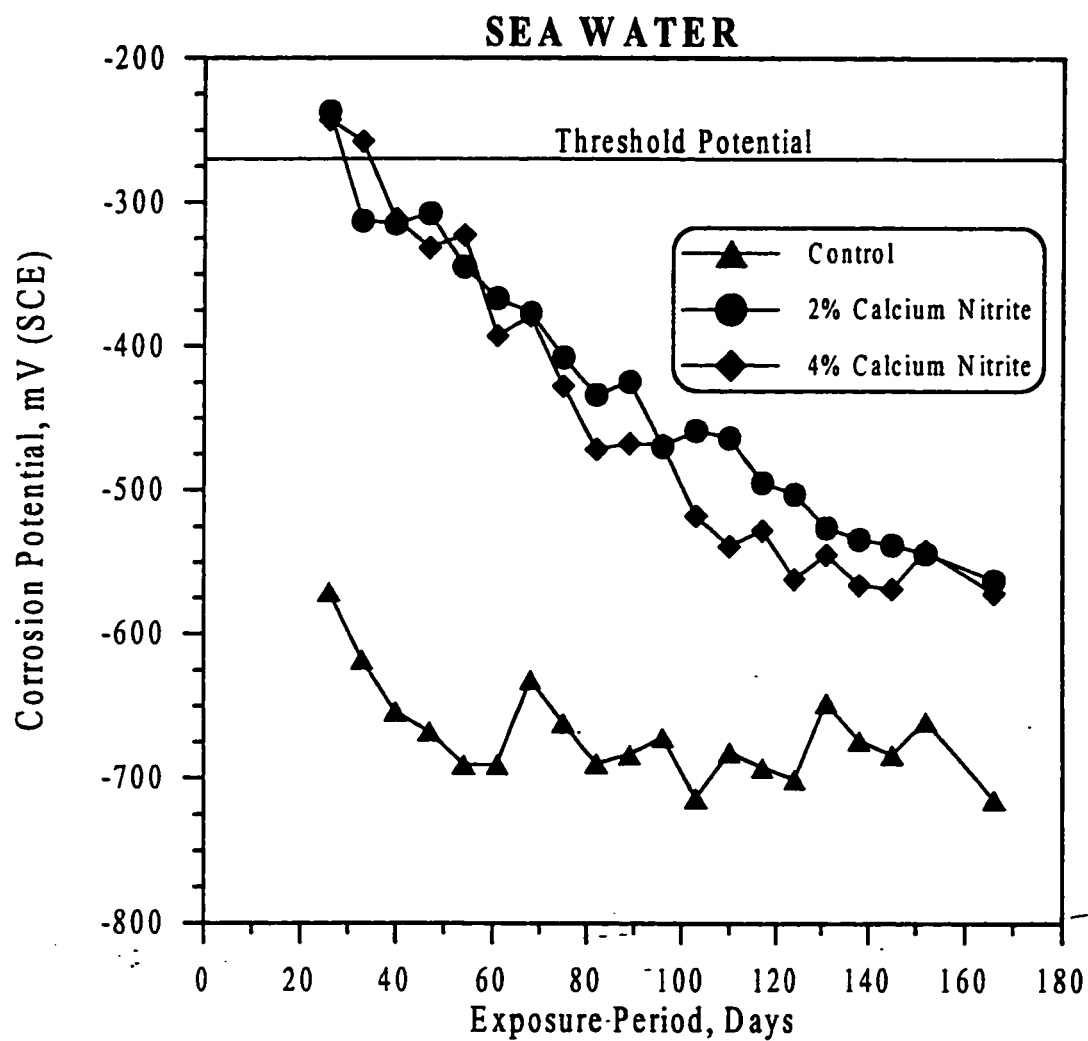


Figure 4.4: Corrosion Potentials on Steel in the Concrete Specimens made with Sea Water and Incorporating Calcium Nitrite

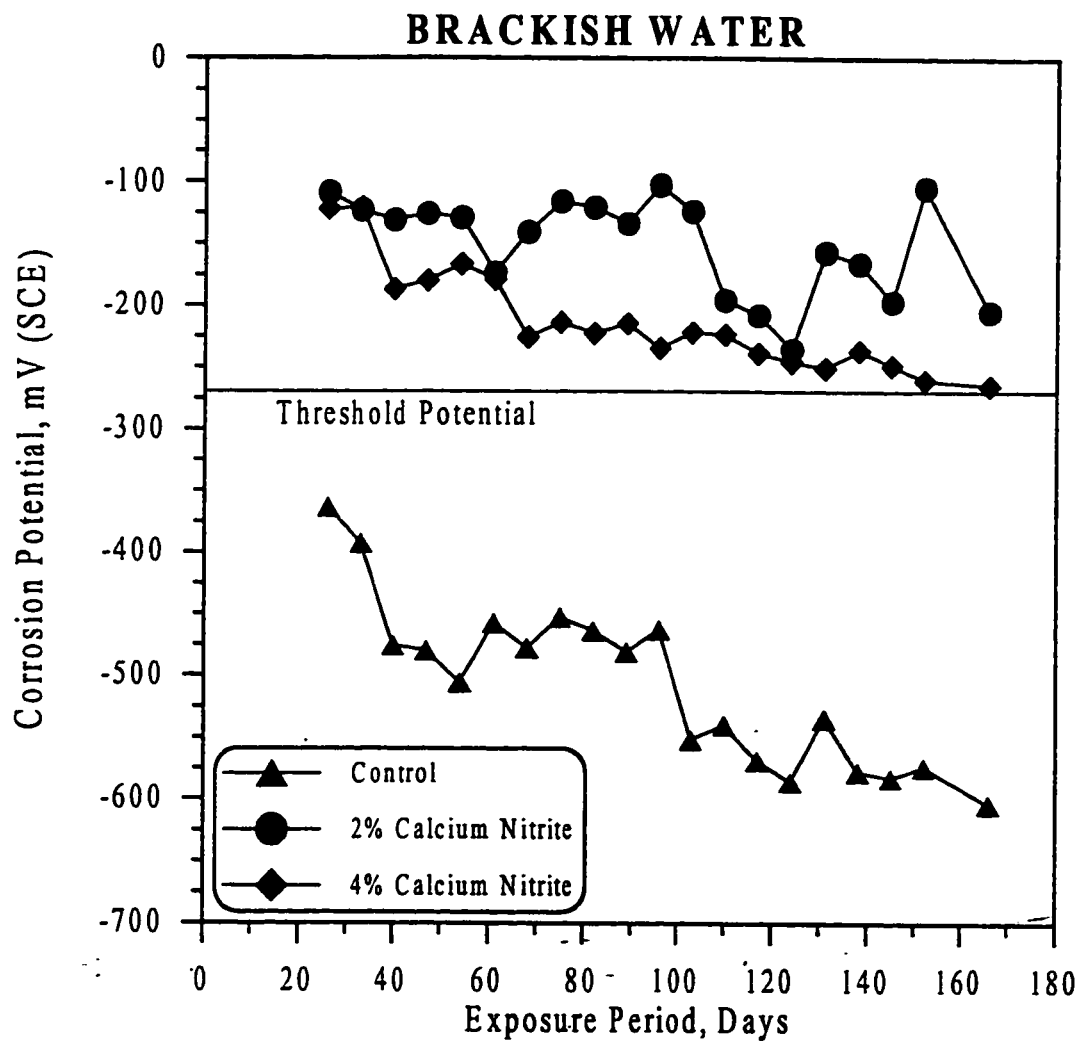


Figure 4.5: Corrosion Potentials on Steel in the Concrete Specimens made with Brackish Water and Incorporating Calcium Nitrite

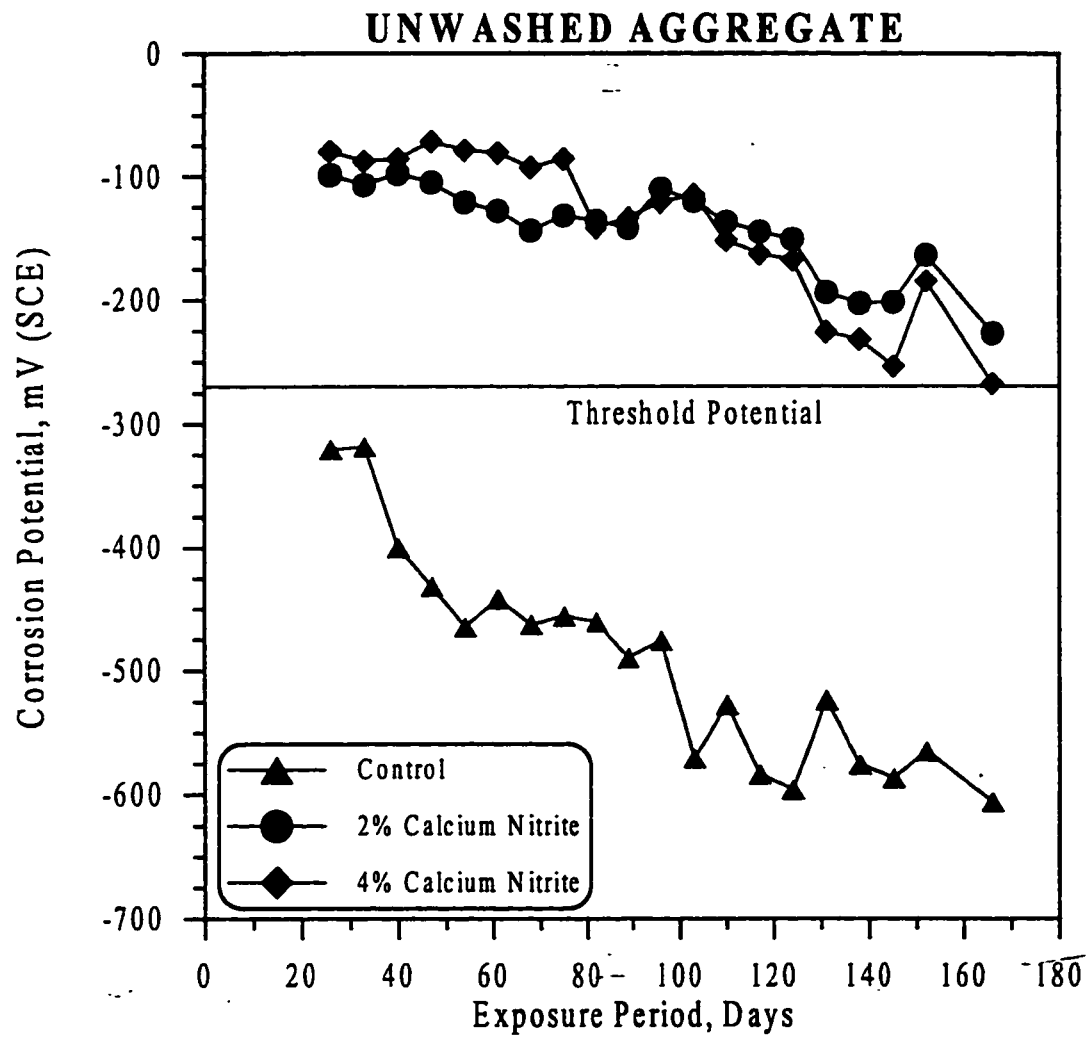


Figure 4.6: Corrosion Potentials on Steel in the Concrete Specimens made with Unwashed Aggregate and Incorporating Calcium Nitrite



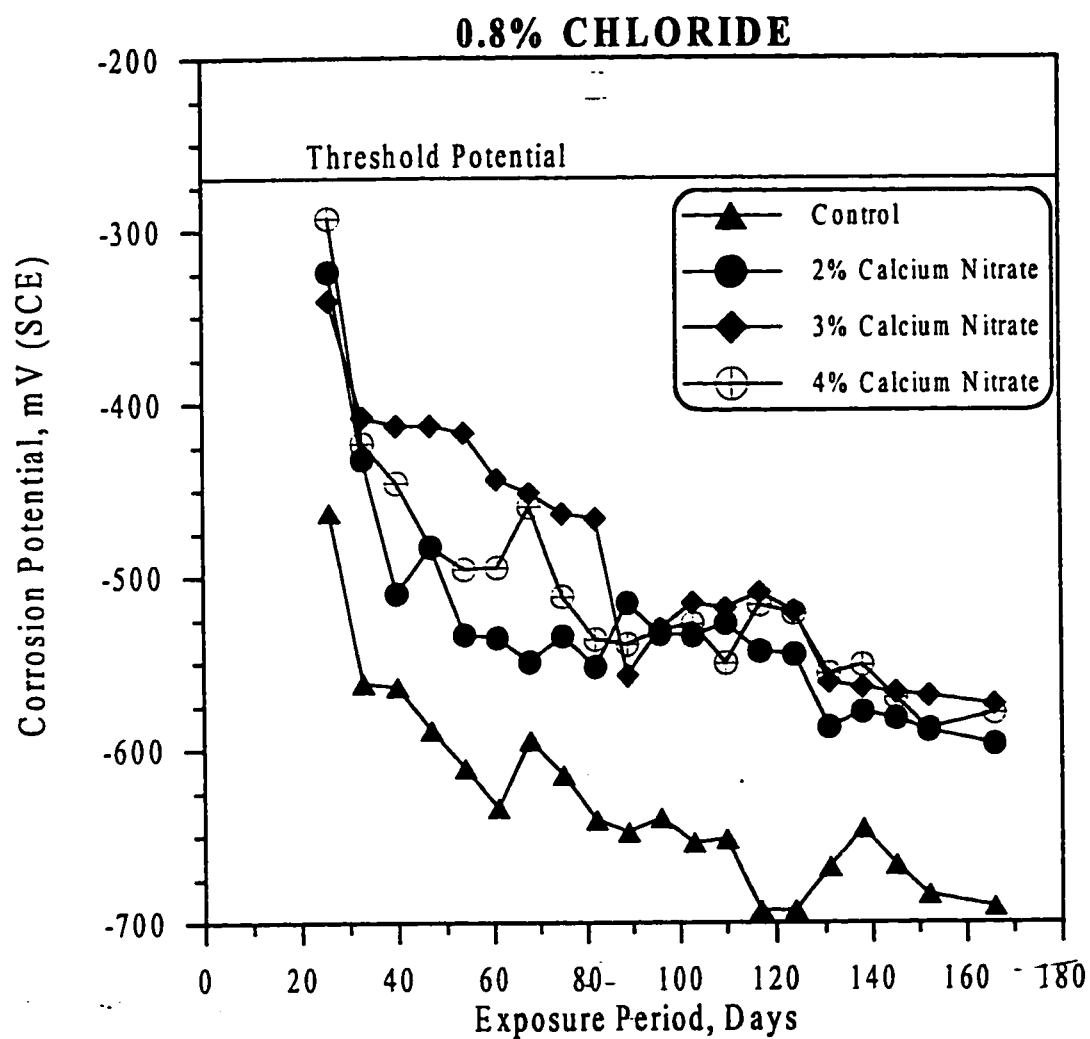


Figure 4.7: Corrosion Potentials on Steel in the Concrete Specimens Contaminated with 0.8% Chloride and Incorporating Calcium Nitrate

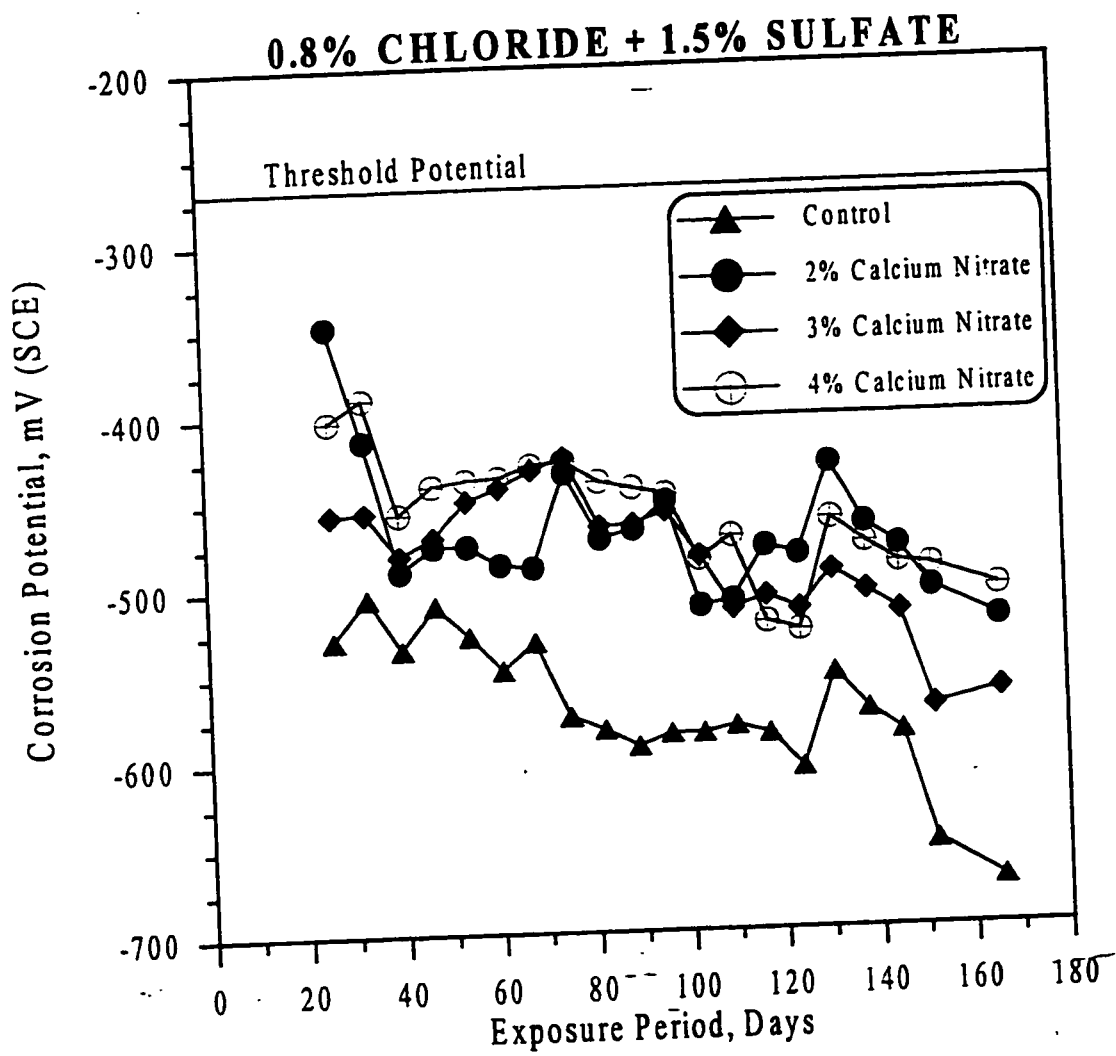


Figure 4.8: Corrosion Potentials on Steel in the Concrete Specimens Contaminated with 0.8% Chloride plus 1.5% Sulfate and Incorporating Calcium Nitrate

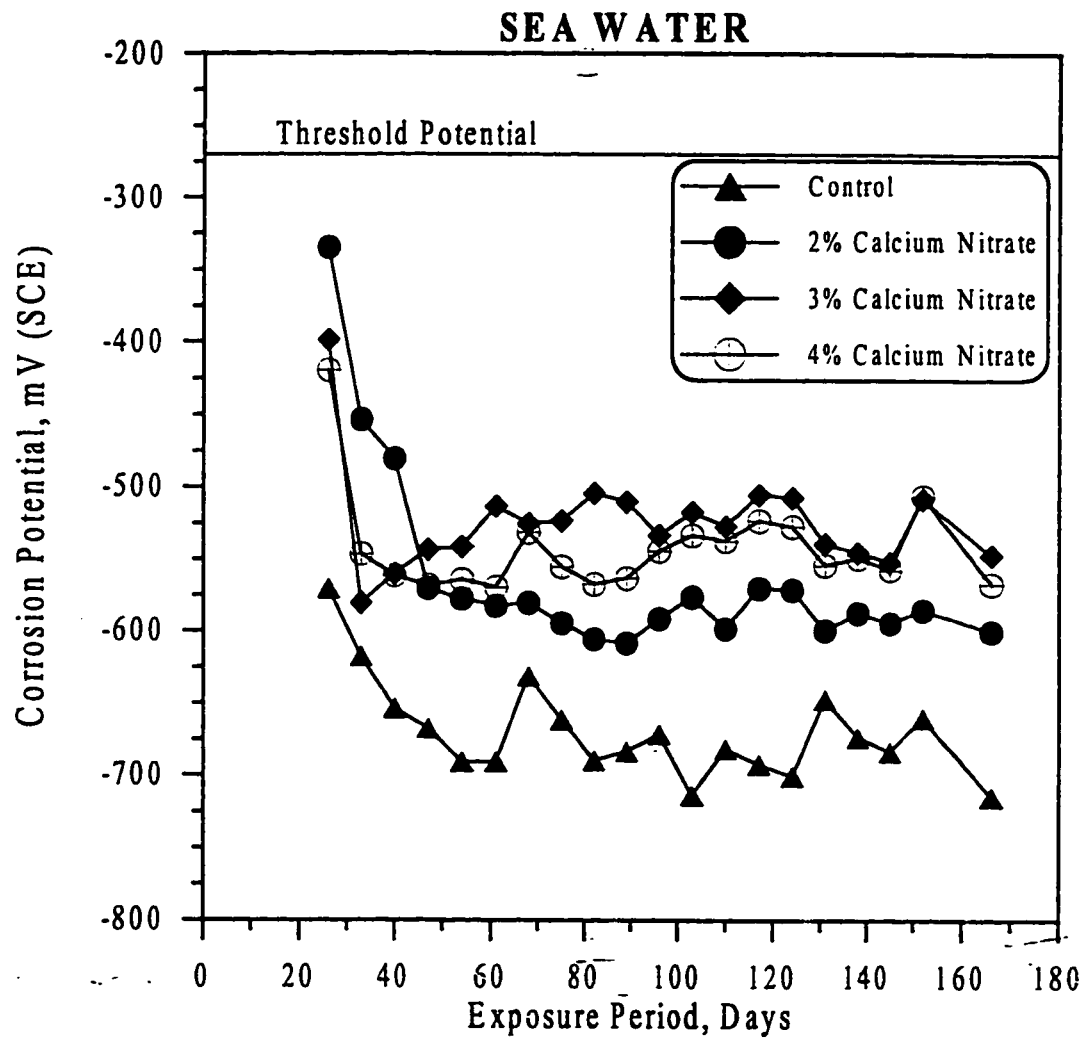


Figure 4.9: Corrosion Potentials on Steel in the Concrete Specimens made with Sea Water and Incorporating Calcium Nitrate

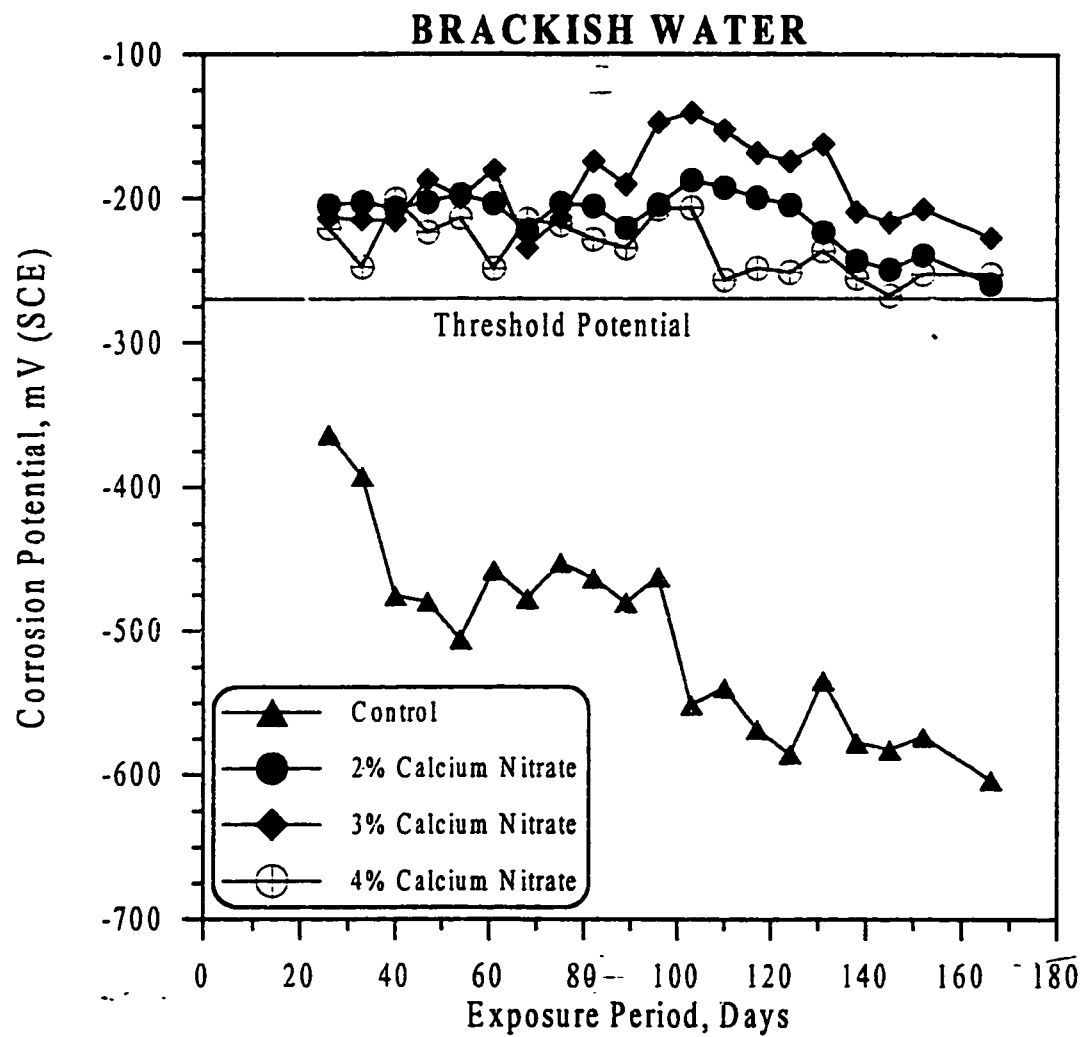


Figure 4.10: Corrosion Potentials on Steel in the Concrete Specimens made with Brackish Water and Incorporating Calcium Nitrate

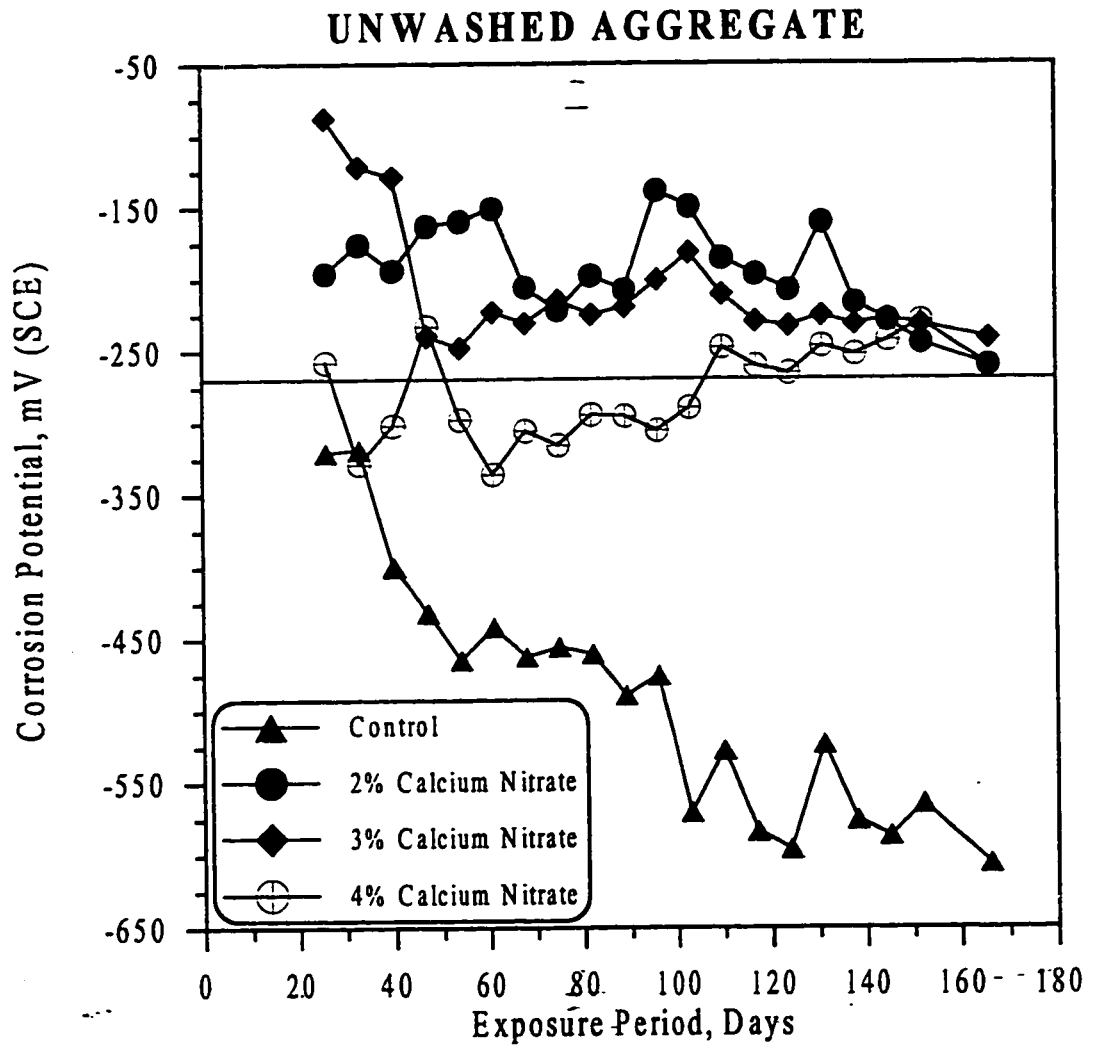


Figure 4.11: Corrosion Potentials on Steel in the Concrete Specimens made with Unwashed Aggregate and Incorporating Calcium Nitrate

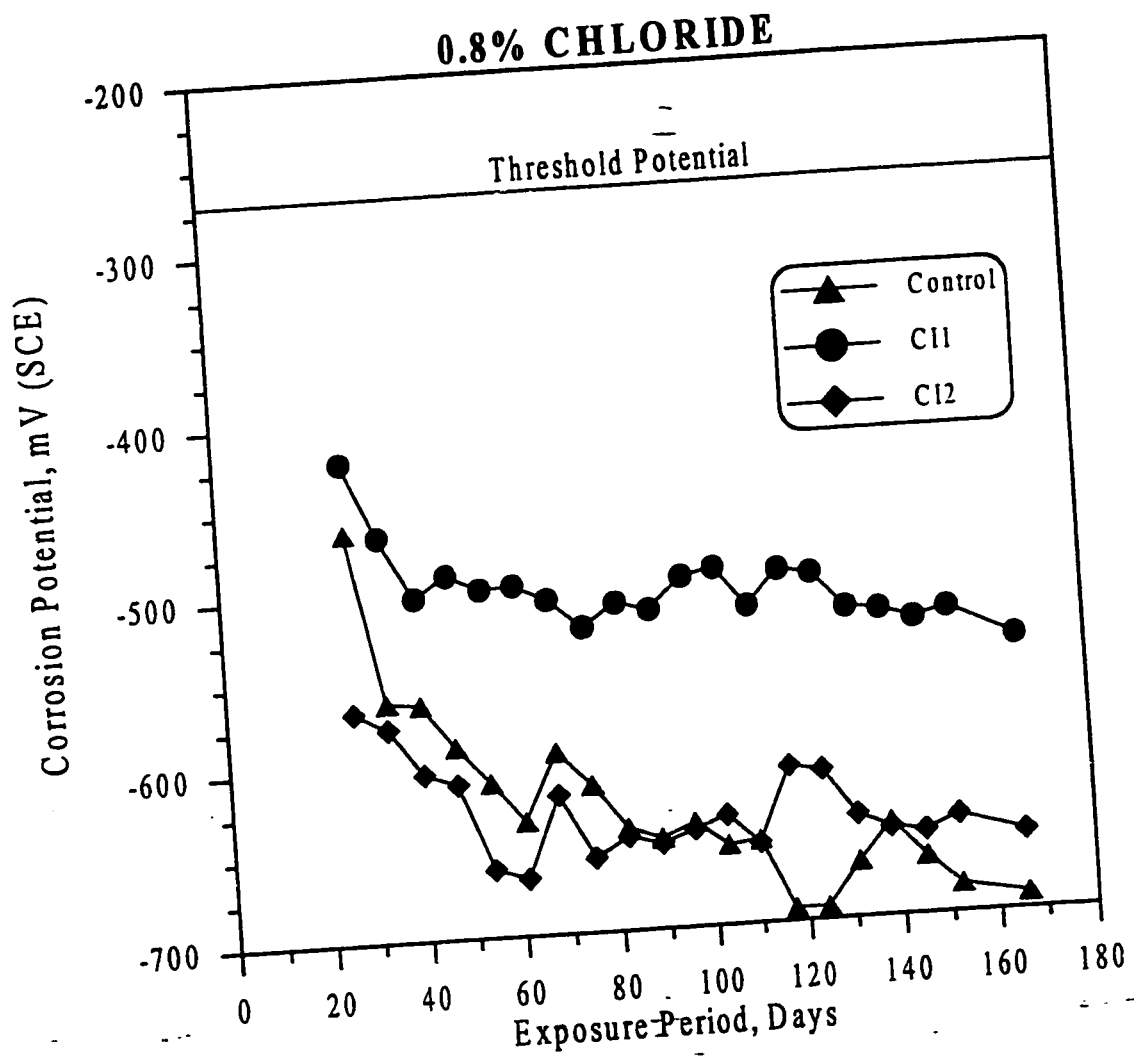


Figure 4.12: Corrosion Potentials on Steel in the Concrete Specimens Contaminated with 0.8% Chloride and Incorporating CI1 and CI2 Inhibitors

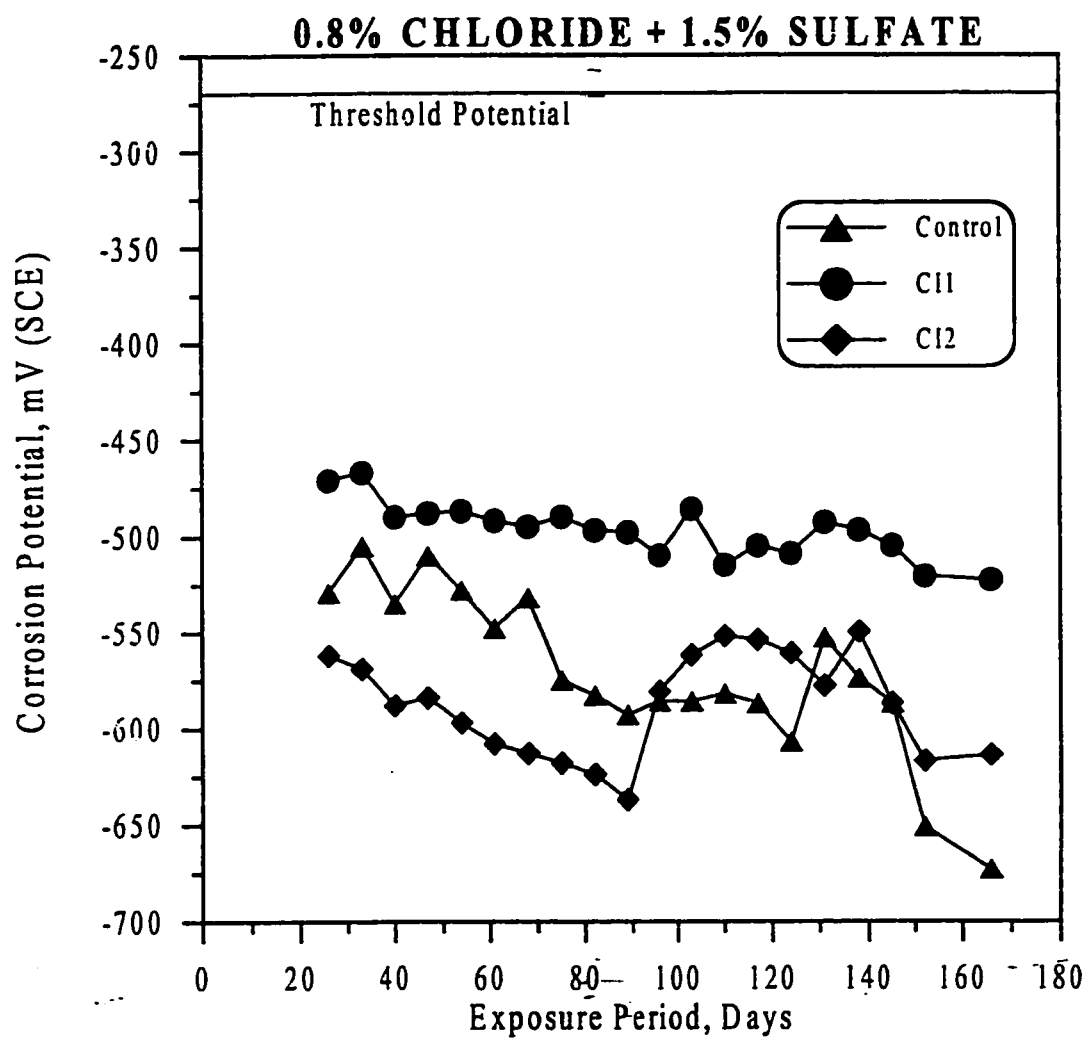


Figure 4.13: Corrosion Potentials on Steel in the Concrete Specimens Contaminated with 0.8% Chloride plus 1.5% Sulfate and Incorporating CI1 and CI2 Inhibitors

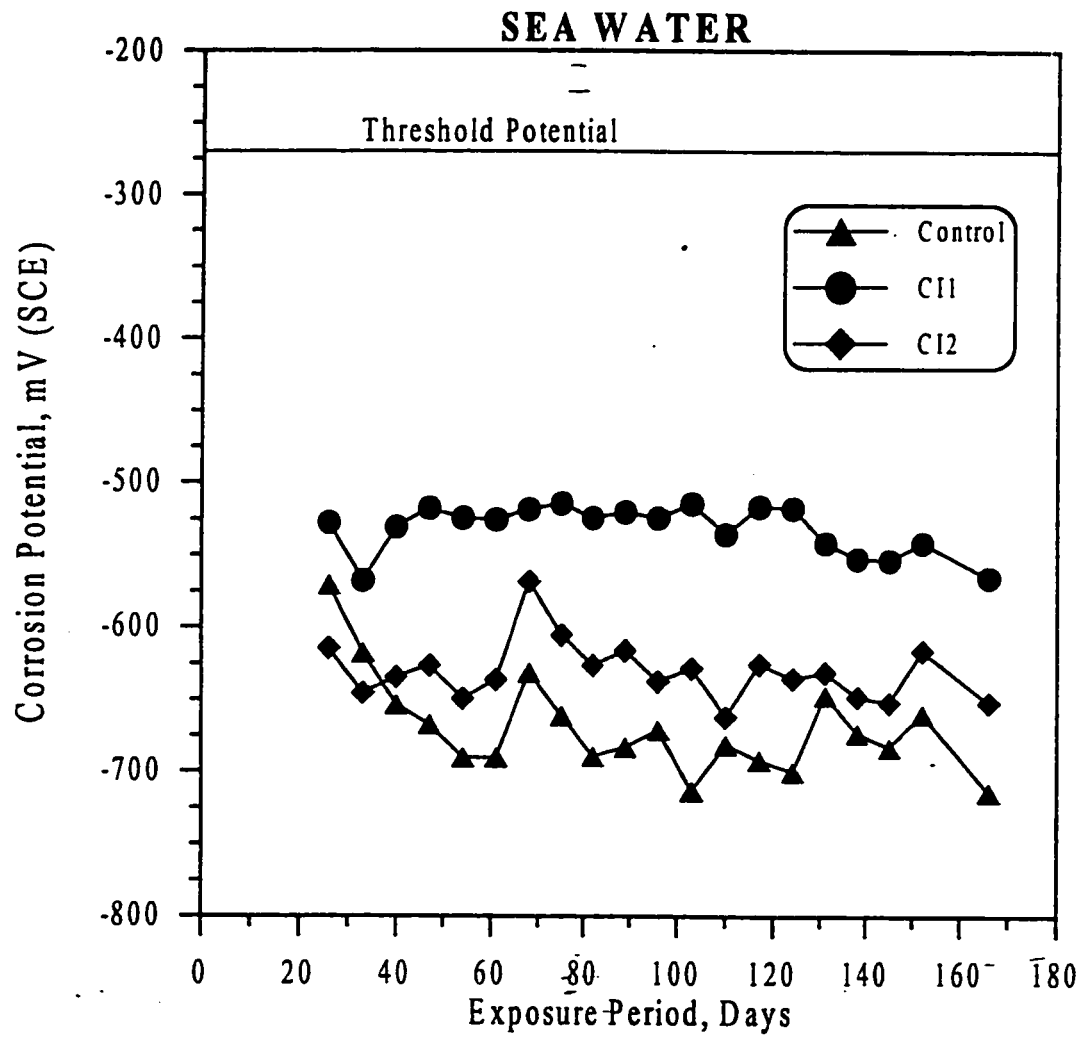


Figure 4.14: Corrosion Potentials on Steel in the Concrete Specimens made with Sea Water and Incorporating CI1 and CI2 Inhibitors



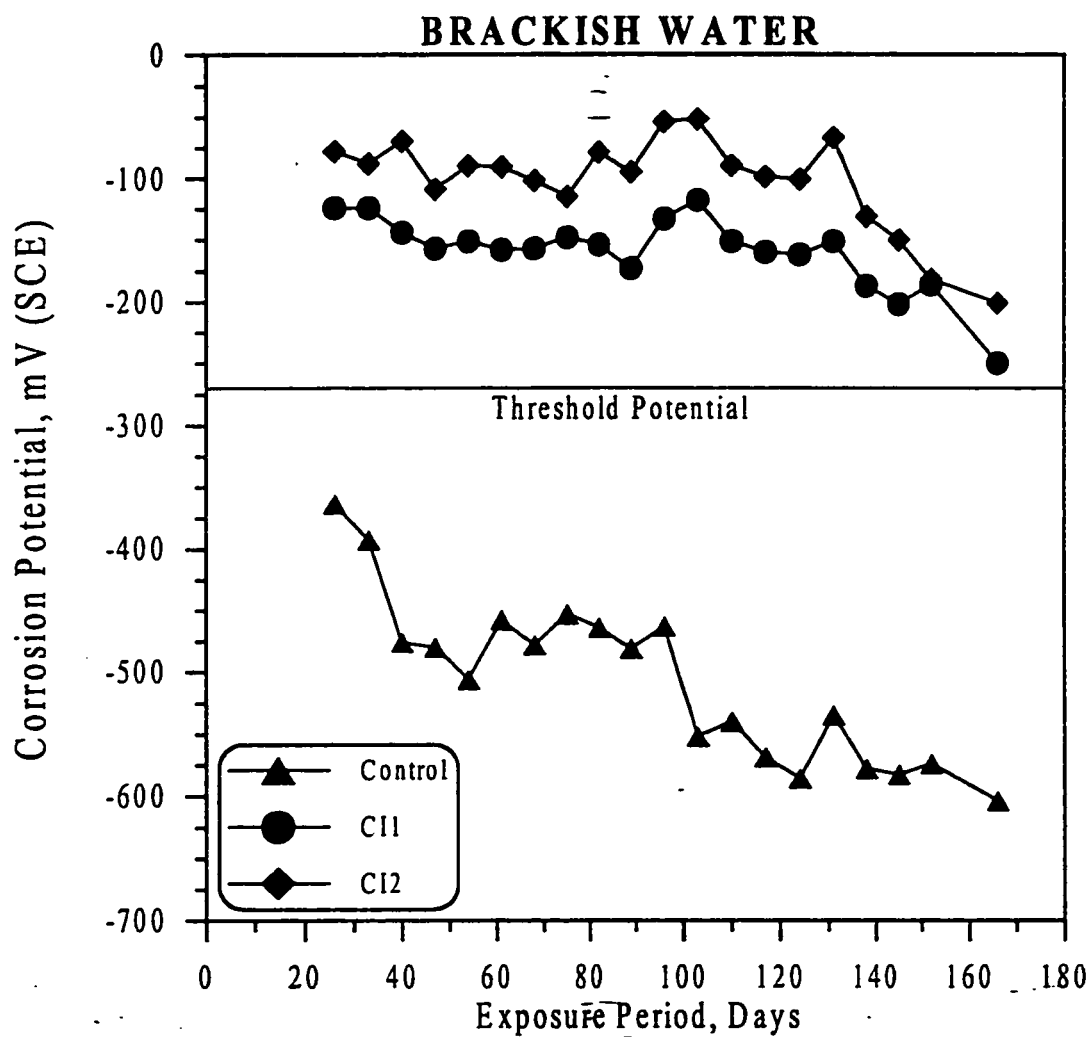


Figure 4.15: Corrosion Potentials on Steel in the Concrete Specimens made with Brackish Water and Incorporating CI1 and CI2 Inhibitors

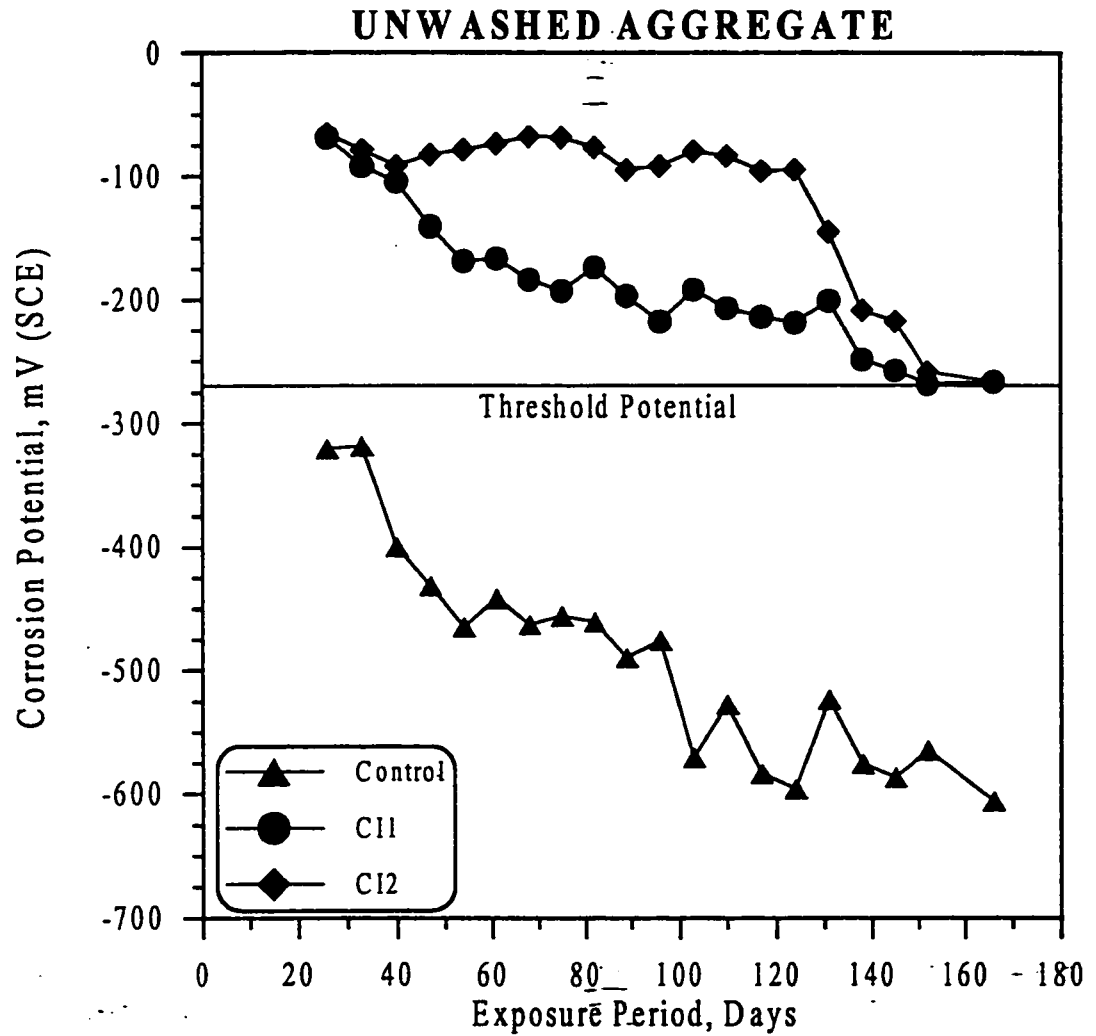


Figure 4.16: Corrosion Potentials on Steel in the Concrete Specimens made with Unwashed Aggregate and Incorporating CI1 and CI2 Inhibitors

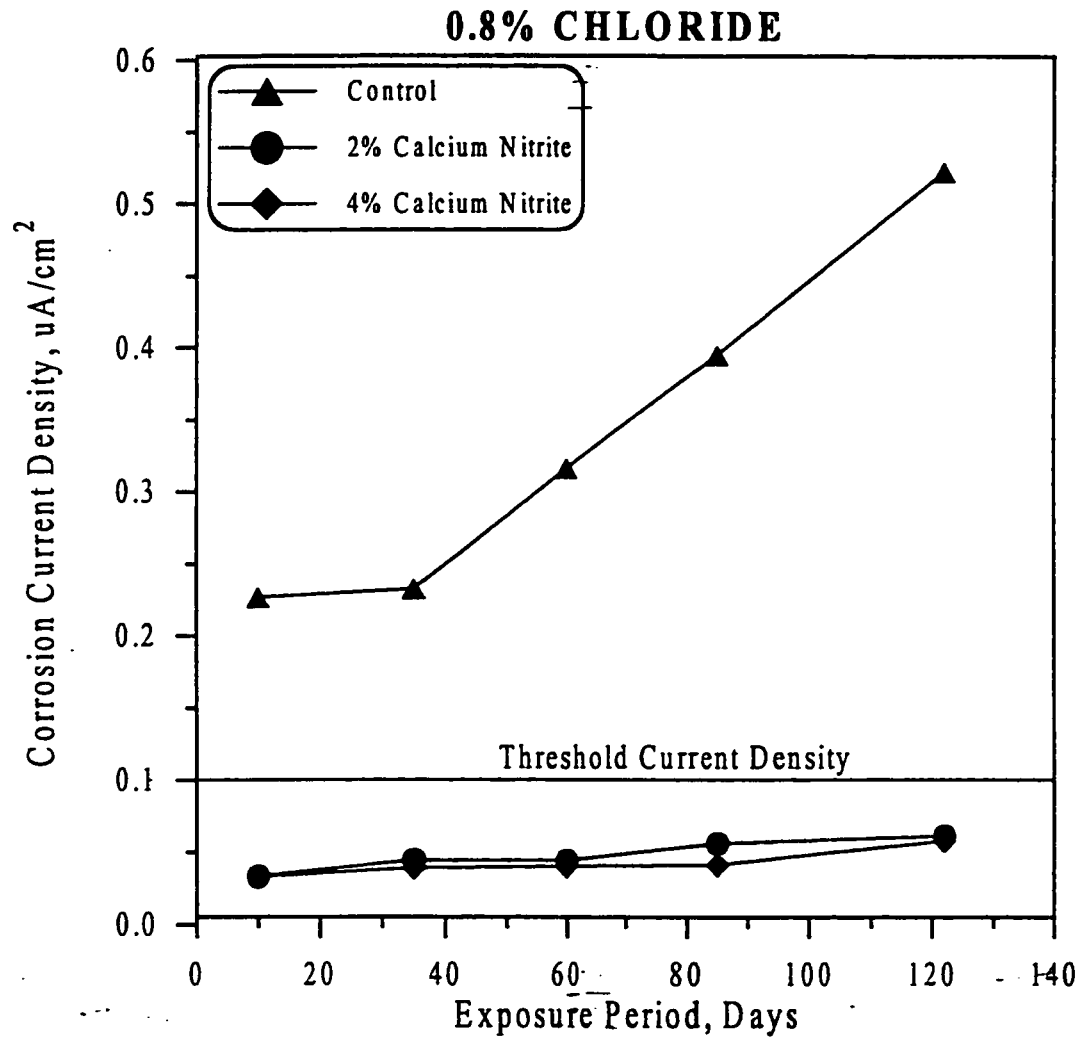


Figure 4.17: Corrosion Current Density in the Concrete Specimens Contaminated with 0.8% Chloride and Incorporating Calcium Nitrite

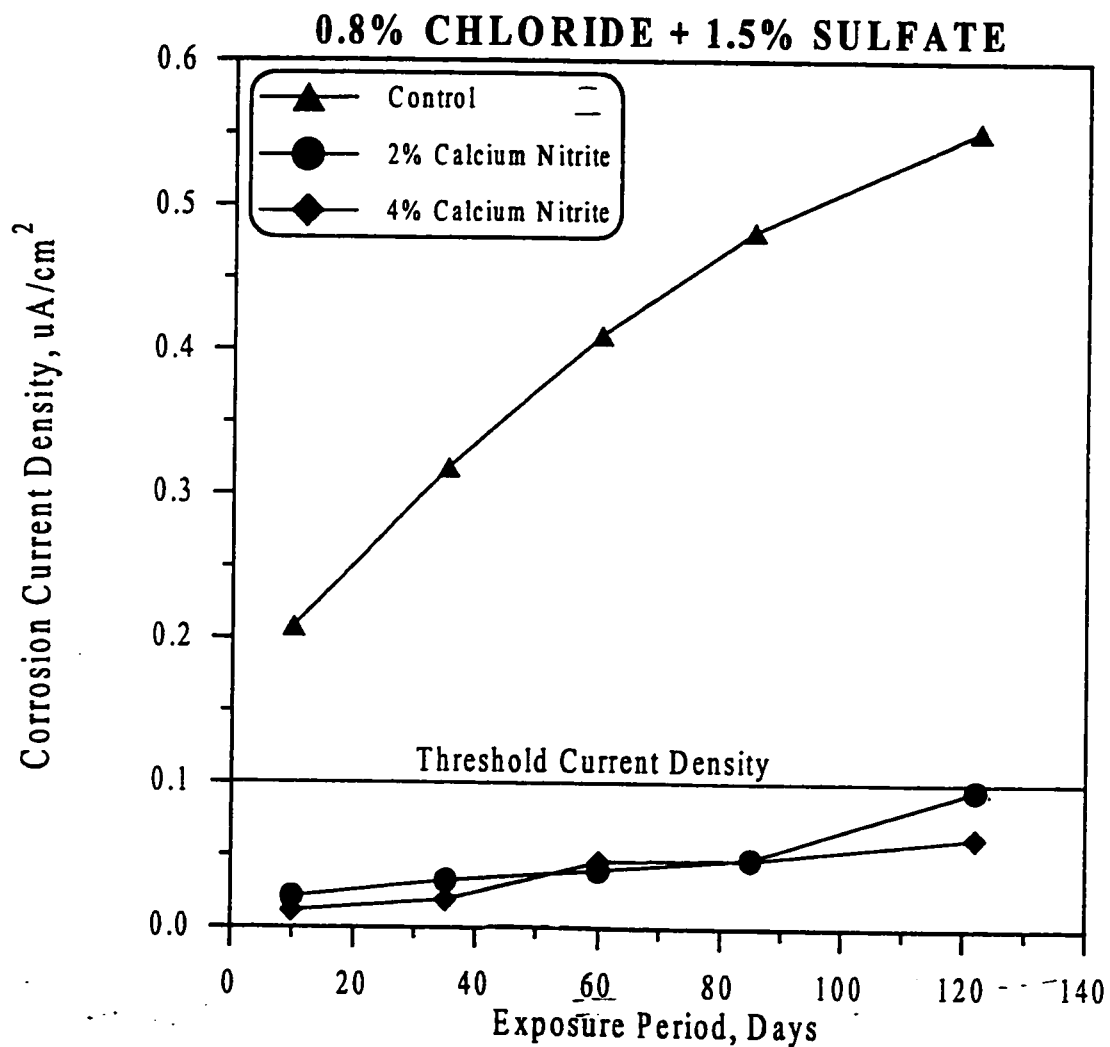


Figure 4.18: Corrosion Current Density in the Concrete Specimens Contaminated with 0.8% Chloride plus 1.5% Sulfate and Incorporating Calcium Nitrite

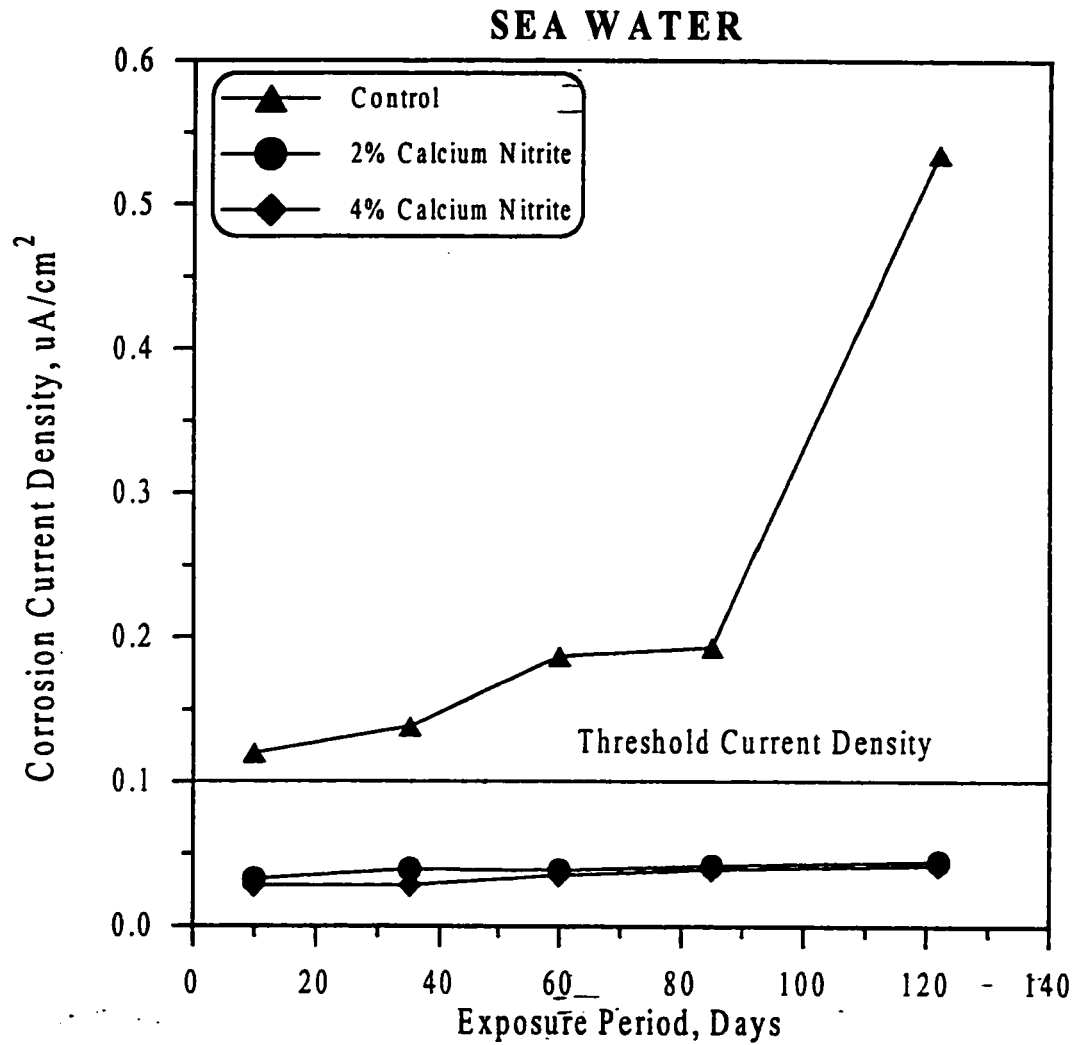


Figure 4.19: Corrosion Current Density in the Concrete Specimens made with Sea Water and Incorporating Calcium Nitrite

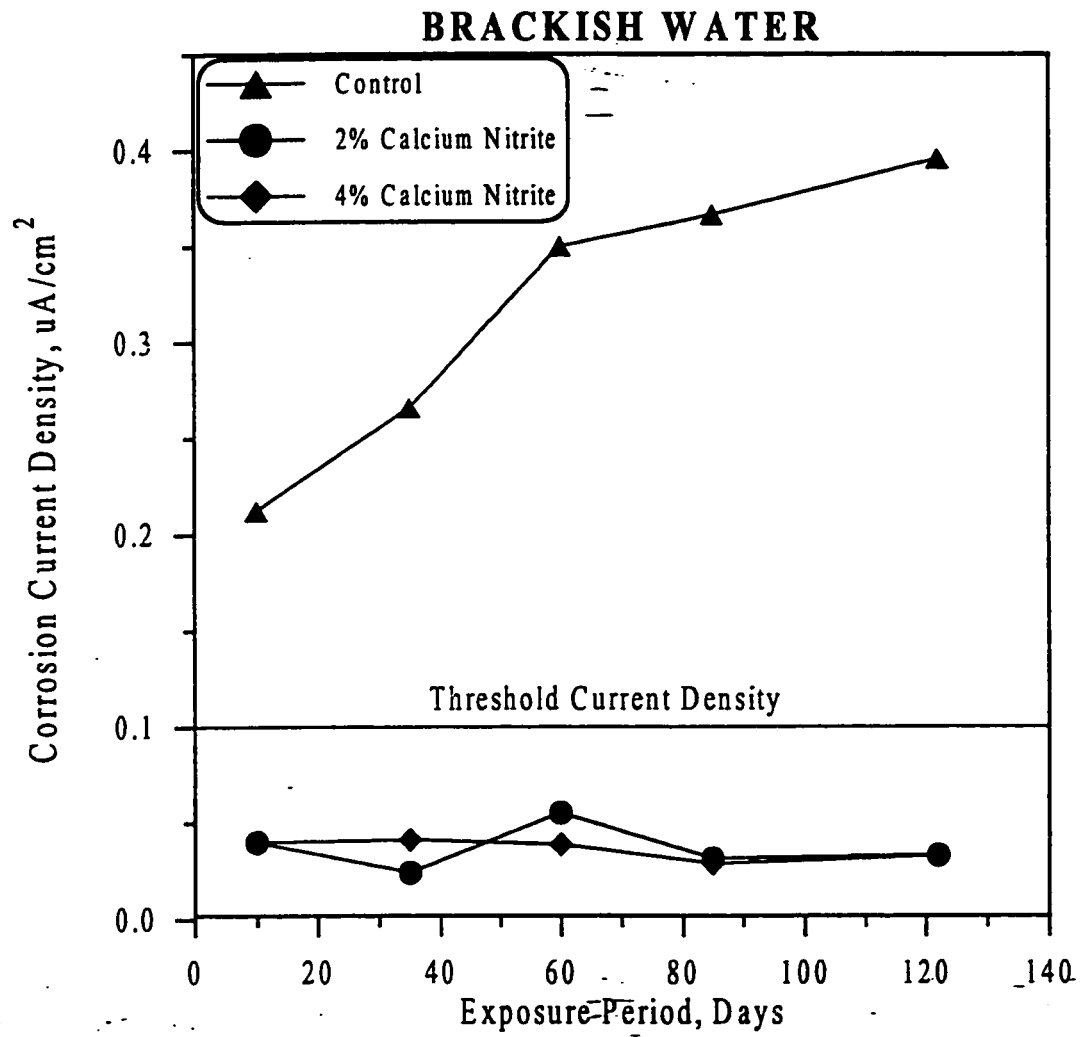


Figure 4.20: Corrosion Current Density in the Concrete Specimens made with Brackish Water and Incorporating Calcium Nitrite

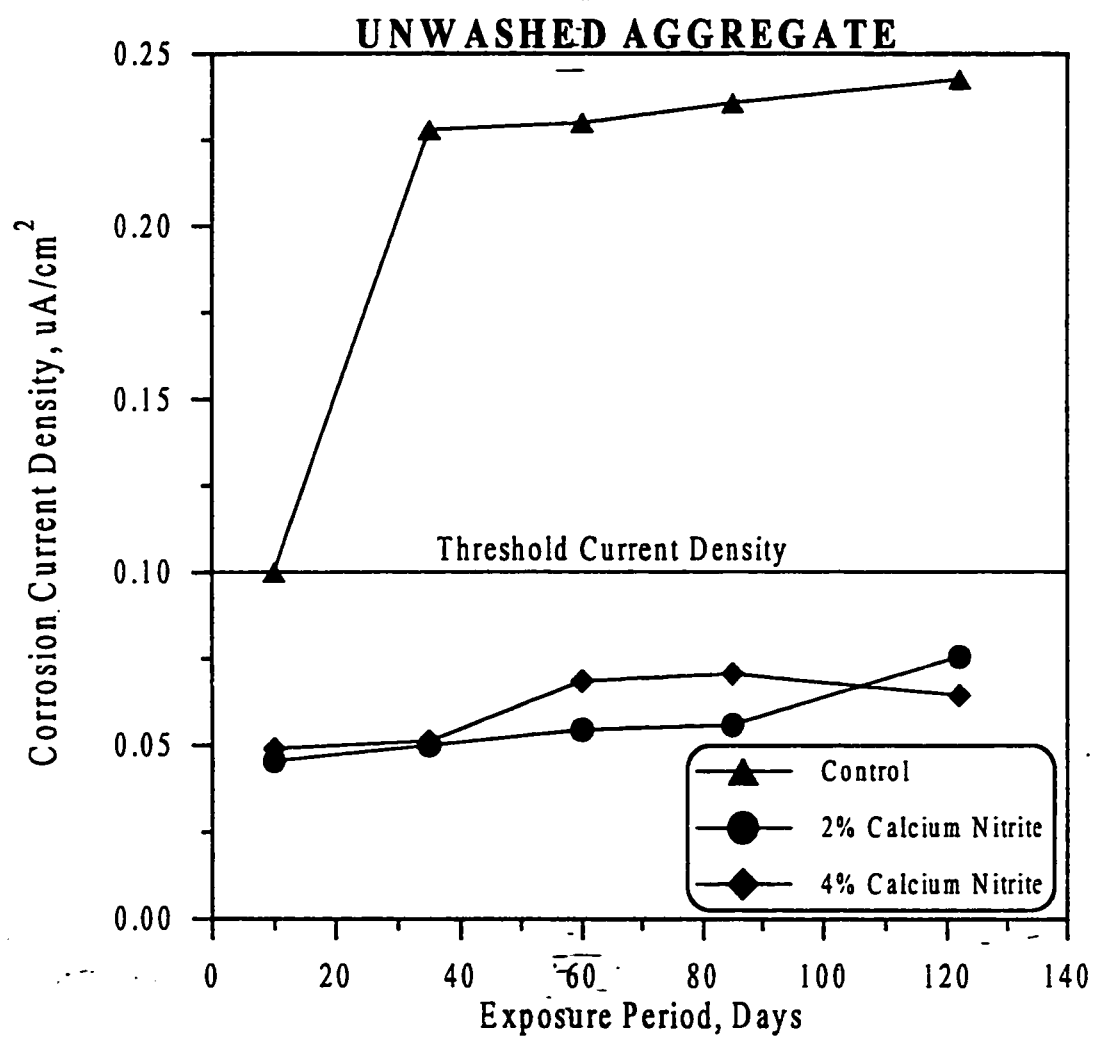


Figure 4.21: Corrosion Current Density in the Concrete Specimens made with Unwashed Aggregate and Incorporating Calcium Nitrite

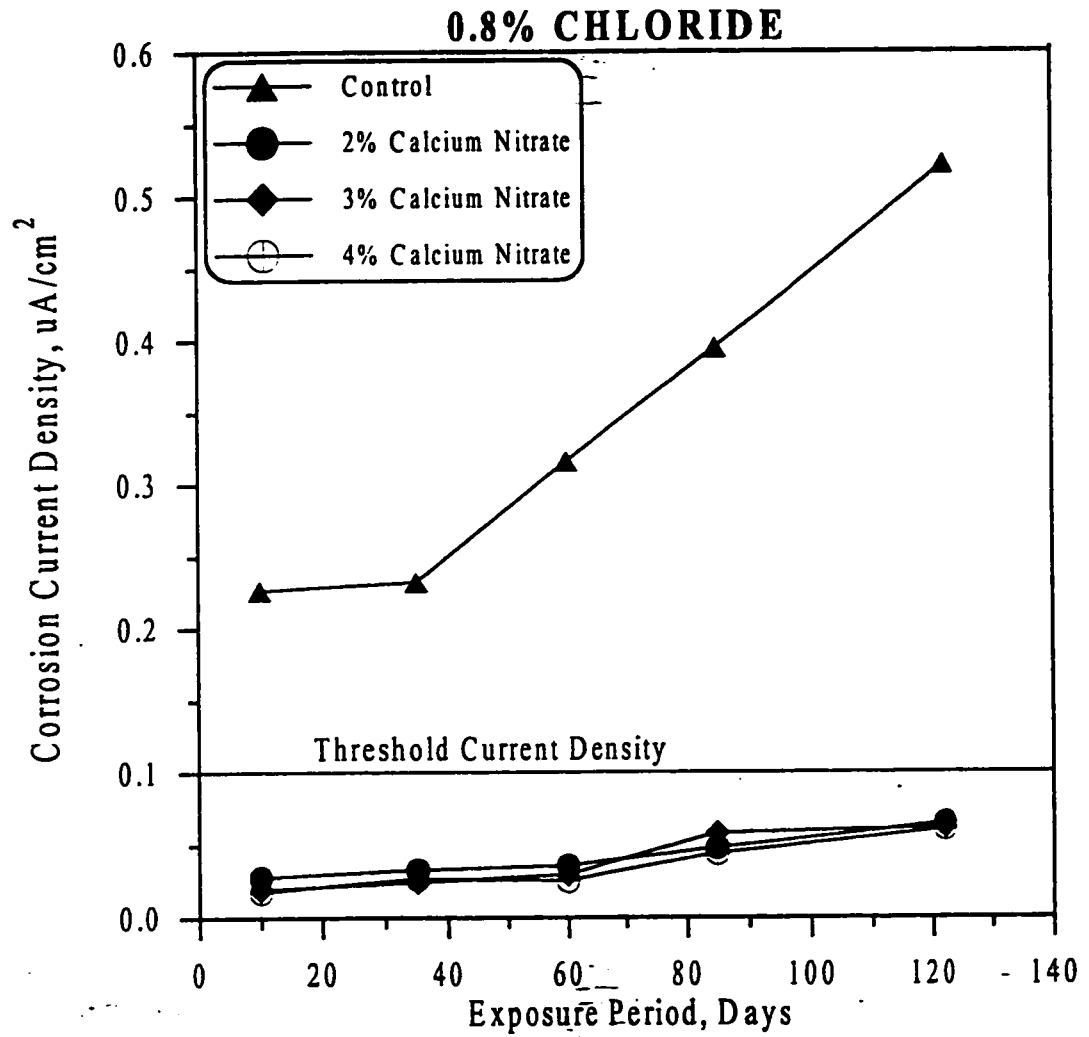


Figure 4.22: Corrosion Current Density in the Concrete Specimens Contaminated with 0.8% Chloride and Incorporating Calcium Nitrate



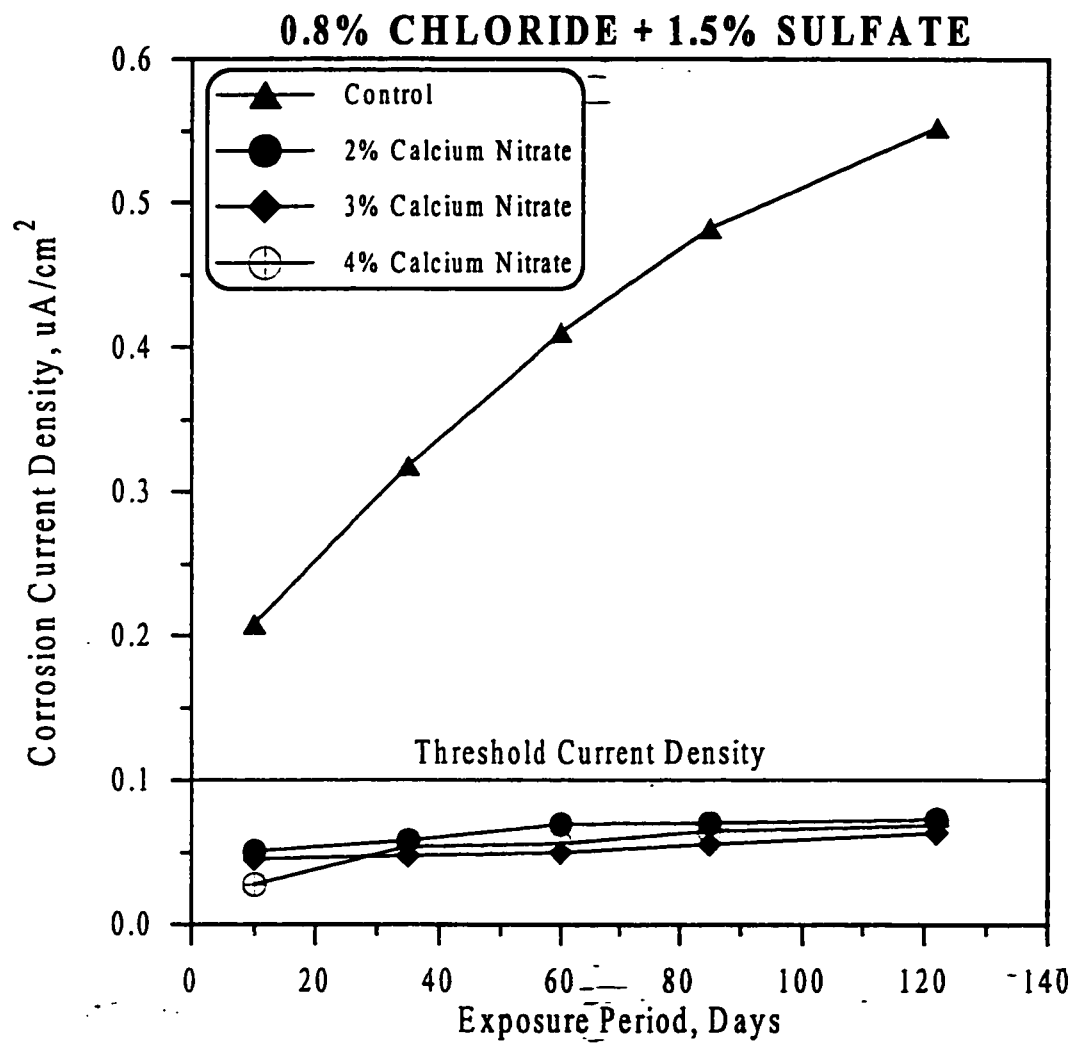


Figure 4.23: Corrosion Current Density in the Concrete Specimens Contaminated with 0.8% Chloride plus 1.5% Sulfate and Incorporating Calcium Nitrate

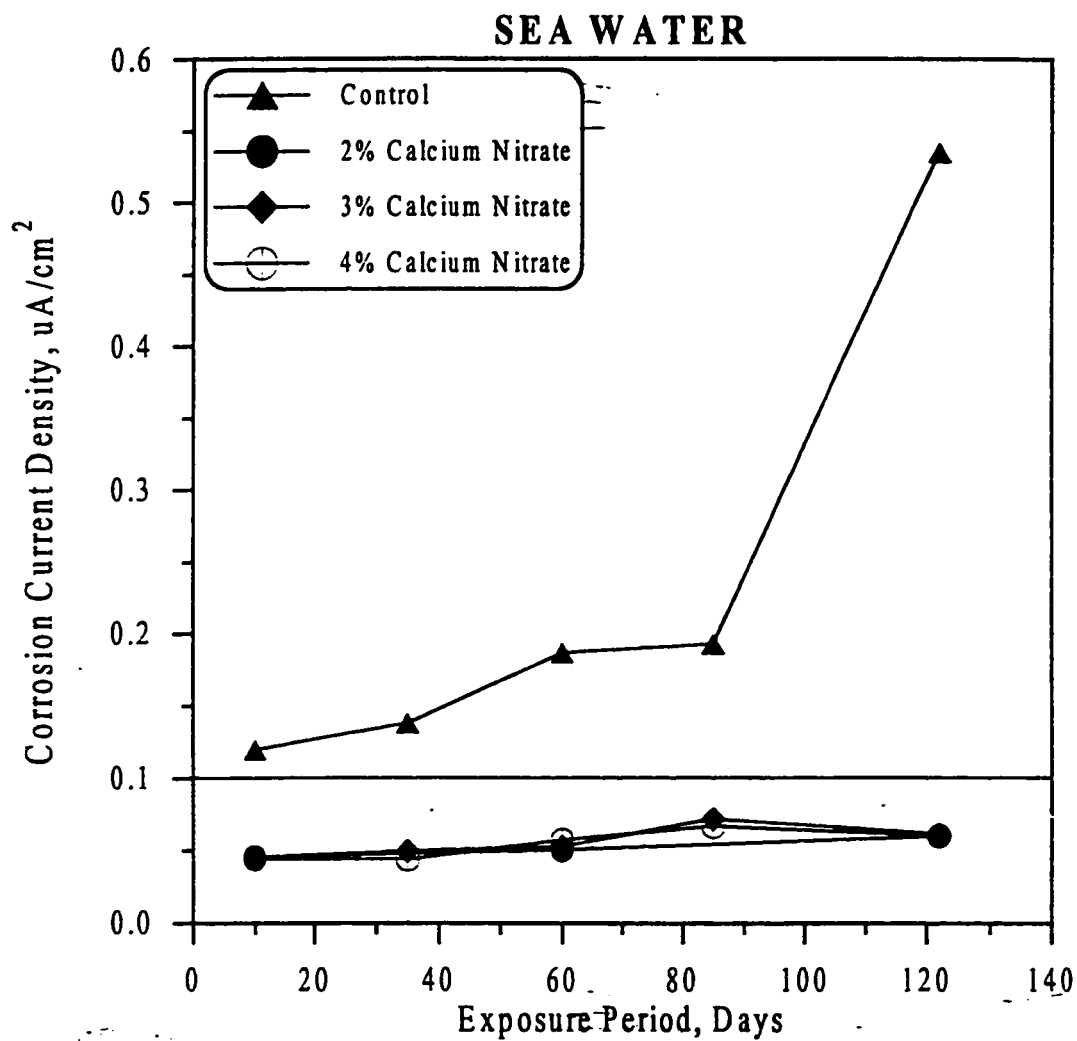


Figure 4.24: Corrosion Current Density in the Concrete Specimens made with Sea Water and Incorporating Calcium Nitrate

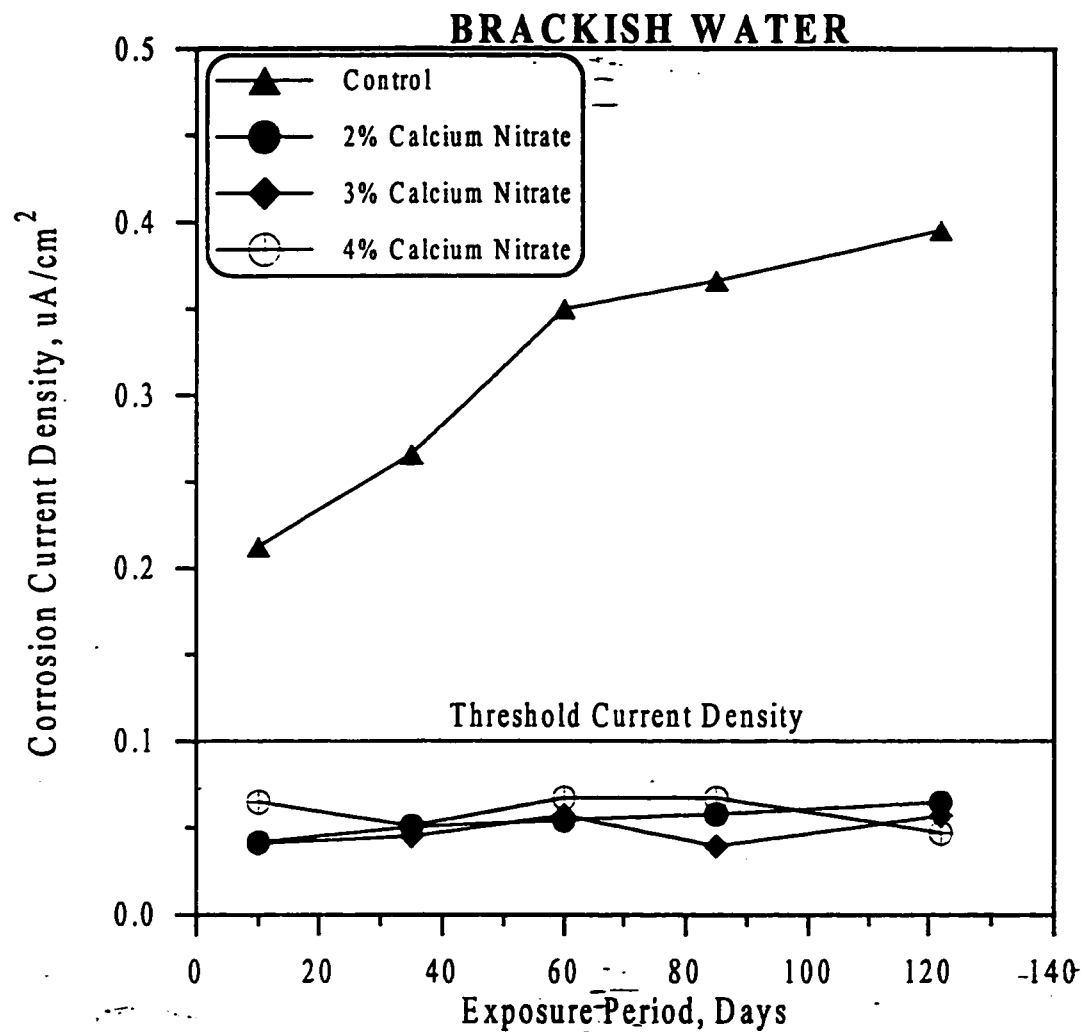


Figure 4.25: Corrosion Current Density in the Concrete Specimens made with Brackish Water and Incorporating Calcium Nitrate

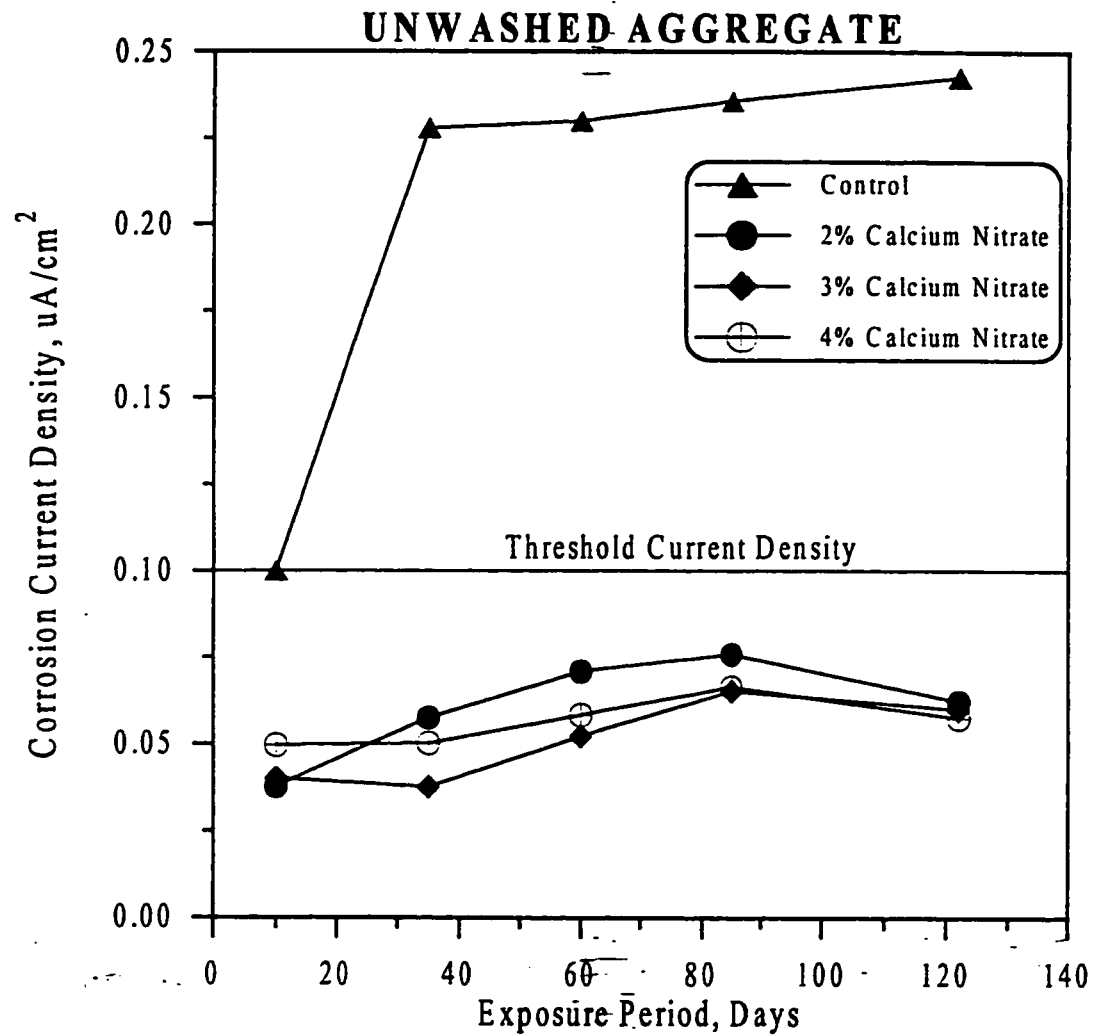


Figure 4.26: Corrosion Current Density in the Concrete Specimens made with Unwashed Aggregate and Incorporating Calcium Nitrate

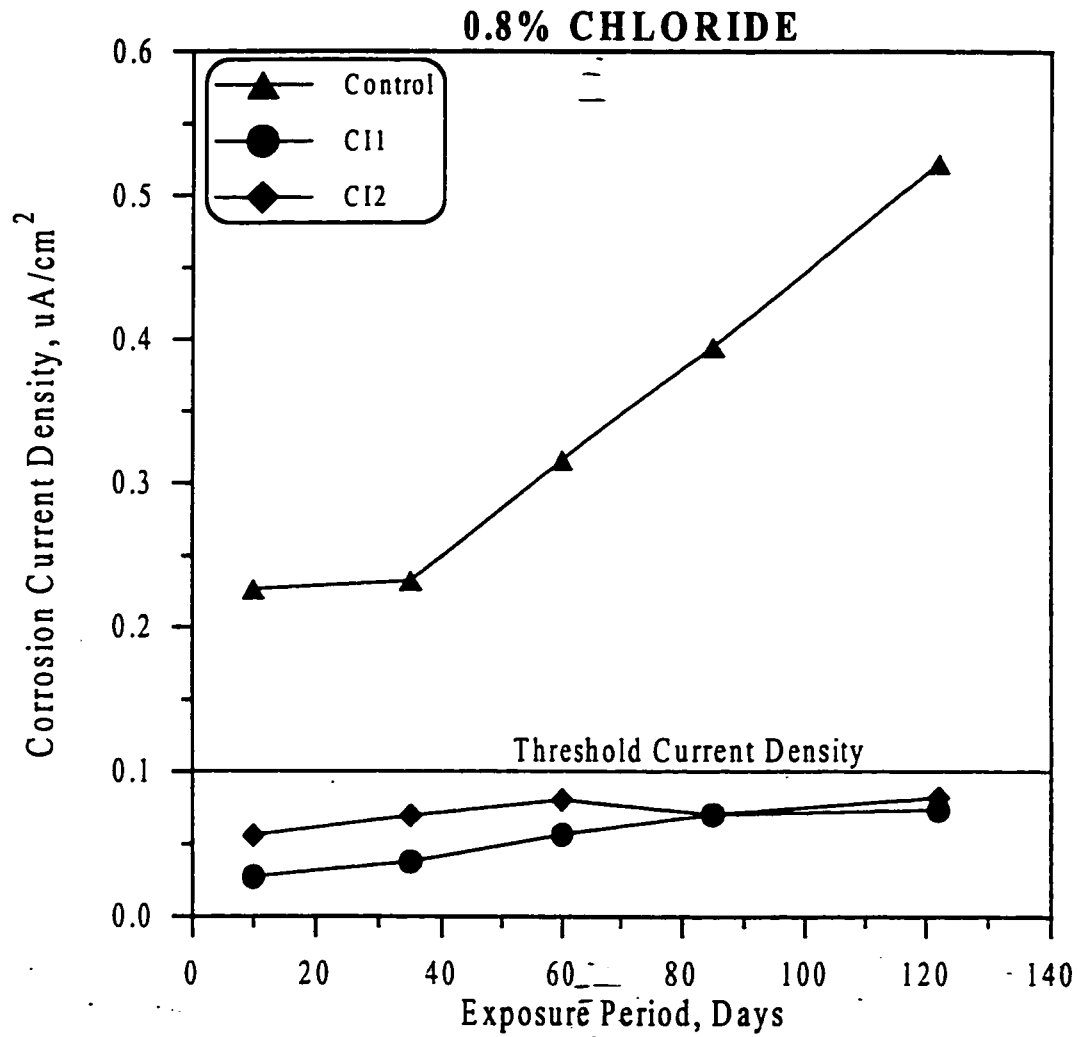


Figure 4.27: Corrosion Current Density in the Concrete Specimens Contaminated with 0.8% Chloride and Incorporating CI1 and CI2 Inhibitors

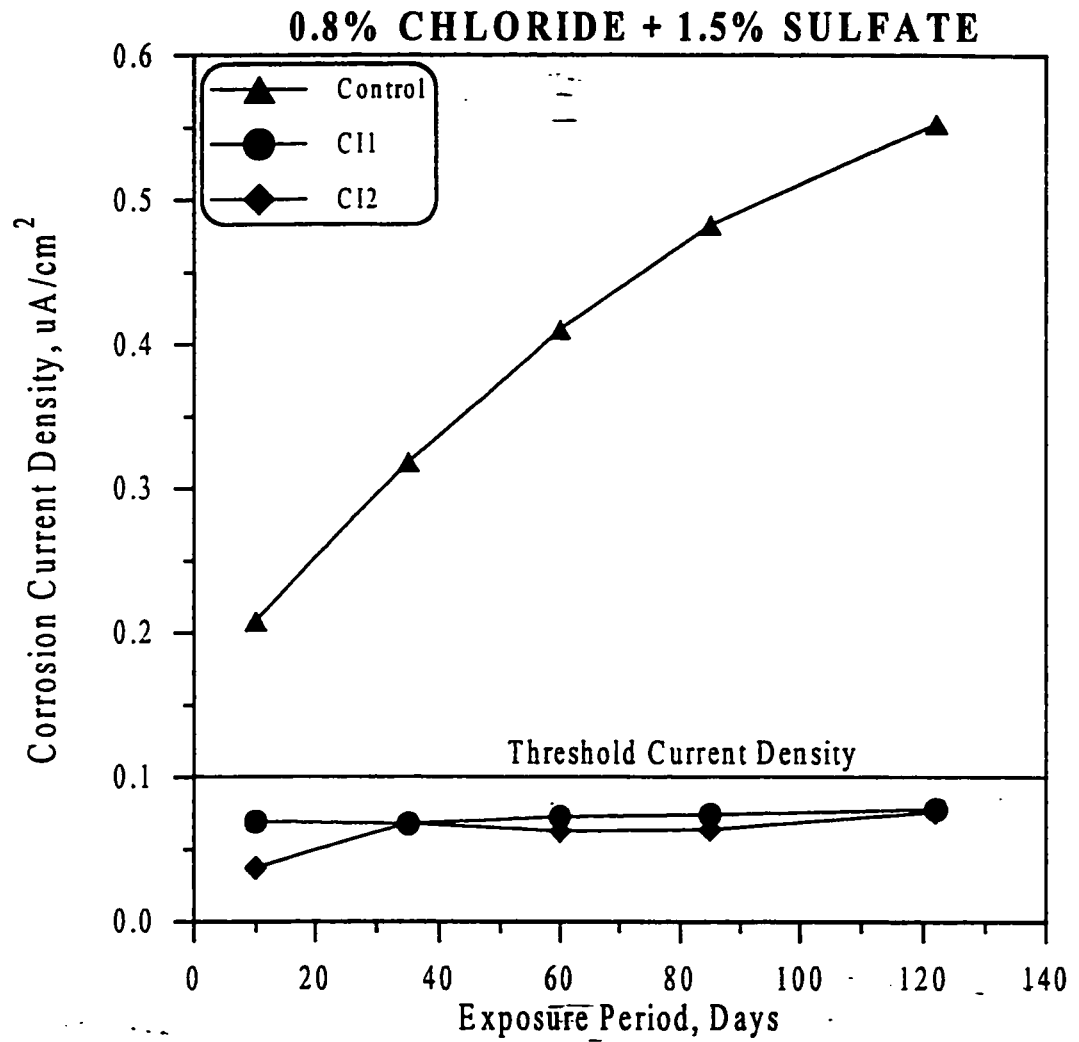


Figure 4.28: Corrosion Current Density in the Concrete Specimens Contaminated with 0.8% Chloride plus 1.5% Sulfate and Incorporating CI1 and CI2 Inhibitors

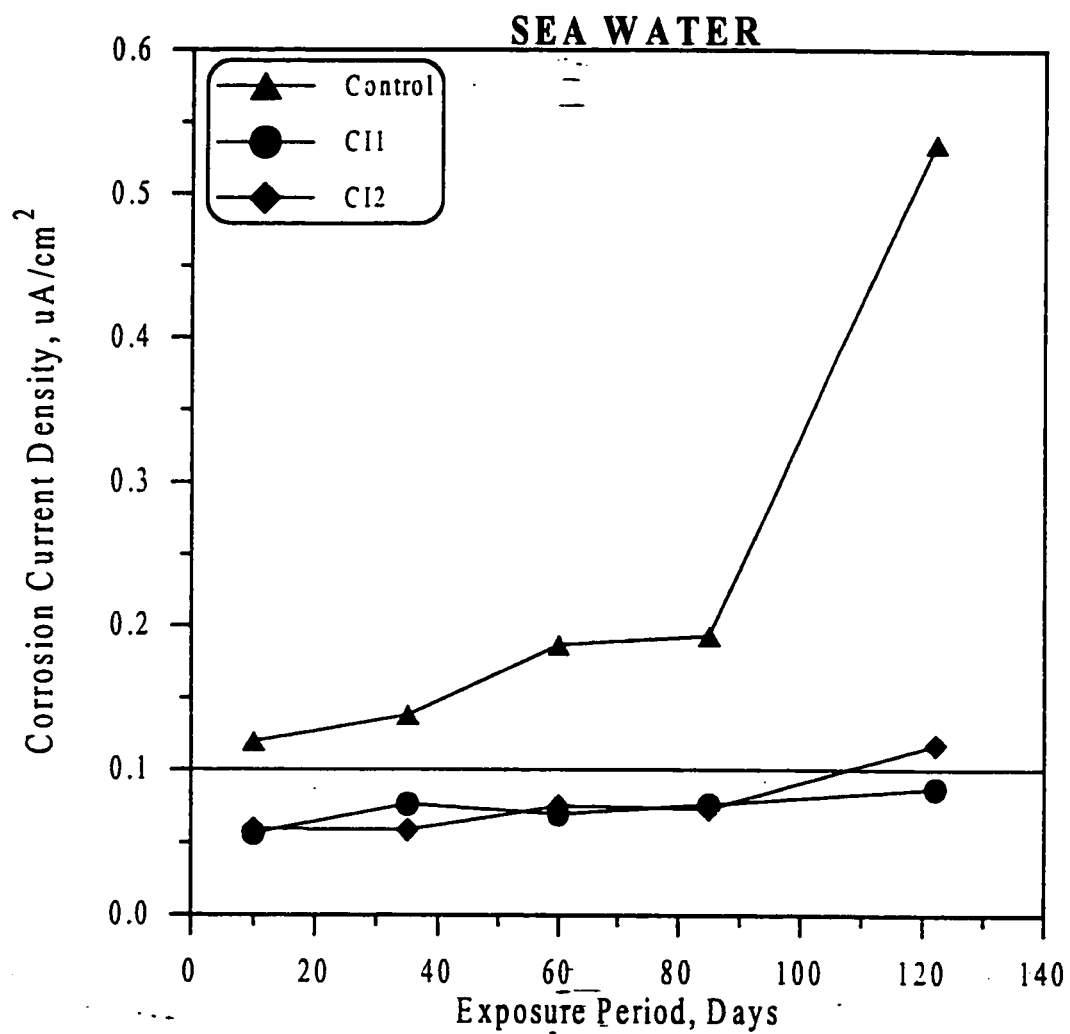


Figure 4.29: Corrosion Current Density in the Concrete Specimens made with Sea Water and Incorporating CI1 and CI2 Inhibitors

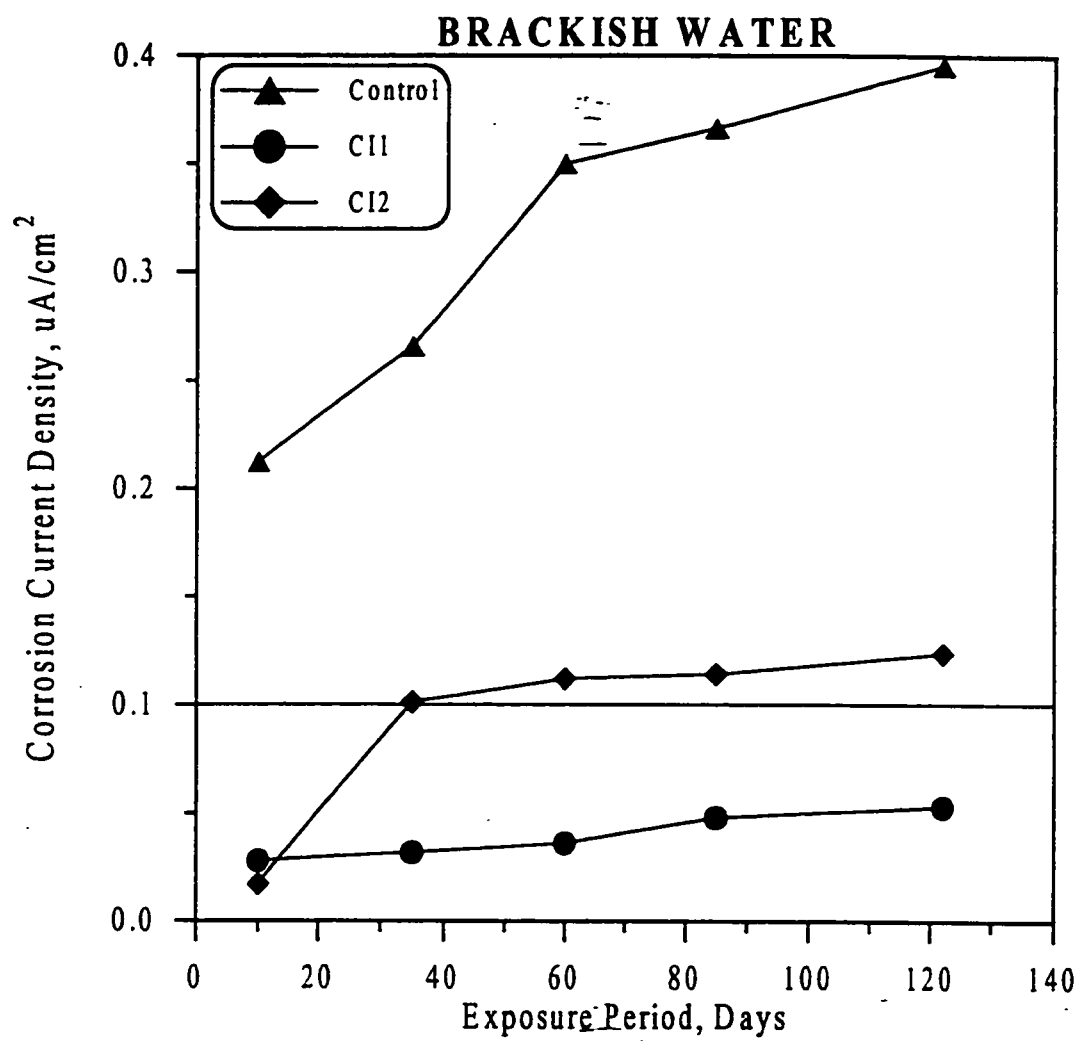


Figure 4.30: Corrosion Current Density in the Concrete Specimens made with Brackish Water and Incorporating CI1 and CI2 Inhibitors



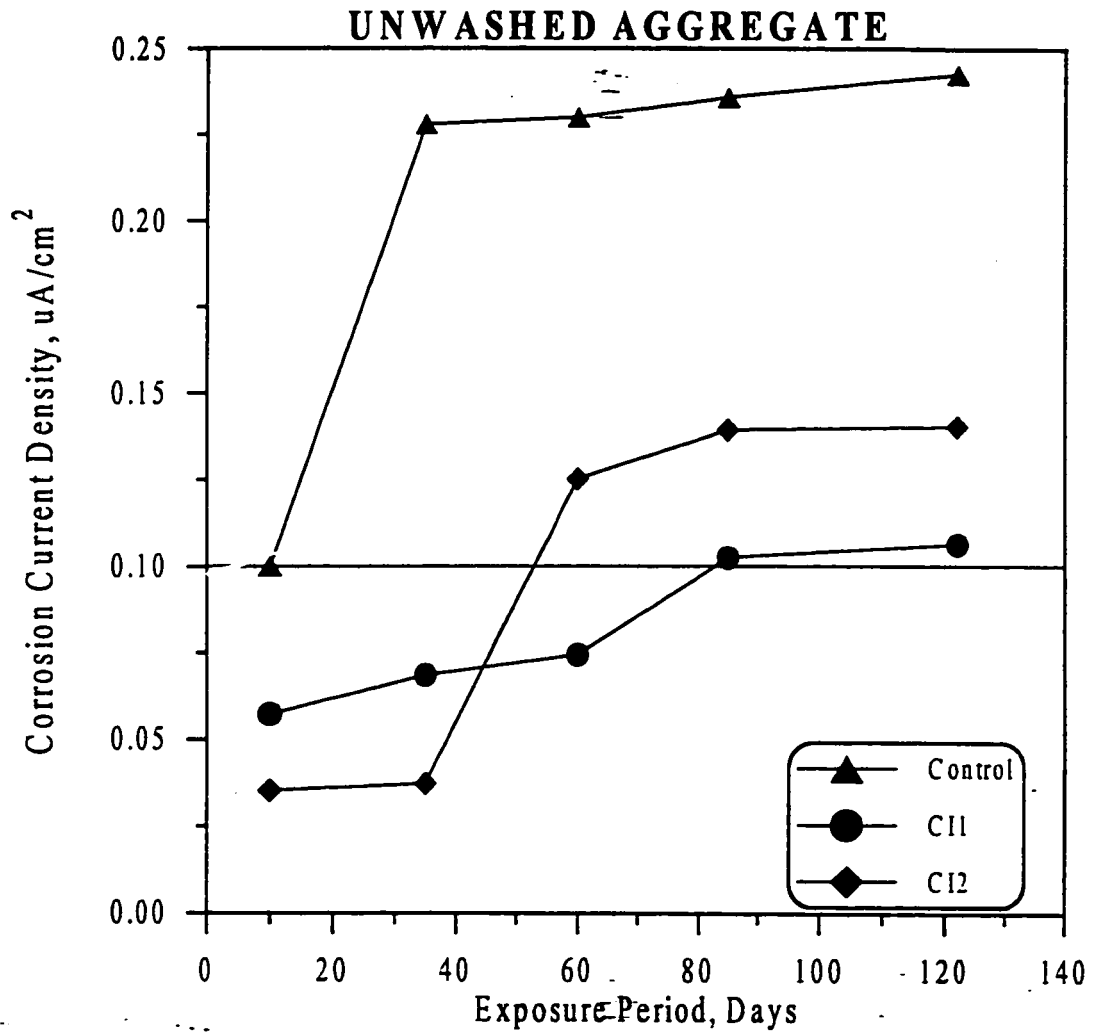


Figure 4.31: Corrosion Current Density in the Concrete Specimens made with Unwashed Aggregate and Incorporating CI1 and CI2 Inhibitors

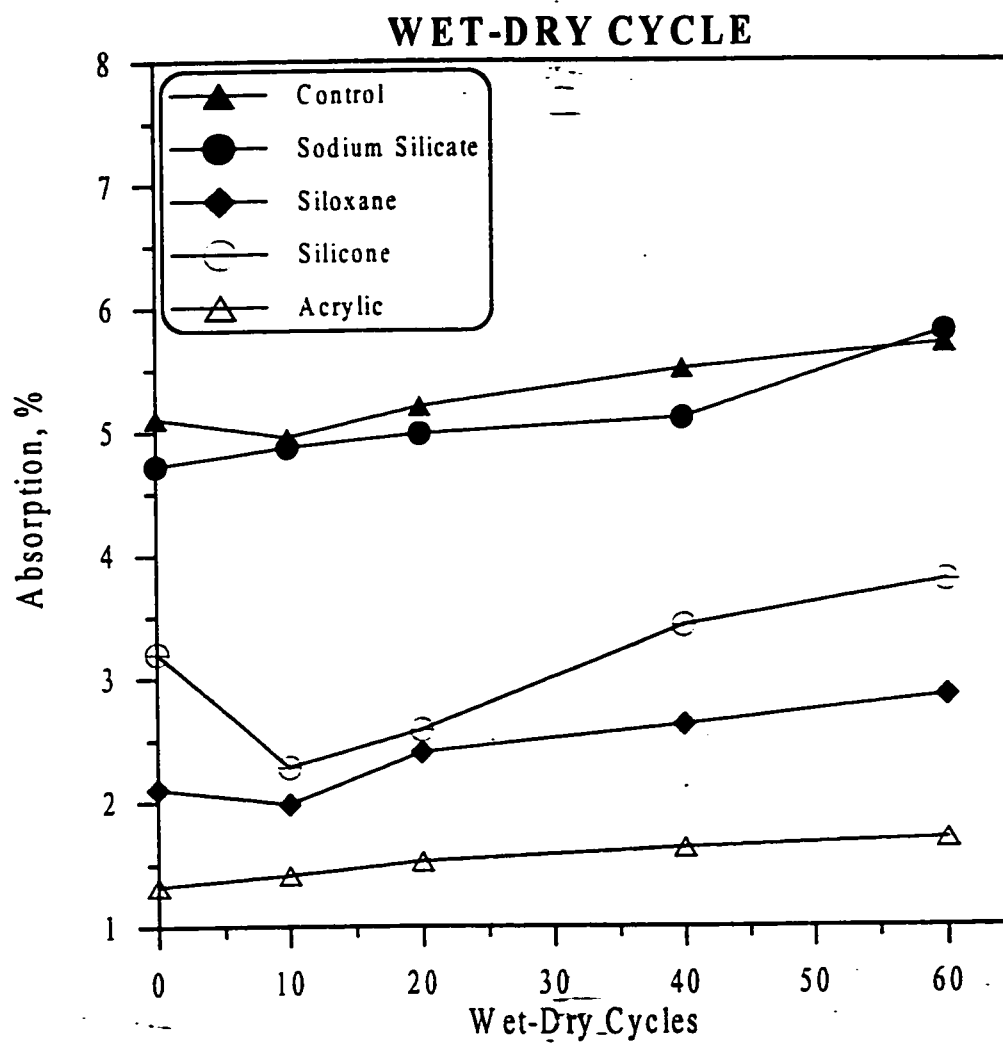


Figure 4.32: Water Absorption of the Coated and Uncoated Concrete Specimens Subjected to Wet-Dry Cycling

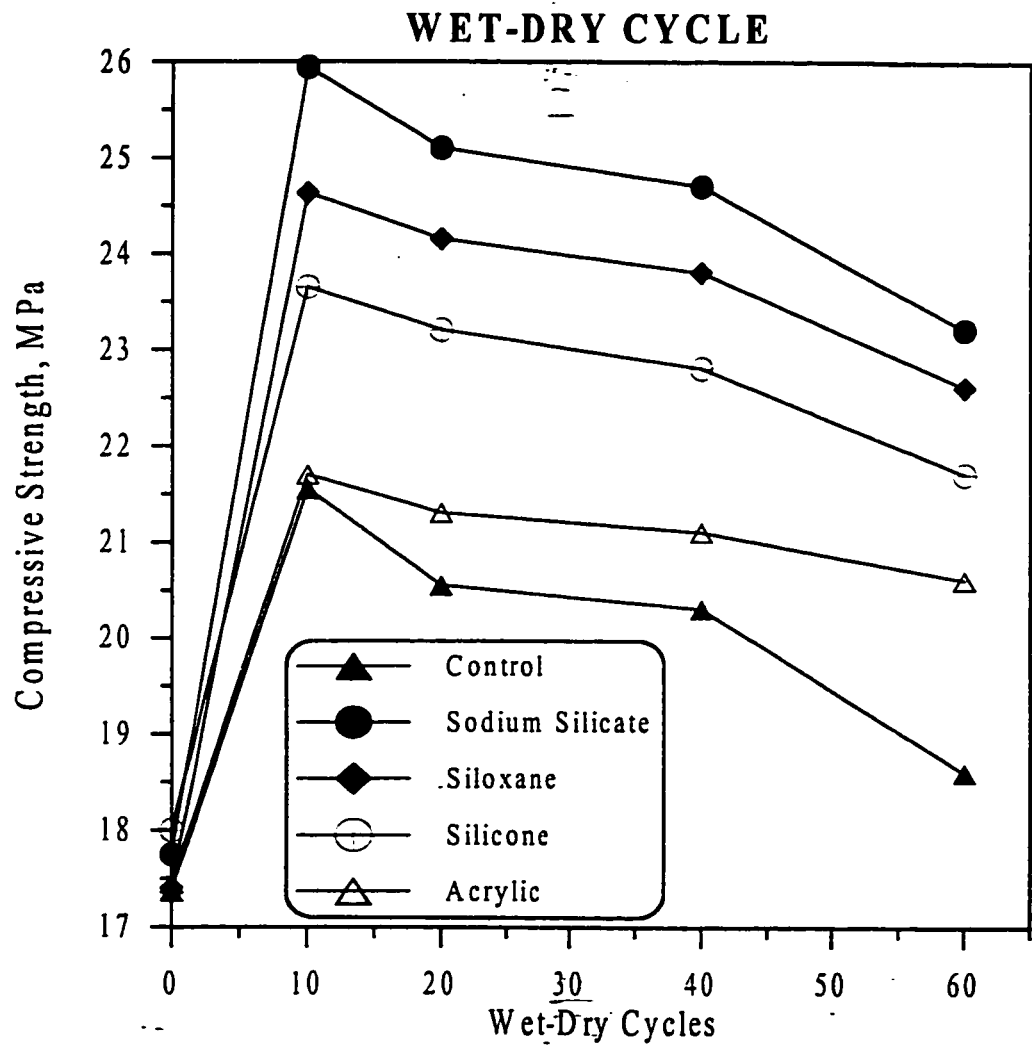


Figure 4.33: Compressive Strength of the Coated and Uncoated Concrete Specimens Subjected to Wet-Dry Cycling

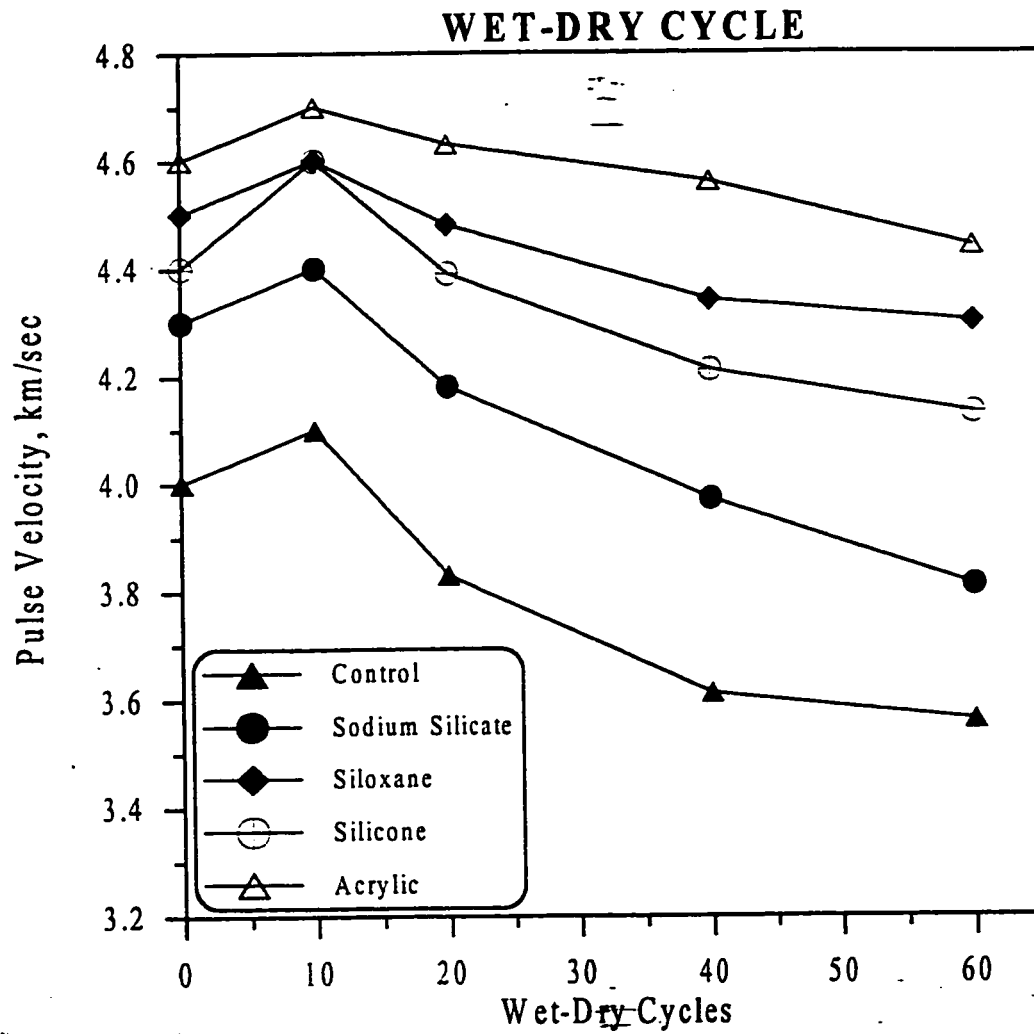


Figure 4.34: Pulse Velocity of the Coated and Uncoated Concrete Specimens Subjected to Wet-Dry Cycling

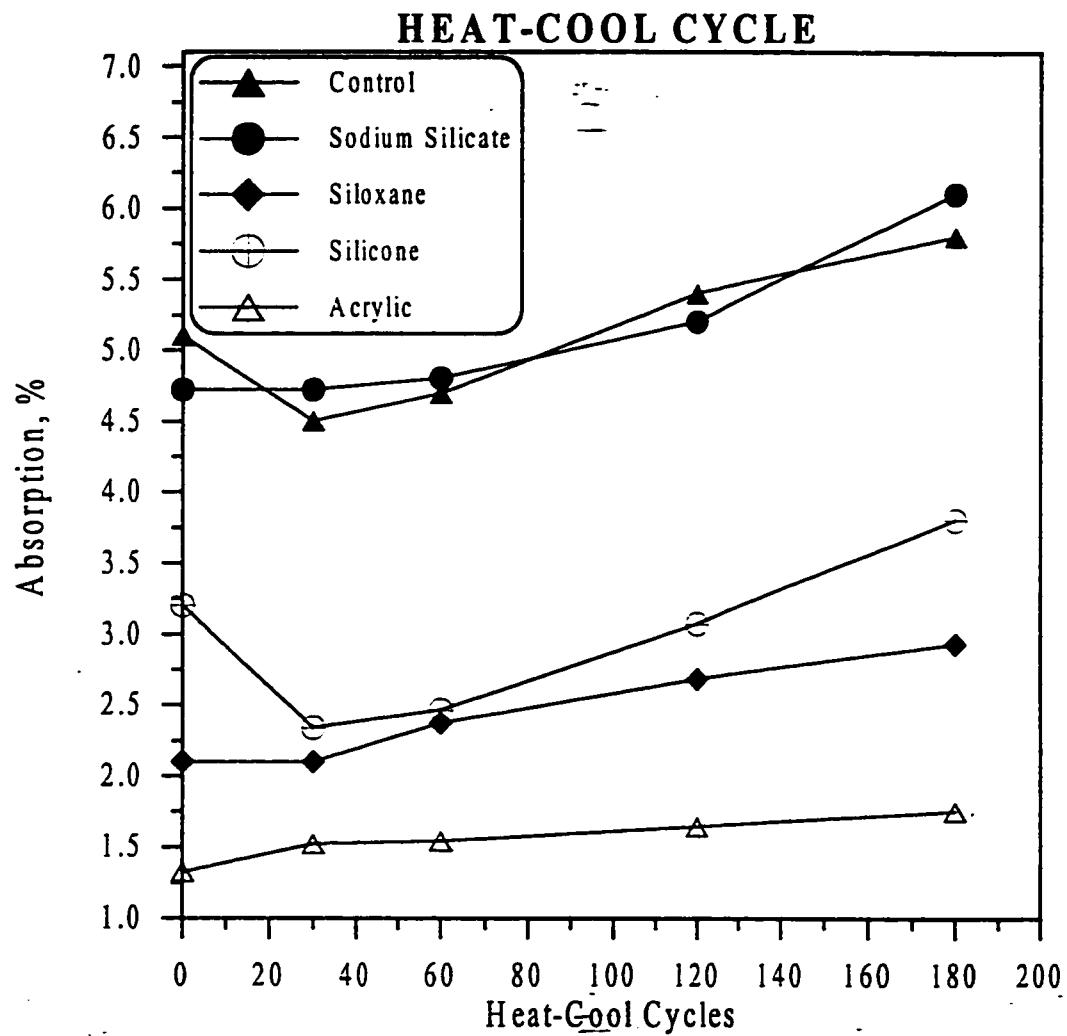


Figure 4.35: Water Absorption of the Coated and Uncoated Concrete Specimens Subjected to Heat-Cool Cycling

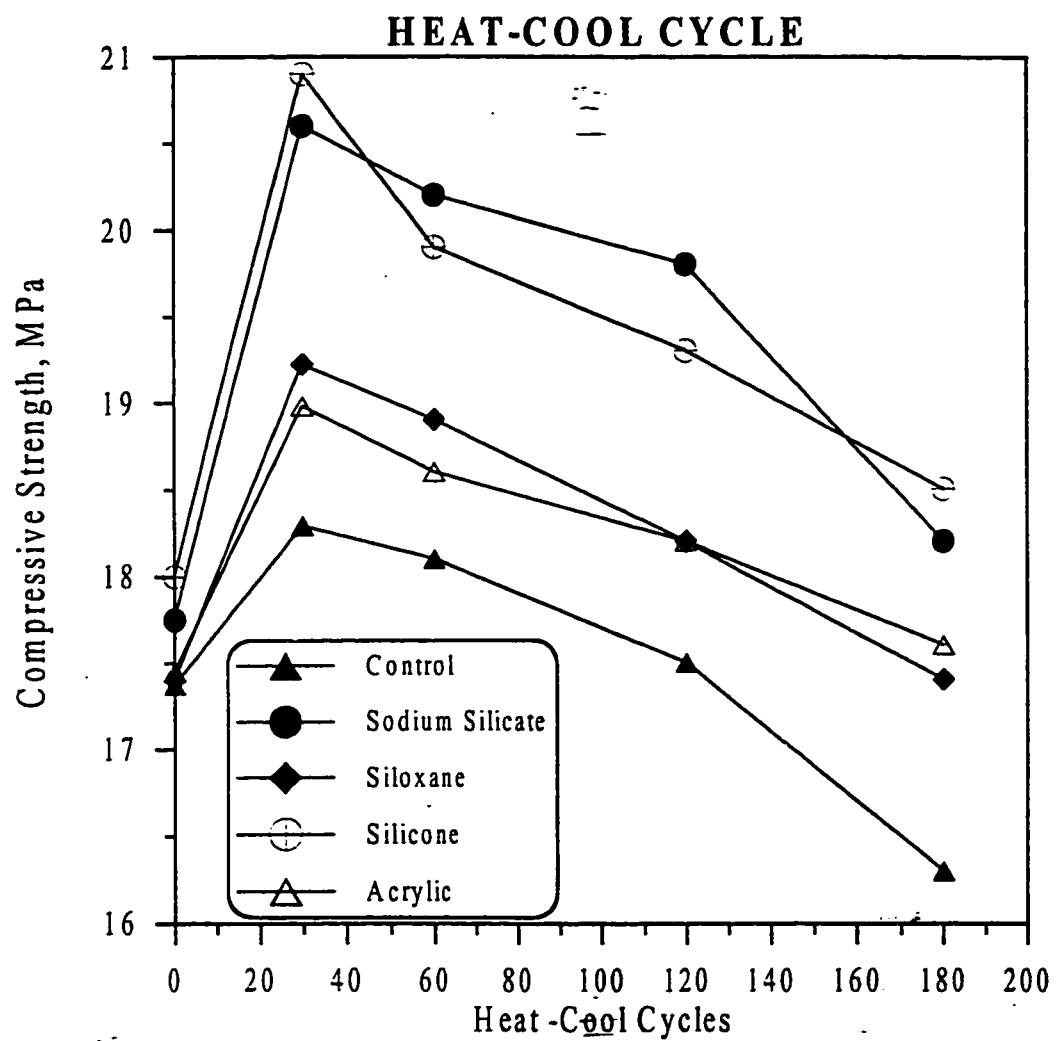


Figure 4.36: Compressive Strength of the Coated and Uncoated Concrete Specimens Subjected to Heat-Cool Cycling

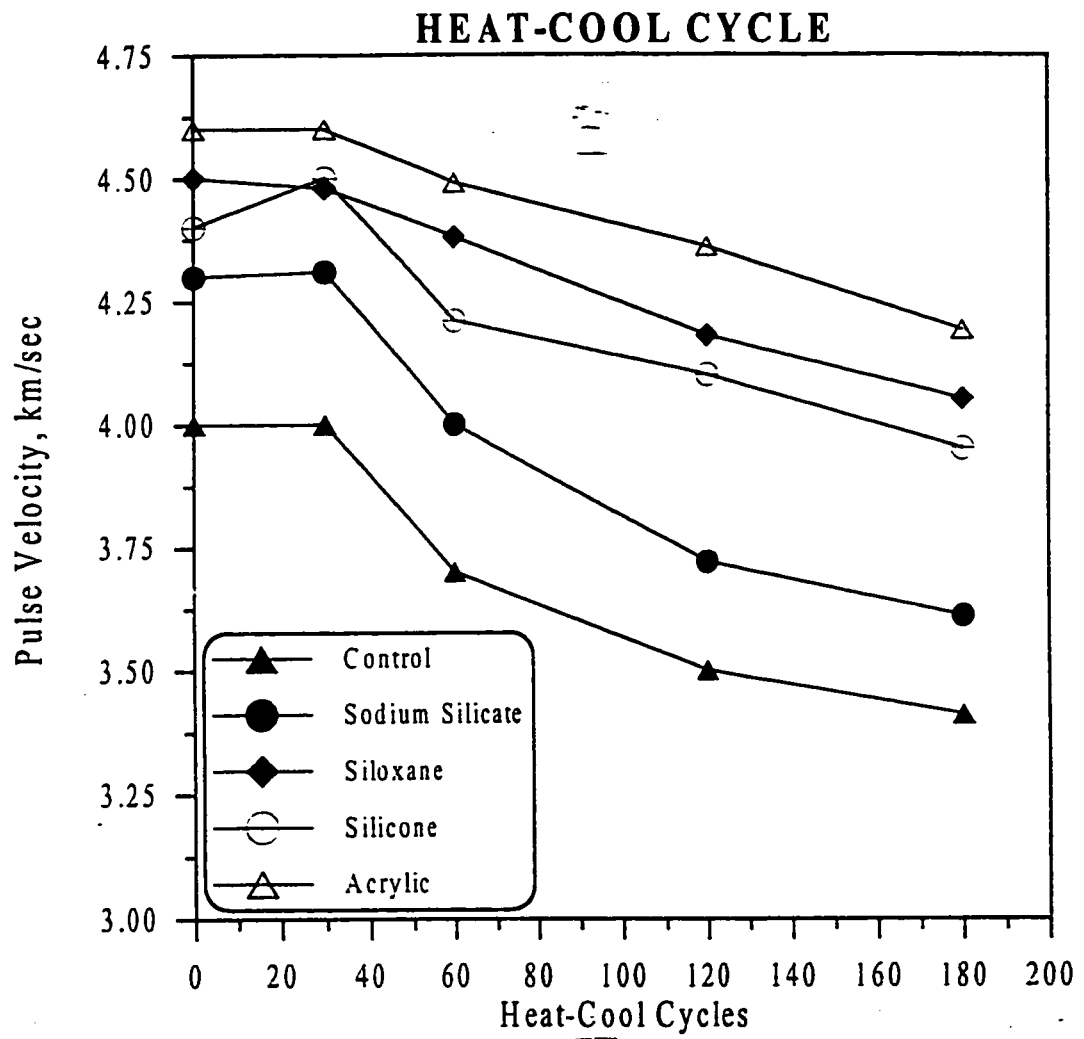


Figure 4.37: Pulse Velocity of the Coated and Uncoated Concrete Specimens Subjected to Heat-Cool Cycling

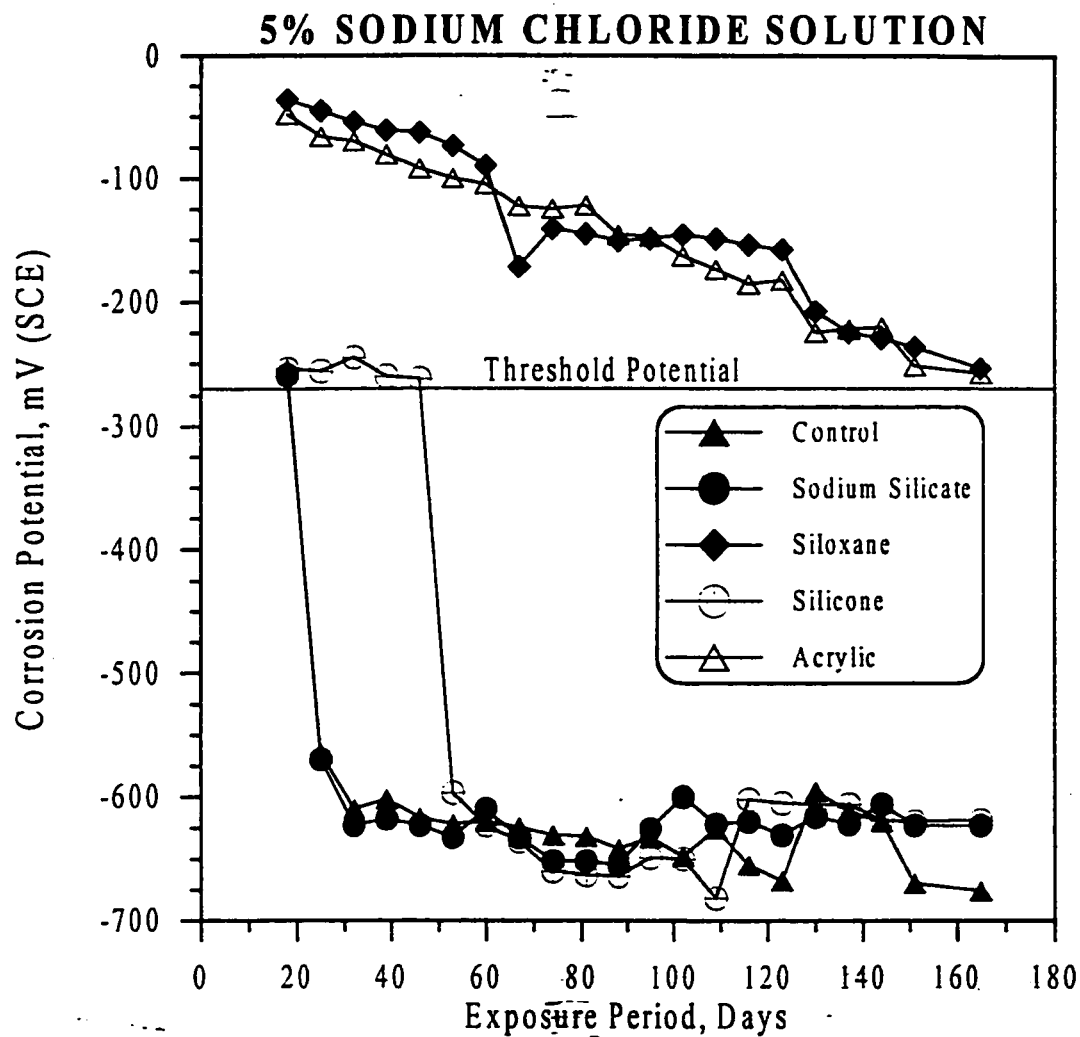


Figure 4.38: Corrosion Potentials on Steel in the Coated and Uncoated Concrete Specimens Exposed to 5% Sodium Chloride Solution



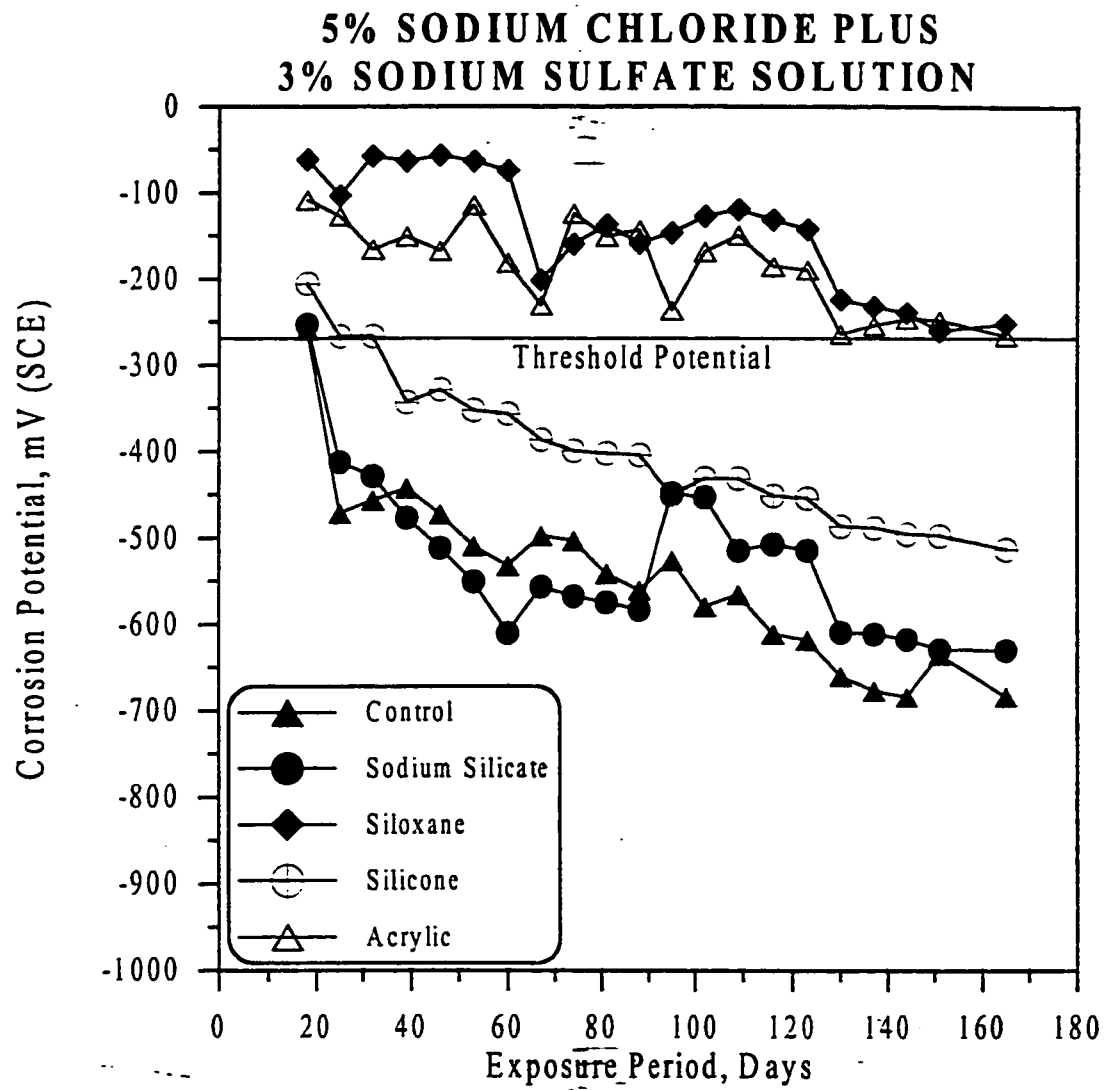


Figure 4.39: Corrosion Potentials on Steel in the Coated and Uncoated Concrete Specimens Exposed to 5% Sodium Chloride plus 3% Sodium Sulfate Solution

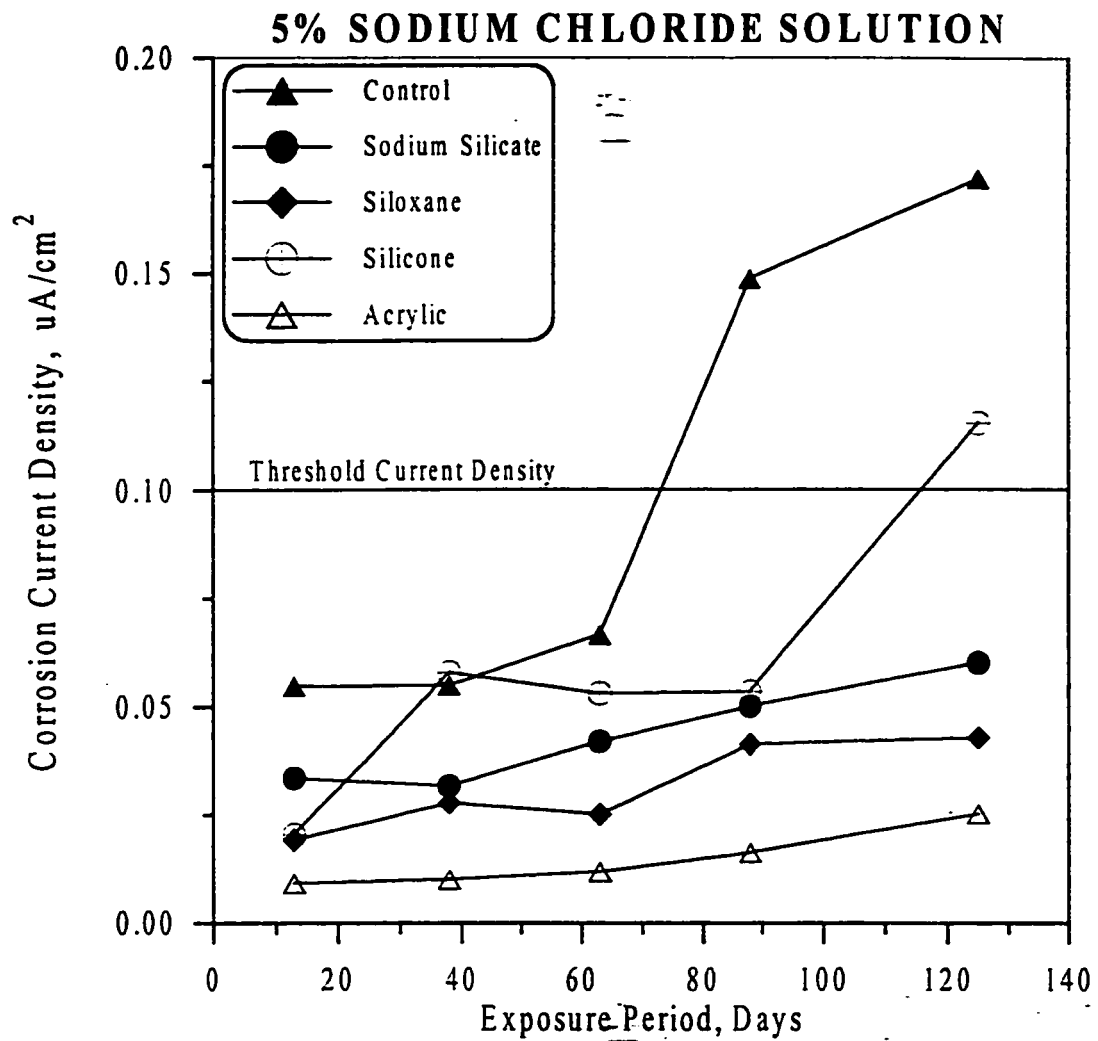


Figure 4.40: Corrosion Current Density on Steel in the Coated and Uncoated Concrete Specimens Exposed to 5% Sodium Chloride Solution

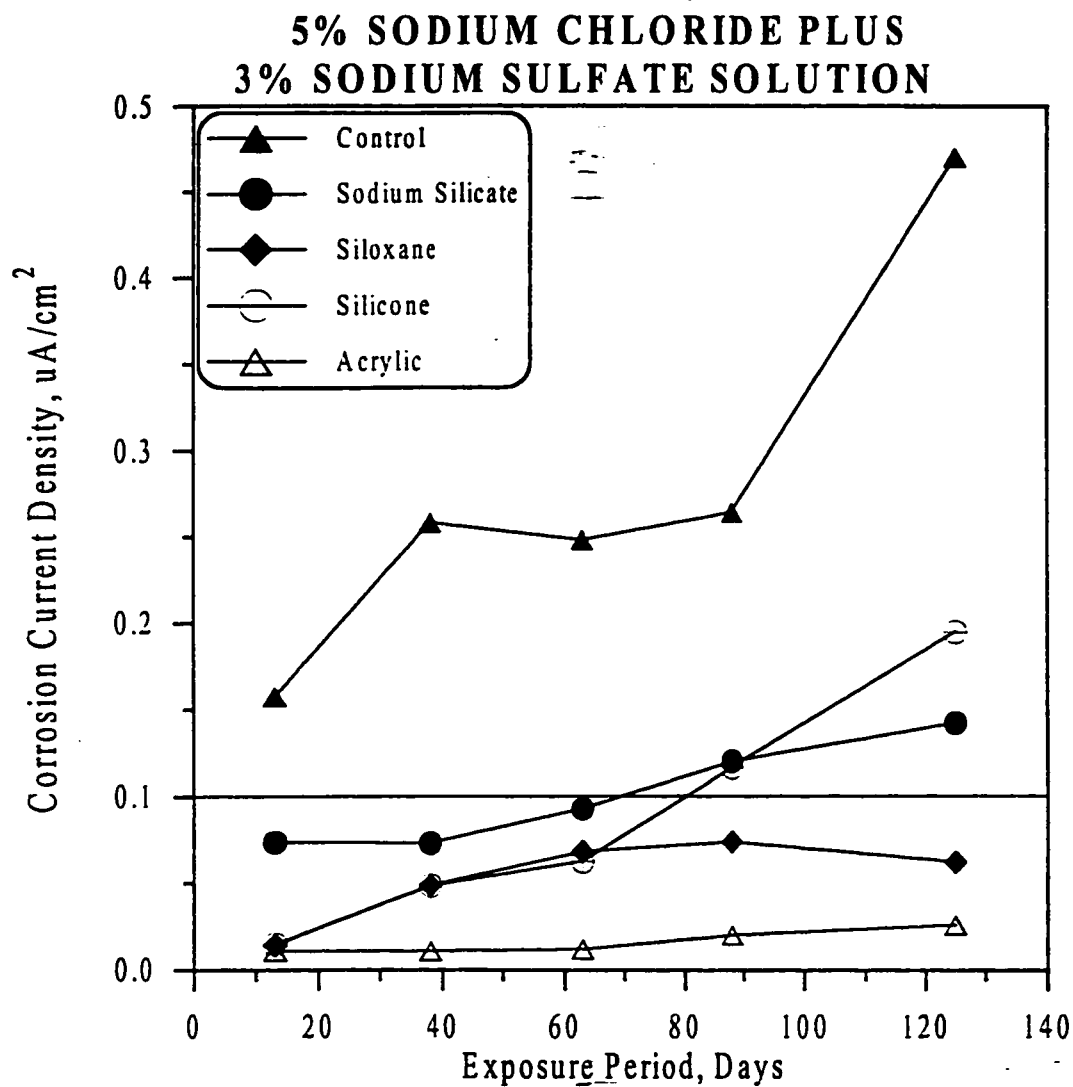


Figure 4.41: Corrosion Current Density on Steel in the Coated and Uncoated Concrete Specimens Exposed to 5% Sodium Chloride plus 3% Sodium Sulfate Solution

## CHAPTER 5

### CONCLUSIONS

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This research program was conducted to assess the effectiveness of corrosion inhibitors and concrete surface coatings in retarding reinforcement corrosion. Based on the results developed in this investigation, the following conclusions can be drawn:

1. The compressive strength of the concrete specimens incorporating all the inhibitors investigated in this study was more than that of the control specimens. The increase in strength varied from 4% in the specimens incorporating CII inhibitor, to 14.5% in the specimens made with 4% calcium nitrate. This indicates that all the corrosion inhibitors used in this study do not adversely affect the compressive strength of concrete.
2. Calcium nitrite was efficient in delaying the initiation of reinforcement corrosion in the concrete specimens contaminated with chloride, chloride plus sulfate and those made with sea water. In the concrete specimens made with brackish water or unwashed aggregate, however, all the inhibitors were generally effective in delaying the initiation of reinforcement corrosion.

3. The data on corrosion current density ( $I_{\text{corr}}$ ) on steel in the concrete specimens incorporating all the corrosion inhibitors investigated in this study, indicated that the rebars were in a passive state, even after 122 days of exposure. However, active corrosion was indicated on the bars in the concrete specimens without inhibitors right from the initial stages of exposure.
4. All the inhibitors were generally effective in retarding the rate of reinforcement corrosion in the chloride-contaminated concrete specimens.
5. In the concrete specimens contaminated with 0.8% chloride plus 1.5% sulfate, the minimum  $I_{\text{corr}}$  values were observed on the steel in the specimens incorporating 4% calcium nitrite and 3% calcium nitrate.
6. In the concrete specimens made with sea water, 2% calcium nitrite was more effective in minimizing reinforcement corrosion than the other inhibitors.
7. In the concrete specimens made with brackish water, all the inhibitors, except CI2, were efficient in minimizing reinforcement corrosion. In the concrete specimens made with unwashed aggregate, CI1 and CI2 inhibitors were not effective in retarding reinforcement corrosion. In the concrete specimens made with brackish water, calcium nitrite and calcium nitrate inhibitors were useful

in maintaining the passivity of the rebars.

8. The depth of carbonation in the control mortar specimens (i.e. without inhibitor) was higher than that in the specimens incorporating the inhibitors. The depth of carbonation in the mortar specimens incorporating the inhibitors increased in the following manner:

**CI2 > CI1 > Calcium Nitrate > Calcium Nitrite**

9. The depth of carbonation increased with the exposure period. The depth of carbonation in the mortar specimens, with and without inhibitors, was generally more in the contaminated specimens than the uncontaminated specimens, and increased in the following manner:

**No Contamination < Chloride < Sea Water < Chloride plus Sulfate**

10. The water absorption in the uncoated concrete specimens and those coated with sodium silicate and exposed to wet-dry cycles was more than that in the specimens coated with the other coatings. The lowest water absorption, after 60 wet-dry cycles, was observed in the specimens coated with acrylic coating and siloxane. The water absorption in both the coated and uncoated concrete

specimens increased with the number of wet-dry cycles. This phenomenon may be attributed to the development of micro-cracks ascribable to moisture variation.

11. An initial increase in the compressive strength was observed in the coated and uncoated concrete specimens till 10 wet-dry cycles. Thereafter, there was a reduction in the compressive strength in both the coated and uncoated concrete specimens. This reduction may be attributed to the development of micro-cracks. After 60 wet-dry cycles, the minimum compressive strength was indicated in the uncoated concrete specimens.
12. The pulse velocity in the uncoated concrete specimens was less than that in the coated specimens. The highest pulse velocity was noted in the concrete specimens coated with the acrylic coating. An increase in the pulse velocity was noted in all the specimens till 10 wet-dry cycles. Thereafter, there was a steady reduction in the pulse velocity in all the specimens. Again, such a reduction may be attributed to the development of micro-cracks.
13. A steady increase in the water absorption was observed in all the coated and uncoated specimens due to thermal variations, particularly after 30 heat-cool cycles. This may be attributed to the development of micro-cracks due to

thermal variations.

14. An increase in the compressive strength in all the concrete specimens was observed till 30 heat-cool cycles. This increase may be attributed to the accelerated initial hydration of cement. Thereafter, there was a consistent decrease in the compressive strength of all the coated and uncoated concrete specimens. This may be attributed to the development of micro-cracks created due to temperature variation.
15. The pulse velocity in the uncoated concrete specimens was less than that in the coated specimens. The highest pulse velocity was noted in the specimens coated with the acrylic coating. A steady decrease in the pulse velocity in all the uncoated and coated concrete specimens was observed with increasing heat-cool cycles.
16. The corrosion potentials on steel in the concrete specimens coated with the acrylic coating and siloxane, and exposed to the 5% sodium chloride and 5% sodium chloride plus 3% sodium sulfate solutions, were less negative than the ASTM C 876 threshold value of -270 mV SCE, even after 165 days of exposure. This indicates the excellent performance of siloxane and acrylic coating in delaying the time to initiation of reinforcement corrosion.



compared to the other coatings investigated in this study.

17. The corrosion current density ( $I_{\text{corr}}$ ) on steel in the concrete specimens coated with the acrylic coating and siloxane was less than that in the uncoated concrete specimens and those coated with the other coatings. This indicates that these two coatings are effective in extending the time to initiation of reinforcement corrosion and decreasing its rate, thus enhancing the useful service-life of concrete structures coated with them.
18. Among all the surface coatings used in this study, acrylic coating, which is a two-component cement-based acrylic-modified water proofing coating, and siloxane, which is siloxane-based deep penetrating coating, were the most effective against concrete deterioration.

## CHAPTER 6

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