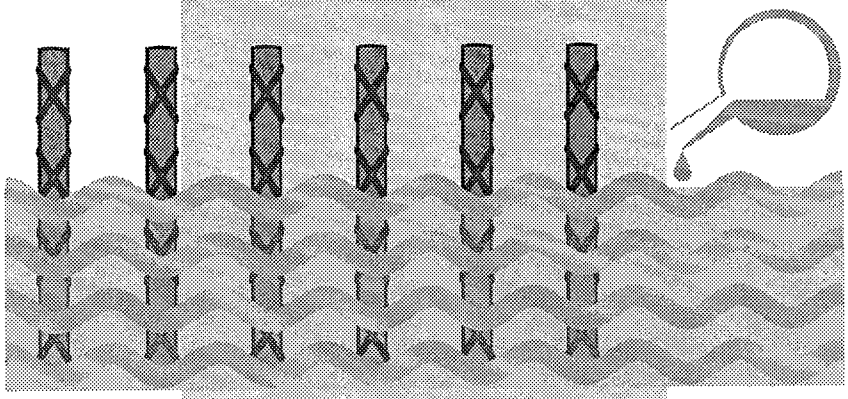
FINAL REPORT

PB98-156037

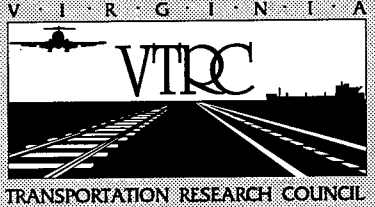
CORROSION PROTECTION PERFORMANCE OF CORROSION INHIBITORS AND EPOXY-COATED REINFORCING STEEL IN A SIMULATED CONCRETE PORE WATER SOLUTION



WIOLETA A. PYĆ
Research Associate
Charles E. Via Department of Civil Engineering
Virginia Polytechnic Institute & State University

RICHARD E. WEYERS
Professor
Charles E. Via Department of Civil Engineering
Virginia Polytechnic Institute & State University

MICHAEL M. SPRINKEL
Research Manager
Virginia Transportation Research Council



REPRODUCED BY:
U.S. Department of Commerce
National Technical Information Service
Springfield, Virginia 22161

Standard Title Page - Report on State Project

Report No.	Report Date	No. Pages	Type Report: Final	Project No.: 9812-010-940
VTRC 98-R42	June 1998	46	Period Covered: 1-1-93 through 6-30-98	Contract No.

Title and Subtitle:
Corrosion Protection Performance of Corrosion Inhibitors and Epoxy-Coated Reinforcing Steel in a Simulated Concrete Pore Water Solution

Key Words:
Corrosion-inhibitor admixtures, epoxy-coated reinforcing steel, corrosion of steel in concrete, concrete pore solution, solution testing

Authors:
W. A. Pyč, R. E. Weyers, and M. M. Sprinkel

Performing Organization Name and Address:

Virginia Polytechnic Institute
Blacksburg, VA

Virginia Transportation Research Council
530 Edgemont Road
Charlottesville, VA 22903

Sponsoring Agencies' Name and Address

Virginia Department of Transportation
1401 E. Broad Street
Richmond, VA 23219

Supplementary Notes

Abstract

We used a simulated concrete pore water solution to evaluate the corrosion protection performance of concrete corrosion-inhibiting admixtures and epoxy-coated reinforcing bars (ECR). We evaluated three commercial corrosion inhibitors, ECR from three coaters removed from job sites, one ECR shipped directly from the coater's plant, and one ECR removed from a job site plus a corrosion inhibitor. The corrosion inhibitors were calcium nitrite, an aqueous mixture of esters and amines, and a mixture of alcohol and amine. Corrosion protection performance was based on the amount of visually observed corroded surface area.

For bare steel tested with and without corrosion inhibitors, corrosion increased with increasing chloride concentration, and specimens saturated with oxygen were more corroded than specimens saturated with breathing air. The amount of corrosion over the 90-day test period was controlled by the amount of oxygen in solution at the higher chloride concentrations. The ester-amine and alcohol-amine did not inhibit corrosion. Calcium nitrite inhibited corrosion at all levels of chloride concentration.

For ECR, corrosion occurred both at sites where the coating was damaged and underneath the coating. Coating debondment was greatest in pore water solutions containing chloride. The least coating debondment and corrosion occurred with the solution containing calcium nitrite and the ECR shipped directly from the manufacturer. Coating debondment and corrosion of ECR are directly related to the amount of damage as holes; mashed, dented, and cracked areas; and holidays.

The researchers recommend that the developed test method be adopted as a standard test for concrete corrosion inhibitors and that calcium nitrite remain the only concrete corrosion inhibitor approved for use in Virginia.

FINAL REPORT

CORROSION PROTECTION PERFORMANCE OF CORROSION INHIBITORS AND EPOXY-COATED REINFORCING STEEL IN A SIMULATED CONCRETE PORE WATER SOLUTION

Wioleta A. Pyć
Research Associate
Charles E. Via Department of Civil Engineering
Virginia Polytechnic Institute and State University

Richard E. Weyers
Professor
Charles E. Via Department of Civil Engineering
Virginia Polytechnic Institute and State University

Michael M. Sprinkel
Research Manager
Virginia Transportation Research Council

(The opinions, findings, and conclusions expressed in this report
are those of the authors and not necessarily those
of the sponsoring agencies.)

Virginia Transportation Research Council
(A Cooperative Organization Sponsored Jointly
by the Virginia Department of Transportation
and the University of Virginia)

Charlottesville, Virginia

VTRC 98-R42
June 1998

Copyright 1998 by the Virginia Department of Transportation.

ABSTRACT

We used a simulated concrete pore water solution to evaluate the corrosion protection performance of concrete corrosion-inhibiting admixtures and epoxy-coated reinforcing bars (ECR). We evaluated three commercial corrosion inhibitors, ECR from three coaters removed from job sites, one ECR shipped directly from the coater's plant, and one ECR removed from a job site plus a corrosion inhibitor. The corrosion inhibitors were calcium nitrite, an aqueous mixture of esters and amines, and a mixture of alcohol and amine. Corrosion protection performance was based on the amount of visually observed corroded surface area.

For bare steel tested with and without corrosion inhibitors, corrosion increased with increasing chloride concentration, and specimens saturated with oxygen were more corroded than specimens saturated with breathing air. The amount of corrosion over the 90-day test period was controlled by the amount of oxygen in solution at the higher chloride concentrations. The ester-amine and alcohol-amine did not inhibit corrosion. Calcium nitrite inhibited corrosion at all levels of chloride concentration.

For ECR, corrosion occurred both at sites where the coating was damaged and underneath the coating. Coating debondment was greatest in pore water solutions containing chloride. The least coating debondment and corrosion occurred in the solution containing calcium nitrite and the ECR shipped directly from the manufacturer. Coating debondment and corrosion of ECR are directly related to the amount of damage as holes; mashed, dented, and cracked areas; and holidays.

The researchers recommend that the developed test method be adopted as a standard test for concrete corrosion inhibitors and that calcium nitrite remain the only concrete corrosion inhibitor approved for use in Virginia.

CORROSION PROTECTION PERFORMANCE OF CORROSION INHIBITORS AND EPOXY-COATED REINFORCING STEEL IN A SIMULATED CONCRETE PORE WATER SOLUTION

Wioleta A. Pyć
Research Associate
Charles E. Via Department of Civil Engineering
Virginia Polytechnic Institute and State University

Richard E. Weyers
Professor
Charles E. Via Department of Civil Engineering
Virginia Polytechnic Institute and State University

Michael M. Sprinkel
Research Manager
Virginia Transportation Research Council

INTRODUCTION

The extent of the rapid deterioration of reinforced concrete bridges from corrosion induced by chloride ion is well known, and a multitude of corrosion abatement techniques have been developed for existing and newly constructed bridges. Epoxy-coated reinforcing steel (ECR) and corrosion-inhibiting admixtures were developed to extend the service life of newly constructed concrete bridge components. ECR is the most used corrosion protection method for concrete bridges in the United States. Corrosion inhibitors have been used for more than 20 years but significantly less frequently than ECR and in Virginia primarily in precast-prestressed members.

Until 1986 when Florida reported that the Long Key Bridge showed signs of corrosion only 6 years after construction, the effectiveness of ECR remained unquestioned. Since then, 12 field studies have been conducted on the effectiveness of ECR.[1] Conclusions have been mixed, but studies in which appropriate evaluation methods and failure criteria were employed concluded that ECR will not provide 50 years of corrosion protection for steel in concrete bridge components.[2,3] More recent studies, including one in Virginia, support this conclusion.[4,5] As a result of these recent findings, interest in the effectiveness of corrosion-inhibiting admixtures has increased.

The Virginia Department of Transportation (VDOT) initiated a study to compare the corrosion protection performance of different systems for newly constructed concrete bridges. These included ECR (present and new coatings), galvanized reinforcing steel, three commercial corrosion-inhibiting admixtures, low-permeability concretes, and two

dual corrosion protection systems (a corrosion inhibitor and ECR, and a corrosion inhibitor and low-permeability concrete).

The corrosion protection effectiveness was assessed in both a simulated concrete pore water solution and in concrete. A field study of three 8-year-old substructures in a marine environment and three 17-year-old bridge decks in a deicer salt environment was also conducted to evaluate ECR. This report presents the results of the study using a simulated concrete pore water solution to assess the effectiveness of corrosion inhibitors and ECR.

PURPOSE AND SCOPE

The purpose of this study was to evaluate the corrosion protection effectiveness of ECR and corrosion inhibitors in a simulated concrete pore water solution. The solution contained concentrations of chloride and corrosion inhibitors equivalent to those in concrete pore water. Corrosion was accelerated by elevating the temperature and oxygen content of the solution. Corrosion protection effectiveness was assessed by visual observation and other corrosion indicators.

ECRs from four coaters were evaluated, three from construction sites in Virginia and one with a new Canadian coating. Three commercial corrosion inhibitors were evaluated: DCI, R222, and A2000.

METHODS

We compared the condition of ECR and bare steel after an immersion test using various solutions. We evaluated the specimens for corrosion using a series of corrosion performance test indicators.

Materials

Bare Steel

The bare steel bars used in this study was manufactured by Resco Steel, Roanoke, Virginia. The bars were No. 5, Grade 60, steel and had a diameter of 16 mm, a tensile strength of 645 to 703 MPa, a yield point of 425 to 473 MPa, and an elongation of 10 percent (using a 200 mm gage length). The chemical composition was 0.38 to 0.43 percent C, 0.83 to 1.00 percent Mn, 0.03 to 0.05 percent S, and 0.01 percent P. The bars were stored indoors, in the laboratory, before they were prepared for the experiment.

A band saw was used to cut the bars into 80 specimens 152 mm long. The specimens were soaked in hexane for 24 hours to remove any grease and dirt on the surface.

ECR

We evaluated ECRs, No. 5 bars, from four sources: three U.S. manufacturers (FS, LNE, and FSC) and one Canadian manufacturer (CGN). The ECR manufactured in the United States was collected at the construction site and stored outside uncovered for 30 days before it was brought into the laboratory and stored under a black plastic cover until used. Thus, they were exposed to the natural environment and had surface damage attributable to the transportation to and handling at the job site. The ECRs from Canada was in perfect condition. Each bar was packed separately and shipped directly from the manufacturer.

ECRs were cut into 120 specimens 152 mm long using a hand-held band saw. The thickness of the coating of 3 specimens from each manufacturer was measured in accordance with ASTM G 12-83 using the coating thickness gauge Minitest 500 produced by Elektro-Phisik (Germany). Coating thickness was measured in three locations: on the radial ribs, on the longitudinal ribs, and between ribs. The mean, standard deviation, and coefficient of variation were determined for each set of measurements and for the whole specimen (bar).

Each specimen was evaluated for damage. Any cracks in the coating; holes; and mashed, scraped, or dented areas were recorded. The Tinker & Rasor Model M/1 holiday detector was used in accordance with ASTM G 62-87 to detect any flaws (holidays) in the coating not visible to the unaided eye.

Percent damage was calculated, and specimens were divided into 0 and 1 percent damage groups within each specimen type except for the Canadian bars. The Canadian specimens had only minor defects and single holidays, so the coating was assumed to be perfect with 0 percent damage for the entire group. Each percent damage group was then divided into test groups of three specimens each, and the specimens were exposed to the same solution types.

Plastic caps were attached to the cut ends using a hot melt glue and a glue gun to protect the bare ends from corrosion during the immersion test.

Corrosion Inhibitors

Three corrosion inhibitors were evaluated in this study: DCI, R222, and A2000, produced by three manufacturers, two in the United States and one in Europe. According to the manufacturers, DCI contains 30 percent calcium nitrite and 70 percent water, R222 is an aqueous mixture of amines and esters, and A2000 is a mixture of alcohol and amine. The main difference among them is that R222 and A2000 are organic based and DCI is not.

Test Solutions

The pore solution used in this study was based on work of Diamond.[6] The basic composition was 0.25 M KOH, 0.2 M NaOH, and 0.004 M $Ca(OH)_2$. NaCl was added in various quantities to produce the corrosive environment. Three corrosion inhibitors were added to the pore solution to evaluate their protective properties against corrosion caused by chloride ions present in the solutions.

Four amounts of NaCl were added to the pore solution to give the desired Cl-/OH- ratio. NaCl quantities added to solutions were calculated from the solution composition similar to the expected Cl^-/OH^- ratios.

The pore water content of concrete ranges from 3 to 5 percent by weight.[7] Considering drying effects and the fact that the concrete used in Virginia has a low water-cementitious material ratio (w/c) (0.45), the 3 percent weight was selected and used in this study. The equivalent chloride content in 1 cubic meter of concrete was then calculated based on the chloride content of test solutions considering that all the sodium chloride dissolved in the concrete pore water solution.

The corrosion inhibitors were used in accordance with the manufacturers' recommendations for addition to concrete. We assumed that all of corrosion inhibitors would be dissolved in the concrete pore water. Only one of the corrosion inhibitors (DCI) was used to produce a pore solution for testing ECR specimens with 1 percent damage. Other solutions with all types of corrosion inhibitors were used only to test the bare steel specimens. Table 1 shows the composition of the different pore solutions. Concentrations of the inhibitor in the pore solution were based on manufacturers' recommendations of 5 l/m^3 and 2.5 l/m^3 for R222 and A2000, respectively. For DCI, 20 l/m^3 was used based on the VDOT specification for prestressed members of 17.3 l/m^3 with a pozzolan and 25.7 l/m^3 without a pozzolan.

Immersion Test

Bare steel specimens and ECR specimens were tested through a 90-day immersion test at 40 °C in a simulated concrete pore water solution. The test temperature was determined from a series of measurements taken in concrete at reinforcing steel depths of 25 and 51 mm in Blacksburg, Virginia. Bare steel specimens used in this study were kept outdoors, and the temperature was measured throughout the year. The near highest summer temperature at the depth of the reinforcing steel was 40 °C. During a 7-day pretreatment period, specimens were kept in pore solution or pore solution with corrosion inhibitor.

After pretreatment, NaCl was added and the solutions were aerated with compressed oxygen (O_2) or breathing air (air) for 1 minute. Subsequently, the solutions were aerated with O_2 or air once a week throughout the 90-day test period during which

Table 1. Solution Composition

solution type	solution number, chlorides, kg/m^3	corrosion inhibitor concentration, l/m^3	Cl^-/OH^- ratio, 100% dissolution
PS (pore solution)	0.00	---	---
PS + NaCl	0.73 (17.4)[a]	---	0.5
PS + NaCl	1.47 (34.8)[a]	---	1
PS + NaCl	2.93 (69.6)[a]	---	2
PS + NaCl	5.86 (139.2)[a]	---	4
PS* + DCI	0.00	20 (370)[b]	---
PS* + DCI + NaCl	0.73 (17.4)[a]	20 (370)[b]	0.5
PS* + DCI + NaCl	1.47 (34.8)[a]	20 (370)[b]	1
PS* + DCI + NaCl	2.93 (69.6)[a]	20 (370)[b]	2
PS* + DCI + NaCl	5.86 (139.2)[a]	20 (370)[b]	4
PS + R222	0.00	5 (70)[a]	---
PS + R222 +NaCl	0.73 (17.4)[a]	5 (70)[a]	0.5
PS + R222 +NaCl	1.47 (34.8)[a]	5 (70)[a]	1
PS + R222 +NaCl	2.93 (69.6)[a]	5 (70)[a]	2
PS + R222 +NaCl	5.86 (139.2)[a]	5 (70)[a]	4
PS + A2000	0.00	2.5 (35)[a]	---
PS + A2000 + NaCl	0.73 (17.4)[a]	2.5 (35)[a]	0.5
PS + A2000 + NaCl	1.47 (34.8)[a]	2.5 (35)[a]	1
PS + A2000 + NaCl	2.93(69.6)[a]	2.5 (35)[a]	2
PS + A2000 + NaCl	5.86 (139.2)[a]	2.5 (35)[a]	4

PS* = pore solution with less water because of water in corrosion inhibitor (DCI = 30% solids + 70% water). [a]Grams/1000 g PS. [b]Grams/741 g PS*.

specimens were placed into closed polypropylene containers, covered with various pore solutions, and kept in the oven at 40 °C. Table 2 provides the immersion test configuration. Table 3 provides the number and type of specimens used in the immersion test and the various environments to which they were exposed.

After 4 weeks of immersion, the test specimens were visually examined. Afterward, visual examination was performed every 2 weeks for the remaining 90-day immersion period. Bare steel specimens were examined for the initiation and progress of

Table 2. Exposure Conditions in Immersion Test

solution type	aeration type	specimen type				
		bare steel	ECR-FS	ECR-LNE	ECR-FSC	ECR-CGN
PS	O_2	X	X	X	X	X
	air	X	---	---	---	---
PS + NaCl	O_2	X	X	X	X	X
	air	X	---	---	---	---
PS + CI	O_2	X	X	---	---	---
	air	X	---	---	---	---
PS + CI + NaCl	O_2	X	X	---	---	---
	air	X	---	---	---	---

the corrosion process. ECR specimens were checked for blister formation and the presence of the corrosion products.

Chloride Titration

Chloride ions present in the solutions were first calculated from the solution composition and then determined by solution titration. Hydroxide ions were also calculated from the solution composition and evaluated later by the calculations of OH- from the pH measurements with the electronic pH tester.

pH Testing

Once a week, the polypropylene containers with the specimens were taken from the oven to measure the pH of the solutions. The pH measurements were performed using the electronic pH tester, pHep, manufactured by Hanna Instruments (Mauritius) Ltd. The pH titration of chosen solutions was also performed to evaluate the results of pH measurements with the electronic pH tester.

Evaluation of Corrosion Protection Performance

Bare Steel

Bare steel specimens were visually examined after the 90-day immersion period. Later, microphotographs were taken to document the type of corrosion present on the

Table 3. Immersion Test Matrix

solution	aeration	specimen type											
		BS				ECR-FS			ECR-LNE		ECR-FSC		ECR-CGN
		DCI	R222	A2000	---	0	0.01	1% + DCI	0	0.01	0	0.01	0
PS	air				2								
	O_2				2	3	3		3	3	3	3	3
PS + CI	air	2	2	2									
	O_2	2	2	2				3					
PS + NaCl	air				2								
@ 0.73 kg/m^3	O_2				2	3	3		3	3	3	3	3
PS + CI + NaCl	air	2	2	2									
@ 0.73 kg/m^3	O_2	2	2	2				3					
PS + NaCl	air				2								
@ 1.47 kg/m^3	O_2				2	3	3		3	3	3	3	3
PS + CI + NaCl	air	2	2	2									
@ 1.47 kg/m^3	O_2	2	2	2				3					
PS + NaCl	air				2								
@ 2.93 kg/m^3	O_2				2	3	3		3	3	3	3	3
PS + CI + NaCl	air	2	2	2									
@ 2.93 kg/m^3	O_2	2	2	2				3					
PS + NaCl	air				2								
@ 5.86 kg/m^3	O_2				2	3	3		3	3	3	3	3
PS + CI + NaCl	air	2	2	2									
@ 5.86 kg/m^3	O_2	2	2	2				3					
Sum		80				45			30		30		15
Total		200											

steel surface. The corrosion area was estimated for each specimen, and the percent surface corrosion was calculated.

ECR

ECR specimens were visually examined after the 90-day immersion period. The number of blisters formed on each specimen was recorded. All blisters were opened, and the pH of the solution inside each blister was measured. The area under the blister was determined, and a visual examination for corrosion under the blister was performed.

The hardness of the epoxy coating was determined in accordance with ASTM D 3363-92a.

The adhesion of the epoxy coating to the steel was determined in accordance with the knife peel test (MTO, Draft 93 10 27, Hot Water Test for Epoxy-Coated Reinforcing Bars).

RESULTS AND DISCUSSION

Bare Steel

The corrosion observed on the bare steel specimens was a pitting corrosion. The area covered with corrosion products was larger for the solutions with the higher Cl- ion concentration, and the corrosion pits appeared to be deeper (see Table 4).

The specimens tested in the pore solution with no corrosion inhibitors, aerated with oxygen, developed the larger areas of corrosion on the steel surface in comparison to the specimens evaluated in pore solution aerated with air (see Figure 1).

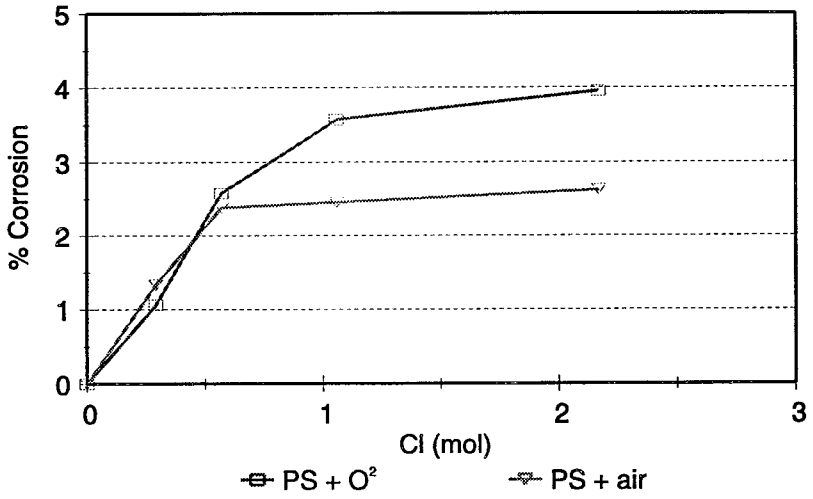


Figure 1. % Corrosion for Bare Steel Specimens Tested in PS; O_2 and Air Aeration

Table 4. Visual Examination of Bare Steel Specimens

specimen type	titrated Cl concentration, moles	corrosion type*	corrosion area, mm^2		% corrosion
			specimen 1	specimen 2	
BS 1 O_2	0	---	0	0	0
BS 2 O_2	0.3	pitting	71	46	1.07
BS 3 O_2	0.6	deeper pitting	141	142	2.58
BS 4 O_2	1.2	deeper pitting	180	212	3.57
BS 5 O_2	2.3	deepest pitting	219	215	3.96
BS 1 air	0	---	0	0	0
BS 2 air	0.3	pitting	76	71	1.34
BS 3 air	0.6	deeper pitting	129	132	2.38
BS 4 air	1.2	deeper pitting	137	132	2.45
BS 5 air	2.3	deepest pitting	154	134	2.62
BS 1 (R) O_2	0	---	0	0	0
BS 2 (R) O_2	0.3	pitting	115	103	1.99
BS 3 (R) O_2	0.6	deeper pitting	163	190	3.22
BS 4 (R) O_2	1.1	deeper pitting	180	170	3.19
BS 5 (R) O_2	2.2	deepest pitting	192	230	3.85
BS 1 (R) air	0	---	0	0	0
BS 2 (R) air	0.3	pitting	104	112	1.97
BS 3 (R) air	0.6	deeper pitting	110	115	2.05
BS 4 (R) air	1.1	deeper pitting	162	120	2.57
BS 5 (R) air	2.2	deepest pitting	230	239	4.27
BS 1 (A) O_2	0	---	0	0	0
BS 2 (A) O_2	0.3	pitting	43	60	0.94
BS 3 (A) O_2	0.5	deeper pitting	130	143	2.49
BS 4 (A) O_2	1.1	deeper pitting	148	140	2.62
BS 5 (A) O_2	2.1	deepest pitting	170	154	2.95
BS 1 (A) air	0	---	0	0	0
BS 2 (A) air	0.3	pitting	72	80	1.39
BS 3 (A) air	0.5	deeper pitting	110	140	2.28
BS 4 (A) air	1.1	deeper pitting	153	150	2.76
BS 5 (A) air	2.1	deepest pitting	150	170	2.92
BS 1 (DCI) O_2	0	---	0	0	0
BS 2 (DCI) O_2	0.3	---	0	0	0
BS 3 (DCI) O_2	0.6	pitting	65	70	1.23
BS 4 (DCI) O_2	0.9	deeper pitting	89	100	1.72
BS 5 (DCI) O_2	2.1	deepest pitting	140	132	2.48
BS 1 (DCI) air	0	---	0	0	0
BS 2 (DCI) air	0.3	pitting	30	50	0.73
BS 3 (DCI) air	0.6	deeper pitting	72	67	1.27
BS 4 (DCI) air	0.9	deeper pitting	88	102	1.73
BS 5 (DCI) air	2.1	deepest pitting	102	105	1.89

R = R222, A = A2000. *Comparison of depth of pitting is relative only to specimens within each group.

For bare steel, the area of corrosion was influenced by the solution type, chloride content, and method of aeration. The pitting corrosion progressed rapidly at the highest chloride ion content; the area covered with corrosion products was larger and the corrosion pits were deeper. The pore solution with no corrosion inhibitor, aerated with oxygen, produced a more corrosive environment than solutions aerated with air. The corrosion process was influenced by the amount and rate of oxygen diffusion. As the amount of chlorides increased, the corrosion rate increased until the process was controlled by the oxygen concentration at the bar.

Chloride concentration in moles was selected as the basis of comparison because it is the chloride concentration in the concrete pore water that causes corrosion, not the Cl/OH ratio. The Cl/OH ratio influences the initiation and progress of the corrosion process either positively or negatively, and this would then be reflected in the concentration of the chlorides in the pore solution.

The corrosion area on the surface for the specimens tested in solutions with all three corrosion inhibitors increased with the increasing concentrations of Cl^- ions for the oxygen and air aeration (see Figures 2 and 3). Of the three corrosion inhibitors tested in this study, only DCI protected bare steel samples from corrosion. Typical corrosion states are illustrated in Figures 4 through 7.

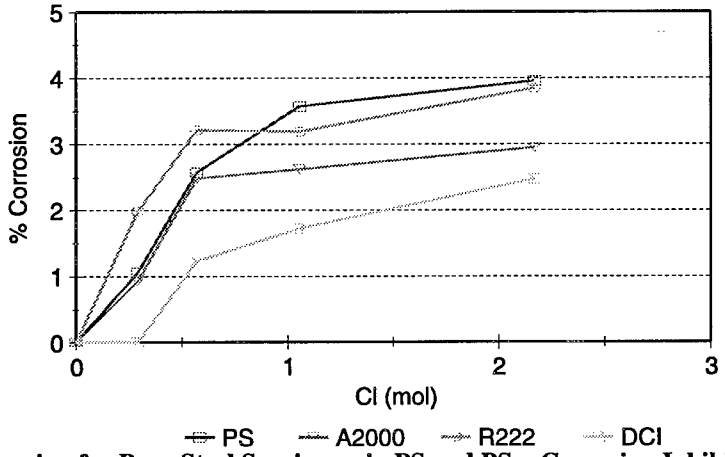


Figure 2. % Corrosion for Bare Steel Specimens in PS and PS + Corrosion Inhibitor; O_2 Aeration

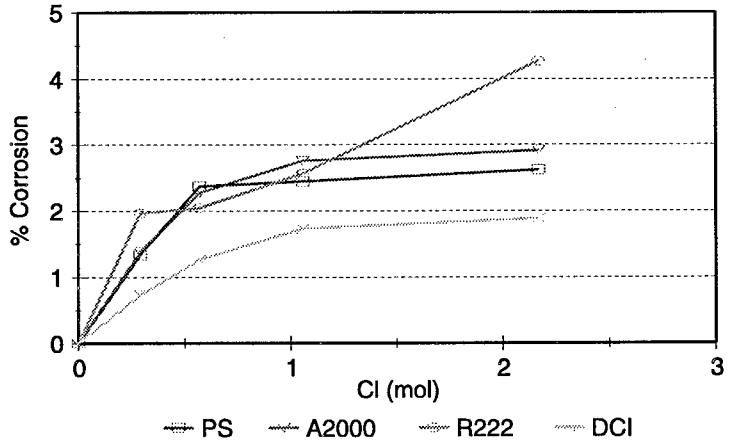


Figure 3. % Corrosion for Bare Steel Specimens in PS and PS + Corrosion Inhibitor; Air Aeration

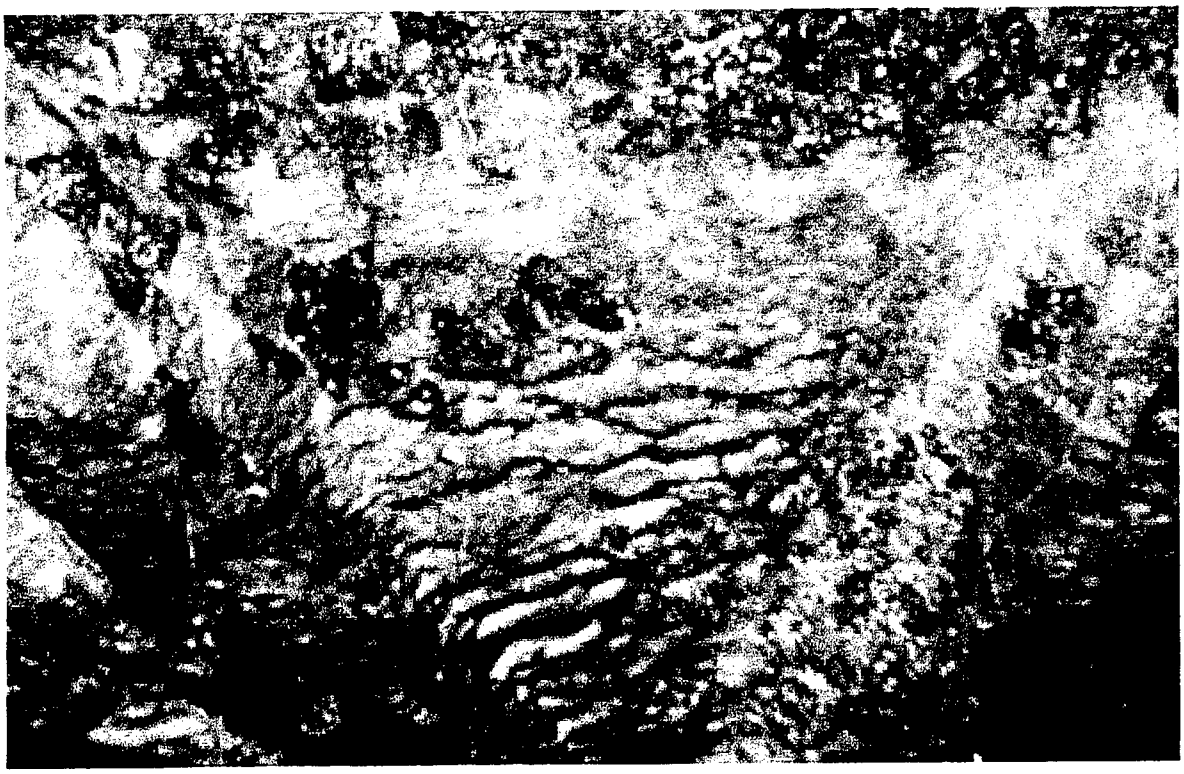


Figure 4. Bare Steel Specimen with Pitting Corrosion; PS + NaCl: Cl = 0.28 mole, O_2 Aeration (20 x)

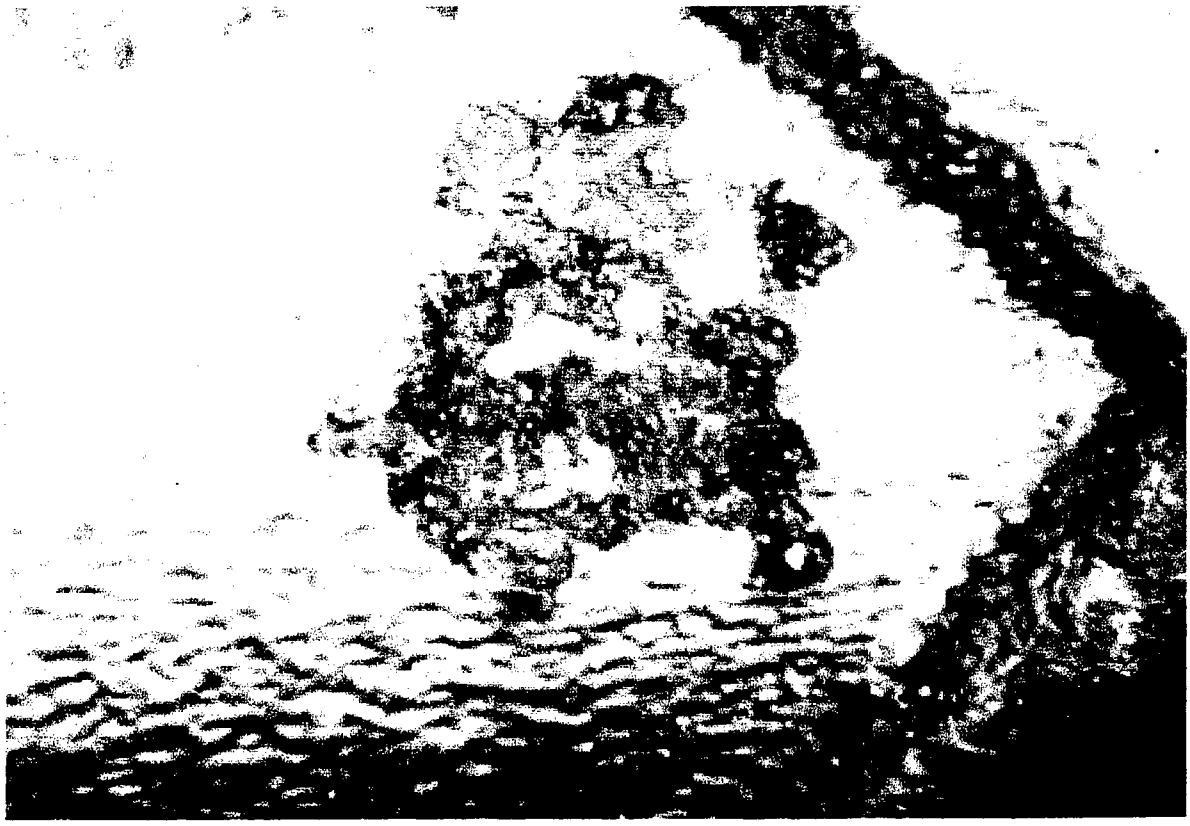


Figure 5. Bare Steel Specimen with Pitting Corrosion; PS + R222 + NaCl: Cl = 0.30 mole, O_2 Aeration (20x)

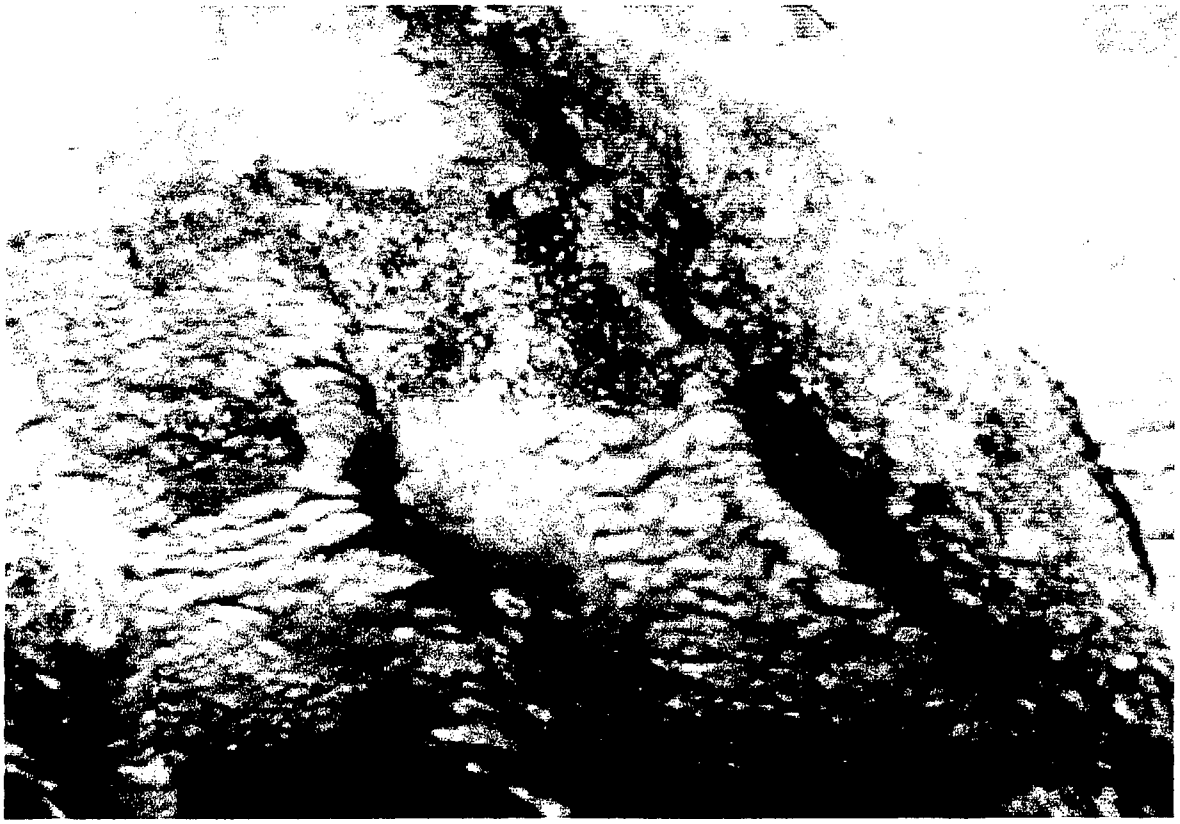


Figure 6. Bare Steel Specimen with Pitting Corrosion; PS + A2000 + NaCl: Cl = 0.29 mole, O_2 Aeration (20 x).

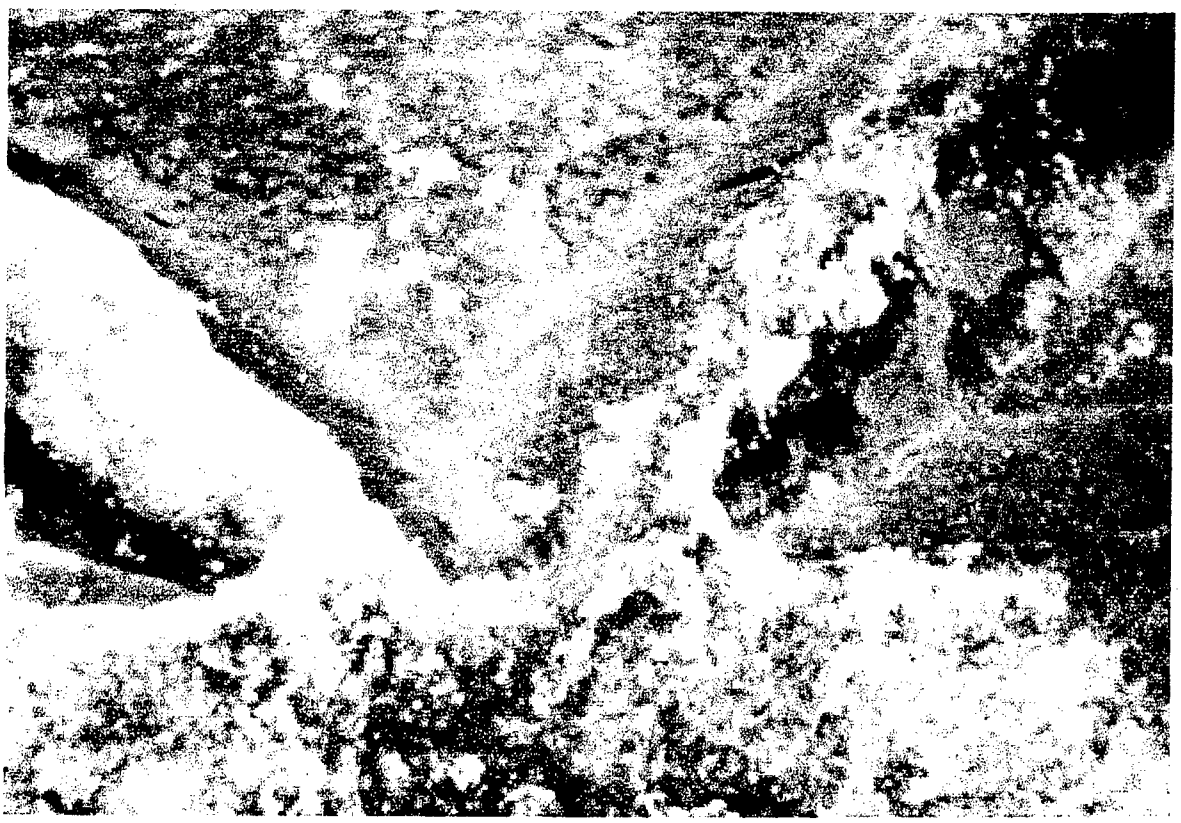


Figure 7. Bare Steel Specimen with No Corrosion; PS + DCI + NaCl: Cl = 0.30 mole, O_2 Aeration (20 x).

ECR

Before Immersion

Thickness Determination

The results of the coating thickness measurements are presented in Tables 5 through 8. The average coating thickness was about 300 μ for the FS specimens, 200 μ for the LNE specimens, 250 μ for the FSC specimens, and 270 μ for the CGN specimens. According to ASTM A 775-95, ECR coating thickness is to be between 175 and 300 μm. Thus, the average coating thickness for each ECR type was within the specification limits. Thickness also varied depending on location (see Figures 8 through 11).

Holiday Detection

The average number of holidays per 152 mm were as follows: for CGN, 0.14; for FSC, 0.19; for FS, 0.22; and for LNE, 10 (see Figure 12). The value of 10 holidays was assigned to the LNE specimens because of the continuous holidays in the epoxy coating.

The FS, FSC and CGN specimens were within the specification limits according to ASTM A 775-95 (smaller than 1 holiday per 152 mm). LNE specimens did not meet the holiday specification limit.

After Immersion

Visual Examination

The results of the visual examination are presented in Tables 9 through 11. Regardless of the chloride content of the solution, no blisters could be found on the CGN specimens, all of which had 0% damage. These specimens and the FS specimens with 1 percent damage immersed in the solutions with DCI showed the least corrosion. The FS and FSC specimens immersed in the pore solution with the various chloride contents showed only some corrosion protection. The LNE specimens had the most corrosion.

Table 5. Coating Thickness of ECR-FS Specimens

steel type	coating thickness, μm			
	radial ribs	between ribs	longitudinal ribs	bar
FS 1	413	260	216	
	397	269	289	
	392	334	245	
	382	304	290	
	410	361	236	
	422	283	231	
	323	328	205	
	405	342	223	
	374	255	250	
	395	234	213	
mean	391	297	240	309
sd	26.55	40.72	28.18	70.39
cov	0.07	0.14	0.12	0.23
FS 5	467	280	237	
	399	273	306	
	467	312	224	
	441	274	233	
	439	316	204	
	392	324	193	
	448	327	286	
	425	251	259	
	411	310	185	
	441	232	265	
mean	433	290	239	321
sd	24.67	31.01	37.81	87.94
cov	0.06	0.11	0.16	0.27
FS 11	476	318	280	
	391	234	312	
	320	223	213	
	426	256	269	
	463	169	235	
	345	369	205	
	394	243	265	
	411	240	310	
	418	402	251	
	408	214	214	
mean	405	267	255	309
sd	44.95	69.35	36.82	85.82
cov	0.11	0.26	0.14	0.28

Table 6. Coating Thickness, ECR-LNE Specimens

steel type	coating thickness, μm			
	radial ribs	between ribs	longitudinal ribs	bar
LNE 1	233	179	160	
	172	149	108	
	197	170	82	
	243	101	131	
	164	132	163	
	262	106	110	
	296	142	127	
	283	131	137	
	165	181	148	
	236	178	102	
mean	225	147	127	166
sd	46.04	28.24	24.98	54.58
cov	0.2	0.19	0.2	0.33
LNE 2	329	164	153	
	270	138	128	
	213	183	121	
	276	115	155	
	282	145	118	
	170	116	137	
	325	120	126	
	305	196	128	
	230	179	138	
	257	182	159	
mean	266	154	136	185
sd	47.69	29.28	14	66.29
cov	0.18	0.19	0.1	0.36
LNE 3	269	171	251	
	294	161	201	
	200	119	254	
	195	161	283	
	237	166	273	
	184	223	194	
	255	115	171	
	209	135	172	
	303	138	205	
	203	127	170	
mean	235	152	217	201
sd	40.98	30.54	41.59	52.28
cov	0.17	0.2	0.19	0.26

Table 7. Coating Thickness of ECR-FSC Specimens

steel type	coating thickness, μm			bar
	radial ribs	between ribs	longitudinal ribs	
FSC 23	253	248	267	
	308	222	358	
	331	177	297	
	312	217	329	
	265	204	369	
	265	220	341	
	262	178	294	
	332	179	344	
	326	210	307	
	293	164	304	
mean	295	202	321	273
sd	29.56	25.11	30.61	58.51
cov	0.1	0.12	0.1	0.21
FSC 21	338	253	290	
	322	168	275	
	299	244	316	
	326	130	348	
	301	148	314	
	320	202	274	
	266	201	296	
	302	175	317	
	317	192	329	
	276	188	301	
mean	307	190	306	268
sd	21.41	36.37	22.24	61.33
cov	0.07	0.19	0.07	0.23
FSC 22	311	162	166	
	344	168	177	
	322	169	138	
	205	182	181	
	322	143	193	
	269	185	192	
	351	171	201	
	268	183	187	
	303	216	158	
	341	121	175	
mean	304	170	177	217
sd	42.66	24.2	17.83	68.43
cov	0.14	0.14	0.1	0.32

Table 8. Coating Thickness of ECR-CGN Specimens

steel type	coating thickness, μm			
	radial ribs	between ribs	longitudinal ribs	bar
CGN 7	271	208	221	
	328	240	220	
	306	216	266	
	331	189	277	
	293	204	280	
	294	183	215	
	256	170	264	
	313	201	202	
	321	169	257	
	263	195	301	
mean	298	198	250	248
sd	25.62	20.42	31.62	48.61
cov	0.09	0.1	0.13	0.2
CGN 2	415	235	261	
	400	283	286	
	392	286	302	
	379	246	298	
	385	279	274	
	387	233	331	
	384	236	287	
	371	265	271	
	398	279	303	
	333	243	287	
mean	384	259	290	311
sd	20.69	20.84	18.84	57.16
cov	0.05	0.08	0.06	0.18
CGN 10	250	255	217	
	299	195	245	
	294	165	235	
	271	214	196	
	248	164	235	
	311	192	245	
	278	206	208	
	312	163	275	
	295	240	277	
	268	201	189	
mean	283	200	232	238
sd	22.03	29.72	28.59	43.56
cov	0.08	0.15	0.12	0.18

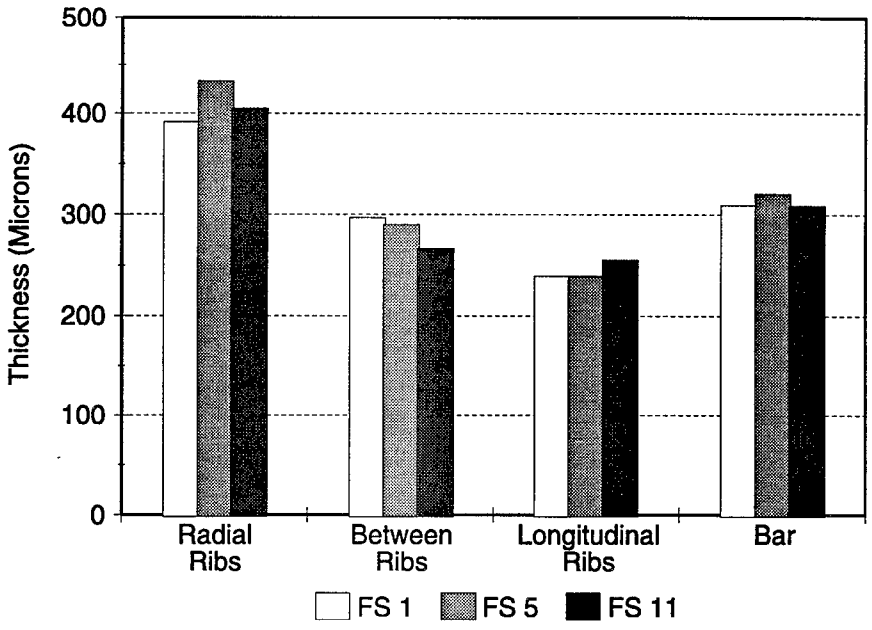


Figure 8. Coating Thickness, ECR-FS Specimen

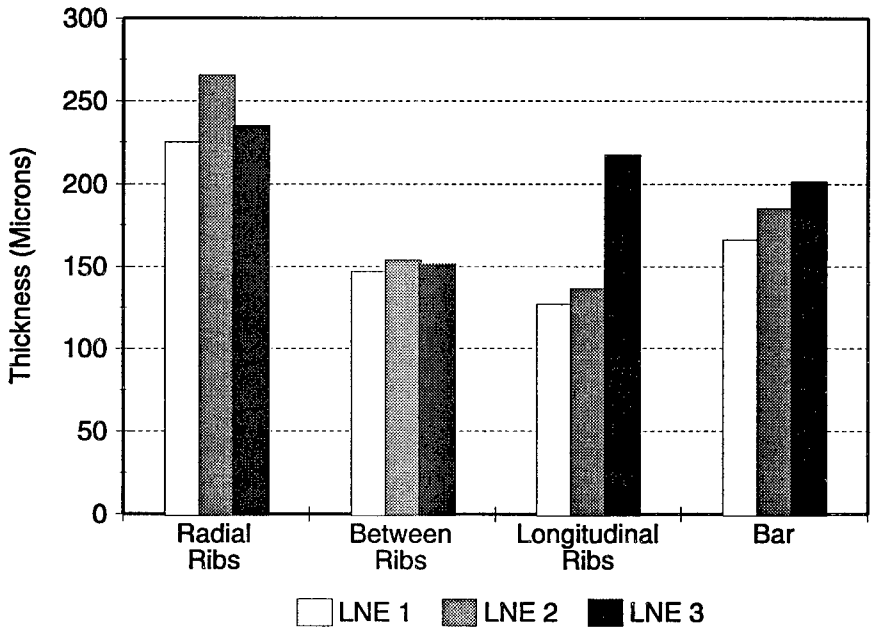


Figure 9. Coating Thickness, ECR-LNE Specimens

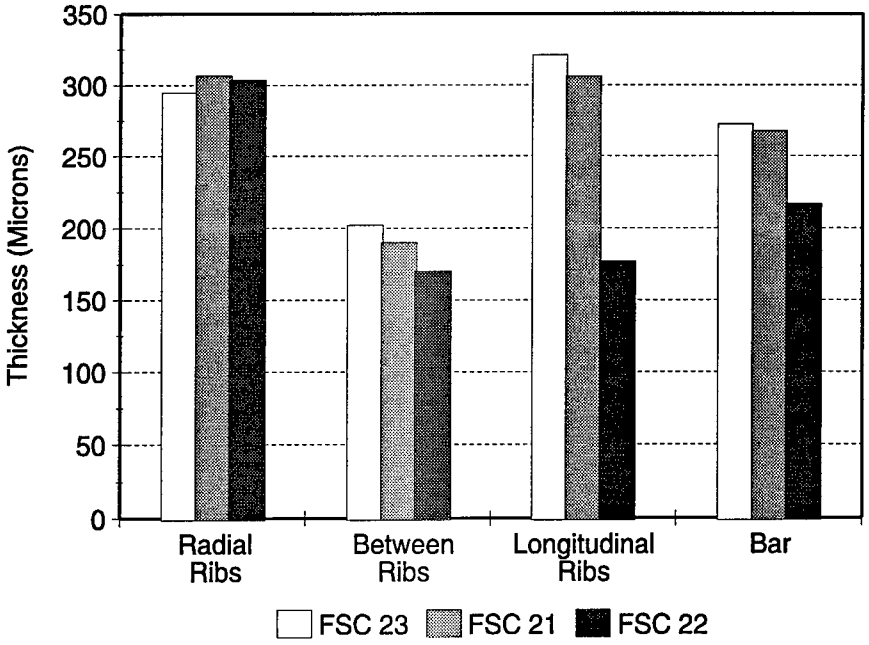


Figure 10. Coating Thickness, ECR-FSC Specimens

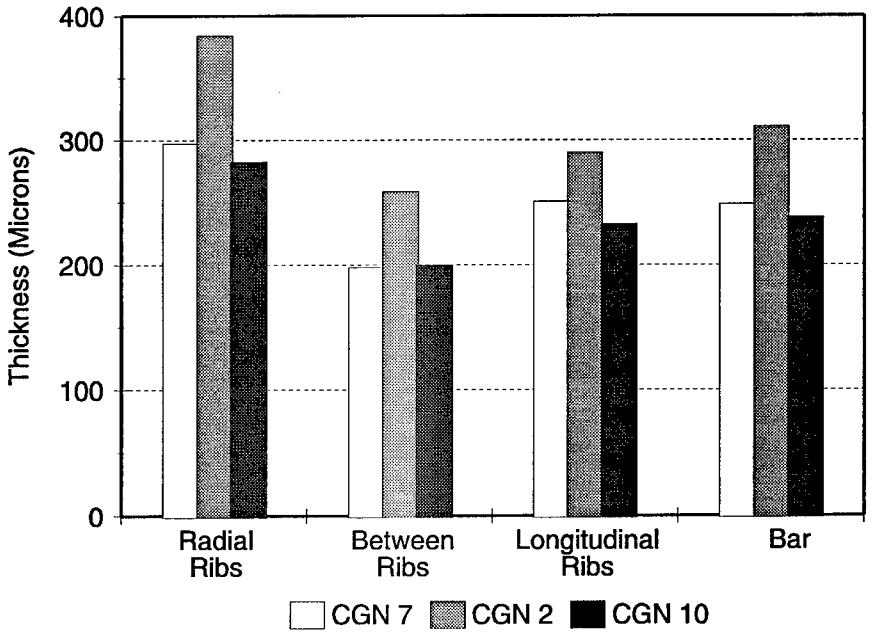


Figure 11. Coating Thickness, ECR-CGN Specimens

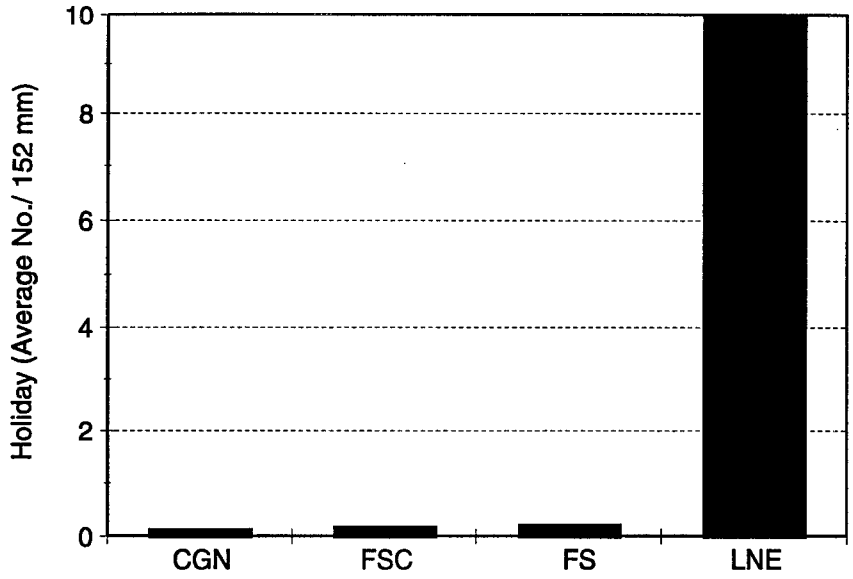


Figure 12. Holiday Detection of ECR Specimens

Table 9. Visual Examination of ECR-FS Specimens

specimen type	specimen symbol	visual observation				% area of blisters
		corrosion	blisters			
			no.	pH	area, mm^2	
ECR-FS 0%	2Q	---	---	---	---	
0.00, O_2	2K	---	---	---	---	
	2R	---	---	---	---	
average						0
ECR-FS 0%	3O	---	---	---	---	
0.73, O_2	3L	---	---	---	---	
	3S	---	---	---	---	
average						0
ECR-FS 0%	3K*	---	2	12	12	
1.47, O_2	3J*	---	2	5 &12	46	
	3F*	+	1	---	18	
average					25.33	0.5
ECR-FS 0%	4G	---	---	---	---	
2.93, O_2	4O	---	---	---	---	
	4S*	+	2	11	10	
average					3.33	0.1
ECR-FS 0%	4H	+	---	---	---	
5.86, O_2	4A*	---	2	12	20	
	4P	---	---	---	---	
average					6.67	0.1

ECR-FS 1%	1C	---	---	---	---	
0.0, O_2	1G	---	---	---	---	
	1N	---	---	---	---	
average						0
ECR-FS 1%	2P	+	---	---	---	
0.73, O_2	2D	+	---	---	---	
	2F*	+	1	12	10	
average					3.33	0.1
ECR-FS 1%	3N	+	1	12	20	
1.47, O_2	3E*	+	1	12	15	
	3B	---	---	---	---	
average					11.67	0.2
ECR-FS 1%	4D *	+	1	5	25	
2.93, O_2	4C	+	---	---	---	
	4L *	+	1	5	12	
average					12.33	0.2
ECR-FS 1%	5N	+	---	---	---	
5.86, O_2	5J	---	---	---	---	
	5K	---	---	---	---	
average						0
ECR-FS 1%	7K	---	---	---	---	
DCI, 0.00, O_2	7B	---	---	---	---	
	7P	---	---	---	---	
average						0
ECR-FS 1%	11	---	---	---	---	
DCI, 0.73, O_2	11O	---	---	---	---	
	11J	---	---	---	---	
average						0
ECR-FS 1%	7I	---	---	---	---	
DCI, 1.47, O_2	7L	---	---	---	---	
	7G*	---	5	---	25	
average					8.33	0.2
ECR-FS 1%	9I	---	---	---	---	
DCI, 2.93, O_2	9K	---	---	---	---	
	9A	---	---	---	---	
average						0
ECR-FS 1%	5S	---	---	---	---	
DCI, 5.86, O_2	5A	---	---	---	---	
	5M*	---	1	---	10	
average					3.33	0.1

ECR-LNE 0% = ECR specimen from LNE manufacturer with 0% damage. *Corrosion under blister. +Corrosion products present on coating surface and/or in mashed areas.

Table 10. Visual Examination of ECR-LNE Specimens

specimen type	specimen symbol	visual observation				% area of blisters
		corrosion	blisters			
			no.	pH	area, mm^2	
ECR-LNE 0%	1Q	---	---	---	---	
0.00, O_2	1O	---	---	---	---	
	1R	---	---	---	---	
average						0
ECR-LNE 0%	1N*	+	7	12	49	
0.73, O_2	1S*	+	4	12	12	
	1A*	+	8	5 & 12	58	
average					39.67	0.72
ECR-LNE 0%	1H*	+	4	12	17	
1.47, O_2	1P*	+	5	12	32	
	1G*	+	8	12	34	
average					27.67	0.5
ECR-LNE 0%	2E*	+	4	12	40	
2.93, O_2	2D*	+	5	12	69	
	2R*	+	4	12	47	
average					52	0.95
ECR-LNE 0%	2F*	+	3	12	55	
5.86, O_2	2Q*	+	9	12	66	
	2O*	+	5	12	52	
average					57.67	1.05
ECR-LNE 1%	2K	---	---	---	---	
0.00, O_2	2I	---	---	---	---	
	2L	---	---	---	---	
average						0
ECR-LNE 1%	1L*	+	9	12	60	
0.73, O_2	1B*	+	3	12	60	
	1C*	+	6	12	64	
average					61.33	1.12
ECR-LNE 1%	1J*	+	8	12	35	
1.47, O_2	1E*	+	3	12	11	
	1I*	+	5	12	80	
average					42	0.77
ECR-LNE 1%	3K *	+	6	12	58	
2.93, O_2	3F *	+	5	12 & 5	58	
	3G *	+	5	12	40	
average					52	0.95
ECR-LNE 1%	3J *	+	5	12	40	
5.86, O_2	3E *	+	3	12	34	
	3I *	+	4	12	60	
average					44.67	0.81

ECR-LNE 0% = ECR specimen from LNE manufacturer with 0% damage. *Corrosion under blister. +Corrosion products present on coating surface and/or in mashed areas.

Table 11. Visual Examination of ECR-FSC Specimens

specimen type	specimen symbol	visual observation				% area of blisters
		corrosion	blisters			
			no.	pH	area, mm^2	
ECR-FSC 0%	21F	---	---	---	---	
0.00, O_2	21Q	---	---	---	---	
	21S	---	---	---	---	
average						0
ECR-FSC 0%	21G	---	---	---	---	
0.73, O_2	21O	---	---	---	---	
	21J	---	---	---	---	
average						0
ECR-FSC 0%	21D	---	---	---	---	
1.47, O_2	21P	---	---	---	---	
	21E*	+	1	6	15	
average					5	0.1
ECR-FSC 0%	23M	+	---	---	---	
2.93, O_2	32R	---	---	---	---	
	23Q	+	---	---	---	
average						0
ECR-FSC 0%	23	---	---	---	---	
5.86, O_2	23P	---	---	---	---	
	23O	---	---	---	---	
average						0
ECR-FSC 1%	21C	---	---	---	---	
0.00, O_2	21N	---	---	---	---	
	21M	---	---	---	---	
average						0
ECR-FSC 1%	22D	---	2	12	18	
0.73, O_2	22N	---	---	---	---	
	22K*	+	1	12	45	
average					21	0.4
ECR-FSC 1%	22H*	+	11	12	71	
1.47, O_2	22O	---	---	---	---	
	22S*	---	2	6	20	
average					30.33	0.6
ECR-FSC 1%	23N*	+	4	6 & 12	42	
2.93, O_2	23H	+	---	---	---	
	23J*	+	2	6 & 8	16	
average					19.33	0.4
ECR-FSC 1%	23S*	+	1	8	20	
5.86, O_2	23B	---	---	---	---	
	23L	---	---	---	---	
average					6.67	0.1

ECR-LNE 0% = ECR specimen from LNE manufacturer with 0% damage.
*Corrosion under blister; +Corrosion products present on coating surface and/or in mashed areas.

The pH of the solution inside the blisters was determined using pH paper. The lowest pH was 5, and the highest was 12. The low pH of 5 or 6 corresponded to the beginning of the corrosion process under the blister: black rust. The pH equal to 11 or 12 was typical for the white metal surface under the coating or the advanced stage of the corrosion process. The changing pH values were typical for all specimen types (see Tables 9 through 11).

After the coating was stripped from the blisters, various corrosion states were observed on the steel surface (see Figures 13 through 17).

Adhesion Testing

The adhesion rating used was as follows:

5 blade tip slides easily under the coating, levering action removes the entire section of the coating

4 total area of steel exposed is larger than 4 mm^2

3 total area of steel exposed is between 2 mm^2 and 4 mm^2

2 total area of steel exposed is smaller than 2 mm^2

1 unable to insert blade tip under the coating.

Before the immersion test, the adhesion of FS, FSC, and CGN specimens was 1, and the adhesion of LNE specimens was 2. Tables 12 through 15 present the results of the adhesion test performed after the immersion test. Except for certain CGN specimens and FS specimens in solutions containing DCI, adhesion worsened for all specimens.

Hardness Test

Coating hardness for all specimens types was B before and after the immersion test. Therefore, this particular hardness test does not seem to be a proper method to evaluate the short-term exposure of ECR specimens.

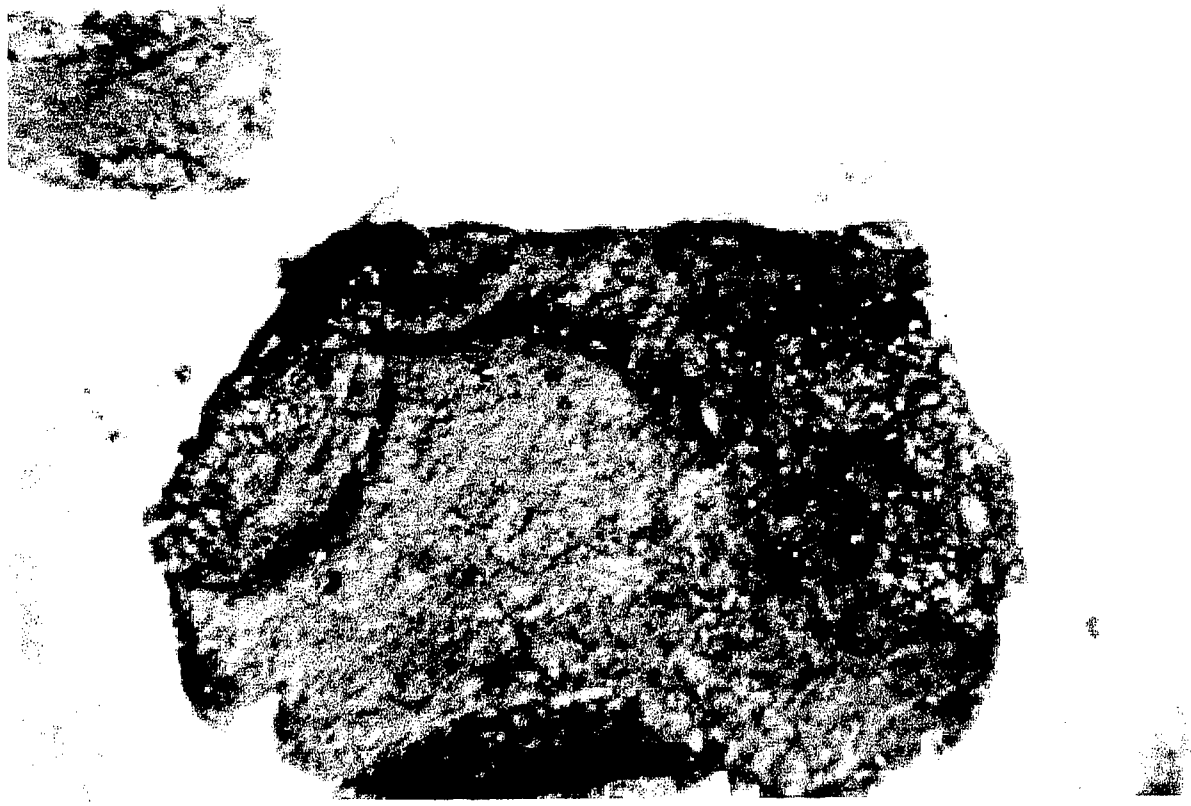


Figure 13. Steel Surface Under a Blister for ECR-FS Specimens with 0% Damage; pH 5 of Blister Solution; PS + NaCl: Cl = 0.59 mole, O2 Aeration

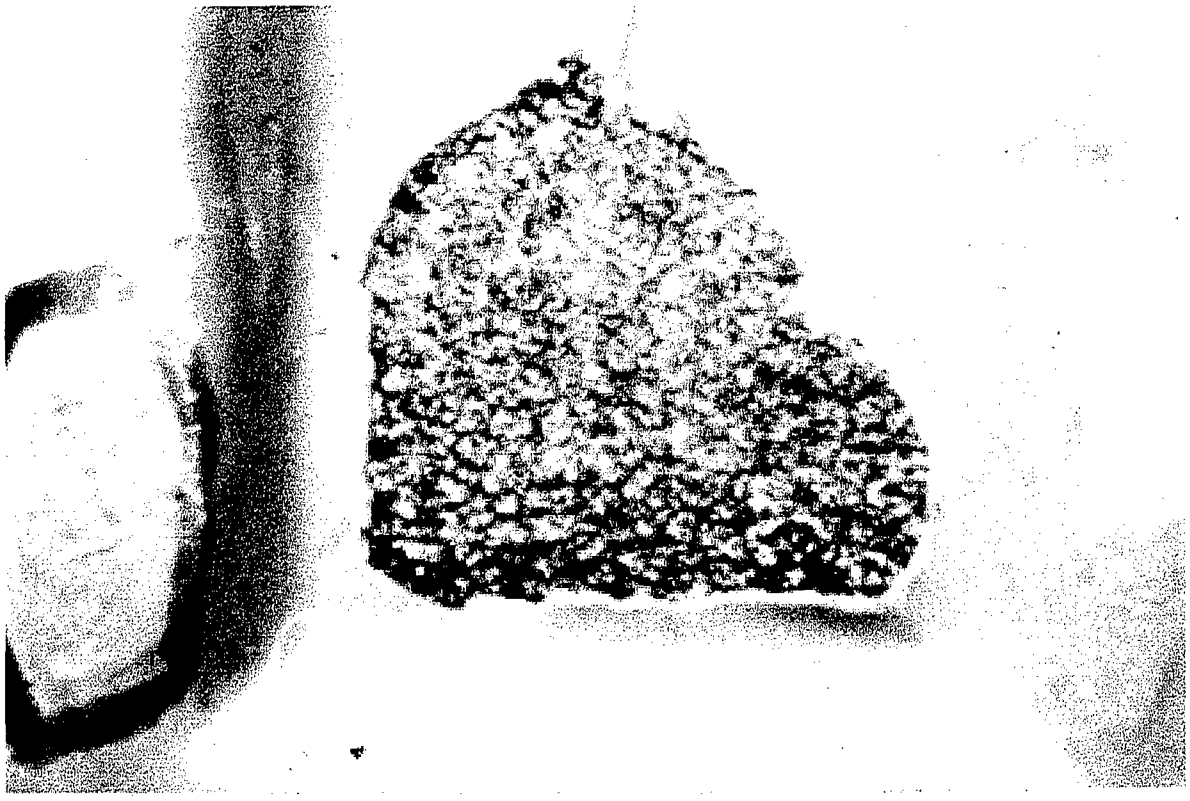


Figure 14. Steel Surface Under a Blister for ECR-FS Specimen with 1% Damage; pH 12 of Blister Solution; PS + NaCl: Cl = 0.59 mole, O_2 Aeration

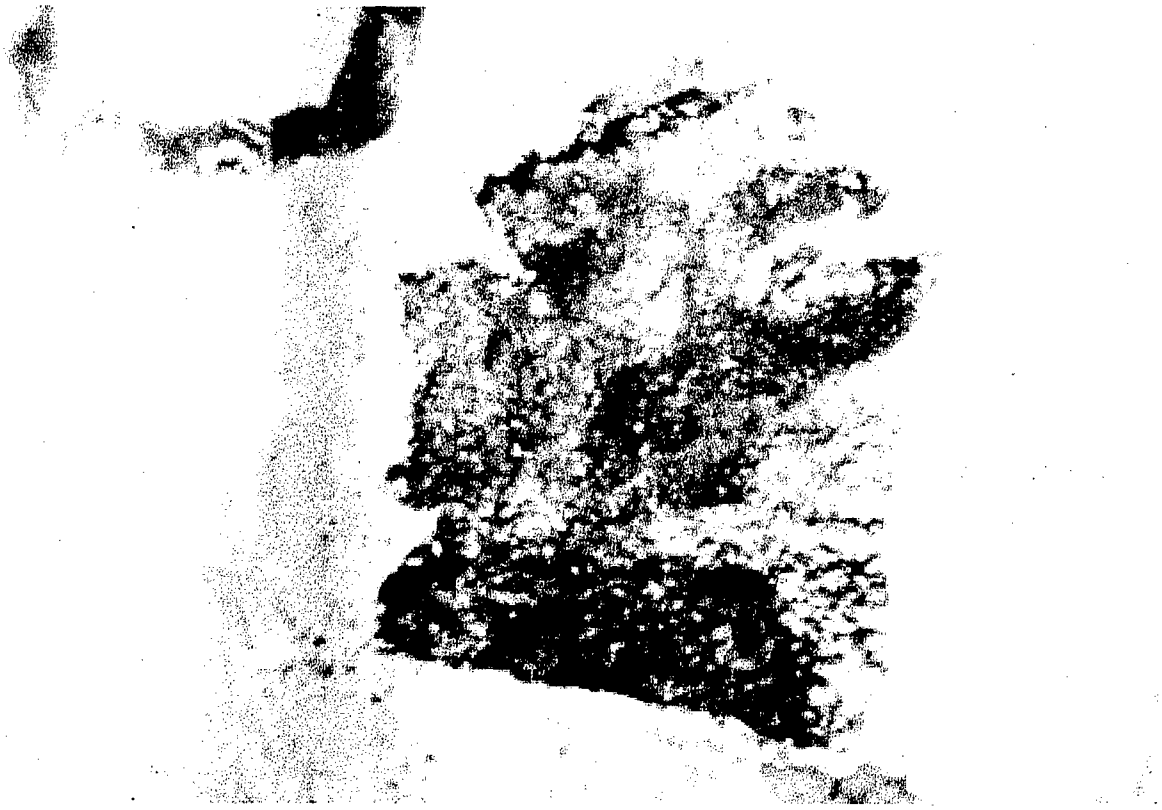


Figure 15. Steel Surface Under Blister for ECR-FS Specimen with 1% Damage; No Blister Solution; PS + DCI + NaCl: Cl = 0.59 mole, O_2 Aeration

Figure 16. Steel Surface Under Blister for ECR-LNE Specimen with 1% Damage; pH 12 of Blister Solution; PS + NaCl: Cl = 0.59 mole, O2 Aeration

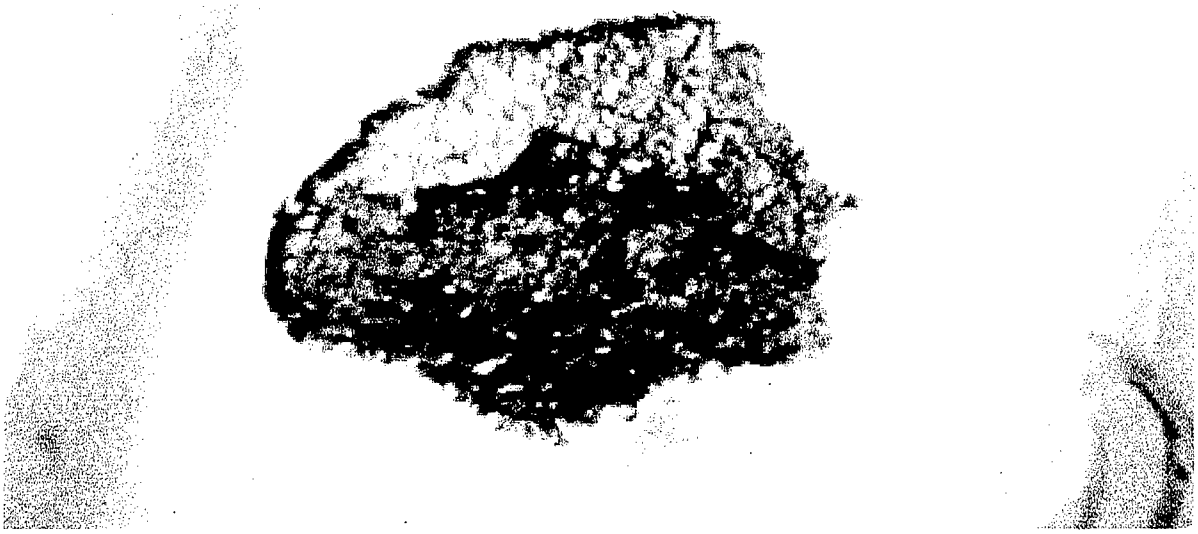


Figure 17. Steel Surface Under Blister for ECR-FSC Specimen with 0% Damage; pH 6 of Blister Solution; PS + NaCl: Cl = 0.59 mole, O_2 Aeration

Table 12. Adhesion Test for ECR-FS Specimens

specimen type	specimen symbol	adhesion			group average
ECR-FS 0%	2Q	4	4	4	
0.00, O_2	2K	4	4	4	
	2R	4	4	4	
average		4	4	4	4
ECR-FS 0%	3O	2	4	4	
0.73, O_2	3L	1	1	2	
	3S	1	2	3	
average		1	2	3	2
ECR-FS 0%	3K	2	4	4	
1.47, O_2	3J	3	4	4	
	3F	4	4	4	
average		3	4	4	4
ECR-FS 0%	4G	1	1	1	
2.93, O_2	4O	1	2	3	
	4S	4	4	4	
average		2	2	3	2
ECR-FS 0%	4H	5	4	4	
5.86, O_2	4A	4	4	5	
	4P	1	1	4	
average		3	3	4	4
ECR-FS 1%	1C	1	1	1	
0.0, O_2	1G	1	1	2	
	1N	1	1	2	
average		1	1	2	1
ECR-FS 1%	2P	5	5	5	
0.73, O_2	2D	5	5	5	
	2F	5	5	5	
average		5	5	5	5
ECR-FS 1%	3N	1	2	4	
1.47, O_2	3E	2	4	4	
	3B	1	2	3	
average		1	3	4	3
ECR-FS 1%	4D	4	5	5	
2.93, O_2	4C	4	4	5	
	4L	1	4	4	
average		3	4	5	4
ECR-FS 1%	5N	2	2	4	
5.86, O_2	5J	4	4	3	
	5K	1	1	2	
average		2	2	3	3

ECR-FS 1%	7K	2	2	2	
DCI, 0.0, O_2	7B	2	2	2	
	7P	2	2	2	
average		2	2	2	2
ECR-FS 1%	11E	1	1	1	
DCI, 0.73, O_2	11O	1	1	1	
	11J	1	1	1	
average		1	1	1	1
ECR-FS 1%	7I	1	1	1	
DCI, 1.47, O_2	7L	1	1	1	
	7G	1	1	2	
average		1	1	1	1
ECR-FS 1%	9I	1	1	1	
DCI, 2.93, O_2	9K	1	1	1	
	9A	1	1	1	
average		1	1	1	1
ECR-FS 1%	5S	1	1	1	
DCI, 5.86, O_2	5A	1	1	1	
	5M	1	1	1	
average		1	1	1	1

Table 13. Adhesion Test for ECR-LNE Specimens

specimen type	specimen symbol	adhesion			group average
ECR-LNE 0%	1Q	2	2	5	
0.00, O_2	1O	5	5	5	
	1R	2	2	2	
average		3	3	4	3
ECR-LNE 0%	1N	5	5	5	
0.73, O_2	1S	5	5	5	
	1A	5	5	5	
average		5	5	5	5
ECR-LNE 0%	1H	5	5	5	
1.47, O_2	1P	5	5	5	
	1G	5	5	5	
average		5	5	5	5
ECR-LNE 0%	2E	5	5	5	
2.93, O_2	2D	5	5	5	
	2R	5	5	5	
average		5	5	5	5
ECR-LNE 0%	2F	5	5	5	
5.86, O_2	2Q	5	5	5	
	2O	5	5	5	
average		5	5	5	5
ECR-LNE 1%	2K	1	2	2	
0.00, O_2	2I	5	5	5	
	2L	1	2	3	
average		2	3	3	3
ECR-LNE 1%	1L	5	5	5	
0.73,	1B	5	5	5	
	1C	5	5	5	
average		5	5	5	5
ECR-LNE 1%	1J	5	5	5	
1.47, O_2	1E	5	5	5	
	1I	5	5	5	
average		5	5	5	5
ECR-LNE 1%	3K	5	5	5	
2.93, O_2	3F	5	5	5	
	3G	5	5	5	
average		5	5	5	5
ECR-LNE 1%	3J	5	5	5	
5.86, O_2	3E	5	5	5	
	3I	5	5	5	
average		5	5	5	5

Table 14. Adhesion Test for ECR-FSC Specimens

specimen type	specimen symbol	adhesion			group average
ECR-FSC 0%	21F	1	1	1	
0.00, O_2	21Q	2	2	5	
	21S	1	1	1	
average		1	1	2	2
ECR-FSC 0%	21G	1	1	1	
0.73, O_2	21O	1	1	5	
	21J	5	5	3	
average		2	2	3	3
ECR-FSC 0%	21D	1	1	1	
1.47, O_2	21P	5	5	3	
	21E	1	1	4	
average		2	2	3	2
ECR-FSC 0%	23M	2	2	2	
2.93, O_2	32R	2	2	2	
	23Q	2	2	5	
average		2	2	3	2
ECR-FSC 0%	23E	2	2	2	
5.86, O_2	23P	2	2	2	
	23O	2	2	2	
average		2	2	2	2
ECR-FSC 1%	21C	1	1	1	
0.00, O_2	21N	1	1	1	
	21M	1	1	1	
average		1	1	1	1
ECR-FSC 1%	22D	5	5	5	
0.73, O_2	22N	2	2	2	
	22K	5	5	5	
average		4	4	4	4
ECR-FSC 1%	22H	5	5	5	
1.47, O_2	22O	3	3	4	
	22S	5	5	5	
average		4	4	5	4
ECR-FSC 1%	23N	2	2	5	
2.93, O_2	23H	2	2	2	
	23J	2	2	5	
average		2	2	4	3
ECR-FSC 1%	23S	2	5	5	
5.86, O_2	23B	2	2	2	
	23L	2	2	2	
average		2	3	3	3

Table 15. Adhesion Test for ECR-CGN Specimens

specimen type	specimen symbol	adhesion			group average
ECR-CGN 0%	2A	1	1	1	
0.00, O_2	2B	1	1	1	
	2C	1	1	1	
average		1	1	1	1
ECR-CGN 0%	4B	1	1	1	
0.73, O_2	4C	1	1	1	
	4D	1	1	1	
average		1	1	1	1
ECR-CGN 0%	4	1	1	1	
1.47, O_2	4F	1	1	1	
	4A	1	1	1	
average		1	1	1	1
ECR-CGN 0%	6F	1	1	1	
2.93, O_2	6	1	1	1	
	6C	1	1	1	
average		1	1	1	1
ECR-CGN 0%	8C	2	2	2	
5.86, O_2	8B	2	2	2	
	8A	2	2	2	
average		2	2	2	2

Test Solutions

Air and Oxygen Saturation

The results of the testing are presented in Table 16. The pore solution with the various chloride contents and the pore solution with admixed DCI and NaCl were evaluated for the oxygen saturation. The temperature of the solutions was about 40 °C, and their measured pH was about 12. The oxygen level was measured first for the solutions before the aeration and then after the four aeration periods of 30, 60, 120, and 240 seconds for the same solutions. The oxygen content in the solutions was determined for the solutions aerated with compressed oxygen and breathing air. In both cases, 60 seconds was a sufficient time for the solutions to become saturated with oxygen.

Chloride Titration

The results of the chloride titration are presented in Table 17. Average chloride concentrations in all solution types, starting from the pore solution with the smallest amount of NaCl, were 0.3, 0.6, 1.1, and 2.2 mole. The expected chloride concentrations from the solution calculation were 0.3, 0.6, 1.2, and 2.4 mole for the same solution types, respectively.

Table 16. Oxygen Saturation Test (945 g)

solution type	chlorides, kg/m^3	aeration type	temp, C	salinity, ppt	oxygen content (ppm) after aeration				
					0 s	30 s	60 s	120 s	240 s
PS	0	O_2	44	12	3.5	14.6	15.4	16	15.8
PS	0.73	O_2	41	29	3	13.2	13.4	13.8	14
PS	1.47	O_2	41	40	2.9	11.4	12.1	12.1	12.6
PS	2.93	O_2	40	40	2.6	10.6	11.6	11.6	11.8
PS	5.86	O_2	40	40	2.3	9	10	10.2	10.2
PS + DCI	0	O_2	43	40	2.35	10.6	10.4	10.8	11
PS + DCI	0.73	O_2	43	40	2.4	9.1	10.1	10.6	10.7
PS + DCI	1.47	O_2	43	40	2.5	9.8	9.7	10.1	10
PS + DCI	2.93	O_2	44	40	2.1	10.2	9.4	10.2	11.4
PS + DCI	5.86	O_2	42	40	1.95	9.6	9.8	9.8	10
PS	0	air	40	12	4.5	4.5	4.9	5	5.2
PS	0.73	air	39	29	3.75	3.9	4.2	4.3	4.4
PS	1.47	air	43	40	3.4	3.1	3.4	3.55	3.75
PS	2.93	air	43	40	3	2.8	3.3	3.1	3.25
PS	5.86	air	44	40	2.8	2.45	2.75	2.35	2.35
PS + DCI	0	air	43	40	2.25	3.4	3.4	3.45	3.55
PS + DCI	0.73	air	43	40	2.05	2.95	3.1	3	3.1
PS + DCI	1.47	air	43	40	2.15	2.6	2.6	2.8	2.9
PS + DCI	2.93	air	43	40	1.9	2.1	2.25	2.3	2.3
PS + DCI	5.86	air	43	40	1.8	2.05	2.1	2.15	2.25

Table 17. Chloride Titration Results

solution type	calculated, mole Cl	chlorides, kg/m^3	titrated chlorides	
			mole	kg/m^3
PS	0	0	0	0
PS	0.3	0.73	0.28	0.69
PS	0.6	1.47	0.59	1.43
PS	1.2	2.93	1.16	2.82
PS	2.4	5.86	2.3	5.6
PS + R222	0	0	0	0
PS + R222	0.3	0.73	0.3	0.73
PS + R222	0.6	1.47	0.56	1.37
PS + R222	1.2	2.93	1.05	2.57
PS + R222	2.4	5.86	2.21	5.39
PS + A2000	0	0	0	0
PS + A2000	0.3	0.73	0.29	0.71
PS + A2000	0.6	1.47	0.54	1.33
PS + A2000	1.2	2.93	1.1	2.68
PS + A2000	2.4	5.86	2.07	5.05
PS + DCI	0	0	0	0
PS + DCI	0.3	0.73	0.3	0.73
PS + DCI	0.6	1.47	0.59	1.44
PS + DCI	1.2	2.93	0.93	2.26
PS + DCI	2.4	5.86	2.1	5.11

pH Testing

Measured values of pH decreased with increasing NaCl content within each solution test series (see Table 18).

Table 18. Cl/OH and pH of Test Solution

solution type	Cl/OH ratio, 100% dissolution	pH calculated, 100% dissolution	titrated solution		titrated supernatant		probe pH
			Cl/OH	pH	*Cl/OH	pH	
PS	0	13.7	0	13.6			12.8
PS	0.5	13.7	0.7	13.6	0.7	13.6	12.7
PS	1	13.7					12.6
PS	2	13.7					12.5
PS	4	13.7	5.74	13.6	5.99	13.6	12.4
PS + R222	0	13.7					13
PS + R222	0.5	13.7	0.75	13.6	0.86	13.5	12.9
PS + R222	1	13.7					12.8
PS + R222	2	13.7					12.7
PS + R222	4	13.7			6.55	13.5	12.6
PS + A2000	0	13.7					13
PS + A2000	0.5	13.7	0.49	13.8	0.51	13.8	12.9
PS + A2000	1	13.7					12.8
PS + A2000	2	13.7					12.6
PS + A2000	4	13.7			3.79	13.7	12.5
PS + DCI	0	13.7					11.8
PS + DCI	0.5	13.7	0.5	13.8	7.05	12.6	11.7
PS + DCI	1	13.7					11.6
PS + DCI	2	13.7					11.5
PS + DCI	4	13.7			64.49	12.5	11.4

*Chloride and hydroxide present in supernatant.

The results of the pH titration for pore solution and pore solution with corrosion inhibitors seem to be more accurate than the measurements obtained with the pH probe since they are equal or in some cases very close to the pH of solutions obtained through the calculation, which was about 13.7.

The pH titration shows also that an error occurs during the solution testing with the pH probe. The pH values obtained with the pH probe are always smaller than the real pH in tested solutions. This lack of accuracy for the pH probe is influenced by the high alkalinity of the pore solution. It is known that the high concentrations of alkali metal ions will cause an alkaline error for glass electrodes.[8]

Possible Mechanism of Corrosion for ECR

Visual examination of the steel surface under the blisters and pH measurements of the solution inside the blister suggested the following mechanism for the corrosion of the steel underneath the epoxy coating. First, pore solution penetrates the coating and causes the coating to disbond in weak adhesion areas. The blister forms and the pH of the solution inside the blister changes to around 12. Next, chloride ions arrive at the clean steel surface at a sufficient concentration to initiate corrosion, and the pH decreases to 5 as the corrosion process proceeds. Corrosion products accumulate underneath the coating, and their expansion causes the coating to crack. Pore solution mixes with the solution inside the blister, and the pH under the coating increases to the previous value of about 12 as more pore solution enters the blister. This corrosion mechanism was first observed and proposed by Sagues.[3]

CONCLUSIONS

- DCI is the only corrosion inhibitor that performs well under the experimental conditions.

- Coating thickness and damage of the coating on ECR influences adhesion loss between the coating and the steel surface and the formation of blisters.

- The least corrosion occurred with the CGN specimens within the group of specimens with 0 percent damage and the FS specimens with 1 percent damage immersed in the solutions with DCI. The FS and FSC specimens show only some corrosion protection. The LNE specimens showed the most corrosion.

- ECR as a corrosion protection method may be able to perform well in a pore solution environment if the ECR has a perfect epoxy coating, with no damage, no holidays, good adhesion, and thickness within the specification limits. With any damage in the coating, ECR performs only slightly better than bare steel.

- The long-term evaluation of tested corrosion inhibitors with ECR in concrete is needed in making the final decision concerning the protective properties of dual corrosion protection system consisting of the epoxy coating and a corrosion inhibitor.

RECOMMENDATIONS

1. VDOT should adopt the corrosion evaluation test method developed in this study as a rapid screening test for corrosion inhibitor admixtures used with bare and coated reinforcing steel. Subsequent testing of those inhibitors which shows satisfactory performance would be in concrete where chloride diffusion and corrosion initiation

levels could be evaluated. DCI should remain as the only commercially produced corrosion inhibitor admixture approved for use in concrete in Virginia at this time.

2. Since ECR will corrode, and the time to corrosion damage is related to the quality of the coating after concrete placement, VDOT should explore the use of an additional corrosion protection system such as polymer concrete, sealers, and coatings on reinforced concrete bridge components built with ECR.

ACKNOWLEDGMENTS

The authors are grateful to the following who peer reviewed this report: Albert Sagues, University of South Florida; Richard Steele, VDOT; and Wallace McKeel, VTRC. Thanks go to Linda Evans for editing the report.

REFERENCES

1. Weyers, R.E. et al. 1995. *Protocol for In-Service Evaluation of Bridges with Epoxy-Coated Reinforcing Steel.* NCHRP 10-37B.

2. Clear, K.C. 1992. *Effectiveness of Epoxy-Coated Reinforcing Steel: Final Report.* Canadian Strategic Highway Research Program, Ottawa, Ontario.

3. Sagues, A.A. et al. 1994. *Corrosion of Epoxy-Coated Rebar in Florida Bridges.* University of South Florida, College of Engineering.

4. Weyers, R.E. et al. 1997. *Field Investigation of the Corrosion Protection Performance of Bridge Decks and Piles Constructed with Epoxy-Coated Reinforcing Steel in Virginia.* VTRC 98-R4. Virginia Transportation Research Council, Charlottesville.

5. Krauss, P.D., D.B. McDonald, and M.R. Sherman. 1996. *Corrosion Investigation of Four Bridges Built Between 1973 and 1978 Containing Epoxy-Coated Reinforcing Steel.* MN/RC-96/25. Minnesota Department of Transportation, St. Paul.

6. Diamond, S. 1981. Effect of Two Danish Flyashes on Alkali Contents of Pore Solutions of Cement-Flyash Pastes. *Cement and Concrete Research*, 11, 388.

7. Stark, D. et al. 1993. *Eliminating or Minimizing Alkali-Silica Reactivity (SHRP-C-343).* National Research Council, Washington,, D.C.

8. Skoog, D.A. and West D.M.. *Analytical Chemistry: An Introduction*, ed 4. Saunders College Publishing.

APPENDIX

STANDARD TEST METHOD FOR EVALUATING CORROSION INHIBITORS IN PORE SOLUTION

1. Scope

1.1 Short Term. This test method is intended for use as a short-term test for evaluating the performance of corrosion inhibitors used in concrete structures through the immersion test in simulated concrete pore solution.

1.2 Values. The values stated in SI units are to be regarded as the standard.

1.3 Safety. This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

2. Significance and Use

The results obtained by this method should serve as a guide in, but not as the sole basis for, selecting a well-performing corrosion inhibitor. An attempt has been made to incorporate into this method the most important factors that may affect the performance of corrosion inhibitor: moisture, oxygen, and chlorides.

3. Apparatus

3.1 Plastic Containers. 1000-ml plastic polypropylene containers are needed to store the bare steel samples immersed in the pore solution during the testing in the oven at 40 °C.

3.2 Balances. An electronic balance sensitive to 0.1 g is needed to weigh the pore solution components and added sodium chloride.

3.3 Band saw. A band saw is needed to cut reinforcing steel into 152-mm specimens.

3.4 Oven. An oven is needed to store the plastic containers during the immersion test at 40 °C.

3.5 Frit. A glass frit is needed for the pore water saturation with oxygen.

3.6 Plastic Tube. A plastic tube is needed to connect the frit with the compressed oxygen tank.

3.7 pH probe or pH electrode. A pH probe or a pH electrode is needed to monitor the pH of tested solutions.

3.8 Stop Watch. A stop watch is needed to measure the time of the solution aeration with oxygen.

4. Materials

4.1 Corrosion Inhibitor. A sample for testing based on the dosage rate used for concrete structures.

4.2 Sodium Hydroxide. Standard grade solid in form of pellets.

4.3 Potassium Hydroxide. Standard grade solid in form of pellets.

4.4 Calcium Hydroxide. Standard grade solid in powder form.

4.5 Sodium Chloride. Certified biological grade having an iodide concentration no greater than 0.0004 percent.

4.6 Deionized Water. Common deionized water produced in a laboratory still.

4.7 Reinforcing Steel. Reinforcing steel cut into 152-mm specimens.

4.8 Oxygen. Compressed oxygen.

4.9 Hexane. Certified grade.

5. Reagents

5.1 Pore Solution. The pore solution is produced by combining sodium hydroxide, potassium hydroxide, calcium hydroxide, and deionized water. The pore solution composition is as follows: 0.4 M KOH, 0.2 M NaOH, and 0.004 M $Ca(OH)_2$. The following amounts of ingredients are needed to produce 1000 g of pore solution:

8 g NaOH
22.4 g KOH
0.3 g $Ca(OH)_2$
977.7 g deionized water.

5.2 Pore Solution with Corrosion Inhibitor. Corrosion inhibitor should be added to the pore solution based on dosage for 1 cubic meter of concrete that has 3 percent by weight of pore water. If corrosion inhibitor contains a large amount of water, the water content in the pore solution should be decreased based on the water present in corrosion inhibitor.

5.3 Pore Solution with Corrosion Inhibitor and Sodium Chloride. Sodium chloride is added to the pore solution containing corrosion inhibitor to produce corrosion prone environments. The following amounts of sodium chloride should be used with 1000 g of pore solution: 17.4 g, 34.8 g, 69.6 g, and 139.2 g. One solution should be left without sodium chloride to serve as a control. The tested solutions will result in chlorides present in the supernatant as follows: 0.69 kg/m^3, 1.43 kg/m^3, 2.82 kg/m^3, and 5.60 kg/m^3.

5.4 Temperature. The temperature should be 40 °C ± 5 °C.

6. Sample Preparation

Using the band saw, cut reinforcing steel into 152-mm specimens and divide them into groups of three for each corrosion inhibitor type tested. Three specimens should come from the same piece of the reinforcement. Before immersion into tested solutions, clean the specimens in hexane.

7. Procedure

1. Place the three reinforcing specimens in a clean plastic polypropylene container.

2. Cover the specimens completely with a prepared pore solution containing tested corrosion inhibitor. The same quantity of pore solution, approximately 900 ml, should be placed in each container. Measure the pH of tested solutions.

3. Saturate the solution with compressed oxygen for 1 minute.

4. Close the container lid, and store the container in the oven for 7 days at 40 °C ± 40 °C.

5. After the 7-day pretreatment period is over, take the containers out of the oven and add the desired amount of sodium chloride.

6. Saturate the solutions with compressed oxygen for 1 minute.

7. Close the container lid, and store the container in the oven for 90 days at 40 °C ± 5 °C.

8. Twice a week, at day 1 and 4, saturate the solution with compressed oxygen for 1 minute, measure the pH, and perform a visual observation of tested specimens. Look for a beginning and development of any corrosion process on the steel surface.

9. After the 90-day immersion test ends, take the specimens out of the solution and perform a visual examination.

8. Visual Examination

1. Examine each specimens for a development of the corrosion process on the steel surface.

2. Estimate the corrosion area for each specimen.

9. Calculation

1. Calculate a percent area corrosion for each specimen.

2. Calculate an average percent corrosion for three specimens tested in the same environment.

3. Construct a graph employing the average percent corrosion for each solution type tested based on the increasing content of moles chloride in solution.

10. Report

10.1 *Contents.* The report should include the following:
Corrosion inhibitor and solution concentrations
Conditioning procedure
Test conditions
Surface appearance of specimens before testing
Duration of the test and the examination periods in days
Average percent corrosion of three specimens tested in the same solution
Graph showing average percent corrosion plotted against increasing chloride concentrations in the tested solution.

10.2. *Examination Period.* For each examination period, the following data are required:
Appearance of the specimens
Measured pH value of the tested solution.

11. Precision and Bias

All test specimen values must be considered.

12. Significance of Results

This test method permits prediction of corrosion inhibitor performance in chloride-contaminated environments.