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

by

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Performance Evaluation of Epoxy-Coated Reinforcing Steel and Corrosion Inhibitors in a Simulated Concrete Pore Water Solution

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(*Abstract*)

Three epoxy-coated reinforcing steel (ECR) types removed from job sites, one shipped directly from the coater's plant, three commercial corrosion inhibitors, and one ECR plus a corrosion inhibitor were evaluated as reinforcing steel corrosion protection systems against chloride induced corrosion. The three corrosion inhibitors were calcium nitrite, an aqueous mixture of esters and amines, and a mixture of alcohol and amine. The ECR was tested in two groups, 0% and 1% coating damage. Corrosion protection performance was evaluated by the amount of visually observed blister surface area, for the ECR, and corroded surface area, for the tested corrosion inhibitors.

Results of the ECR testing demonstrated that coating debondment and corrosion of ECR is directly related to the amount of damage present in the coating, as well as coating thickness. For the bare steel tested with and without corrosion inhibitors, the results showed that corrosion increases with increasing chloride concentrations. Corrosion inhibition characteristics were demonstrated only by the calcium nitrite corrosion inhibitor.

A corrosion protection evaluation test was developed for concrete corrosion inhibitor admixtures. The test solution is a simulated concrete pore water. Corrosion is accelerated by evaluating the temperature to field conditions of 40°C. The test consists of a 7 day pretreatment period followed by a 90 day test period. The corrosive sodium chloride is added to the solution containing the bare or epoxy-coated reinforcing steel specimens after the 7 day pretreatment period. In addition, the solution is periodically saturated with oxygen.

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ABBREVIATIONS AND SYMBOLS

A2000 - tested corrosion inhibitor symbol
ASTM - American Society for Testing and Materials
BS - bare steel reinforcement
CGN - tested epoxy-coated bar symbol
CI - corrosion inhibitor
CRSI - Concrete Reinforcing Steel Institute
C-SHRP - Canadian Strategic Highway Research Program
DCI - tested corrosion inhibitor symbol
ECR - epoxy-coated reinforcement
FHWA - Federal Highway Administration
FS - tested epoxy-coated bar symbol
FSC - tested epoxy-coated bar symbol
LNE - tested epoxy-coated bar symbol
MTO - Ministry of Transportation, Ontario
PS - pore solution
R222 - tested corrosion inhibitor symbol

Chapter 1. INTRODUCTION

1.1 Corrosion of Steel in Concrete

Corrosion is a spontaneous process of returning metals to their natural state by oxidation-reduction reactions. Corrosion of metals results in a loss of both structural integrity and attractive appearance [1]. Corrosion of reinforcing steel in concrete is one of the major causes for deterioration of bridges, buildings and other concrete structures. Corrosion of steel in concrete is attributed to "differential concentration cells caused by non-homogeneity of the concrete and its environment". The main sources of cell potentials are differences in pH, oxygen and chloride content [2].

The high pH environment in concrete, above 12, will normally protect reinforcing steel from corrosion. A passivating film is formed on the steel surface and is maintained in the alkaline environment produced by cement hydration [2]. Steel passivity can be disrupted by chloride presence in the concrete and reduction in pH.

Concrete exposure environments as, $SO_{3,}$ 6 - 10 mg/l, present in rain water, and CO_2, 600 - 1000 mg/m^3, present in air penetrate the concrete, produce acids, and decrease the pH. The carbonation of concrete with CO_2 is known to induce the corrosion process of reinforcing steel in concrete. In the initial stage of carbonation, CO_2 will be bound at the concrete surface according to the following reactions:

$$CO_2 + H_2O \rightarrow H_2CO_3 \qquad (1)$$

$$H_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3 + 2H_2O \qquad (2)$$

The carbonation depth will grow in time until it reaches the reinforcement. The concrete pH will drop to below 10 and the passivity of the reinforcing steel will be destroyed [3].

The other major cause of the corrosion of steel in concrete is the presence of chlorides. Chlorides can either be admixed into the concrete as contaminantes in the concrete aggregates or mixing water, or diffuse into the concrete through exposure to deicing chemicals or marine environments, seawater. In both cases chlorides will react with the hydrated cement matrix, calcium aluminates and calcium alumino ferrites, to form chloroaluminate and chloroferrite hydrates [3]. The stability of solid chloride binding hydrates depends on their chemical equilibrium with chlorides dissolved in the concrete pore water solution. "Free" chlorides present in the pore water solution will promote the corrosion process of the reinforcing steel in concrete. The minimum amount of chlorides required to initiate the corrosion process may be based on the ratio of chloride to hydroxyl ion concentration in the concrete pore water solution. A Cl^- / OH^- ratio equal to 0.6 has been estimated as the corrosion threshold chloride content [3]. Other research has indicated that the threshold chloride concentration is within the range of 0.6 to 0.9 kg of Cl^- per cubic meter of concrete [4].

The presence of Cl^- ions in sufficient concentration at the reinforcing steel depth will destroy the passive layer on the steel surface. The Cl^- ions will react with iron at the surface in the presence of oxygen according to the following anodic and cathodic reactions [2]:

$$Fe \rightarrow Fe^{++} + 2e^- \qquad (3)$$

$$1/2\ O_2 + H_2O + 2e^- \rightarrow 2OH^- \qquad (4)$$

The form of corrosion initiated on the reinforcing steel surface could be either pitting or general attack. If the breakdown of passivity by Cl^- ions occurs locally because of some variations in the passive-film structure and thickness, and there is sufficient amount of oxygen to maintain an oxide film over the majority of the metal surface to sustain the cathodic reaction, pitting corrosion will take place [5, 3]. If the passive layer on the reinforcing steel surface is almost completely destroyed or is not thermodynamically stable, general corrosion will take place given a sufficient supply of oxygen to depolarize the cathodic reaction. For the general corrosion the anodes and cathodes are more closely spaced than in the case of pitting corrosion [3].

While the corrosion process proceeds, metallic iron from the reinforcing steel transforms into oxidation products. In the first state of the oxidation ferrous hydroxide, $Fe(OH)_2$, is formed. Normally white in color when it is pure, ferrous hydroxide will change its color to green or greenish black because of incipient oxidation by air. Access to dissolved oxygen will convert $Fe(OH)_2$ to ferric hydroxide, $Fe(OH)_3$, which is orange to red brown in color, and exists in two forms, nonmagnetic áFe_2O_3 (hematite) or magnetic ãFe_2O_3. The á form is more stable because of the greater negative free energy of formation. A black intermediate layer forms often between hydrous Fe_2O_3 and FeO, a magnetic hydrous ferrous ferrite, $Fe_3O_4 \cdot nH_2O$. Thus rust films consist of three layers of iron oxides representing different states of oxidation [5].

1.2 History of Epoxy-Coated Reinforcing Steel (ECR)

The first tests on nonmetallic coatings were performed by the National Bureau of Standards (now the National Institute for Standards and Technology). Liquid and powdered coatings were examined for their corrosion protective qualities, chemical and physical durabilities, and chloride permeabilitity. Out of the 47 tested materials 36 were epoxies. It was found that epoxy and polyvinyl chloride coatings have the same protecting properties against deicing salt corrosion. The differences exist in the bond strength to the concrete with the epoxy coatings having a greater bond strength. The better performance was also found for powder epoxy coatings than the liquid epoxy coatings [6, 7, 8]. Fusion bonded epoxy coating applied to reinforcing steel was proposed as a method to improve the corrosion resistance of bridge decks in the early 1970s, as a conclusion of this initial research project.

Epoxy-Coated Reinforcement (ECR) was used for the first time in bridge construction in West Conshohocken in Pennsylvania in 1973 [9]. Four spans of this bridge were constructed with the ECR. Since then, the ECR has been used in many other structures in the United States and abroad. It was reported in 1987 that at least 41 state transportation departments were using ECR as the corrosion protection system in concrete decks. Based on 50 years of service and 1986 prices, estimated lifetime costs have shown that only a cover depth of 89 mm was a lower cost corrosion protection method than ECR [10]. The first corrosion failures of the ECR were reported in 1988 in the Florida Keys and in the Middle East. In both cases corrosion of the ECR was attributed to the inadequate surface preparation of the reinforcement, poor quality control, and quality assurance [11].

The performance of ECR is under continuous investigation in the United States and Canada. Failure of the ECR as a long time protection against corrosion was found in marine environments of Florida, and in the Northern US and Canada, where the application of deicing salts is frequent [12, 13].

The presence of microcell corrosion was identified as one of the mechanisms causing the corrosion of the ECR at holidays and bare areas, and underfilm corrosion [13]. The study showed that the main reason for the deterioration of concrete containing ECR is the coating-metal disbondment, which makes ECR more susceptible to the chloride induced corrosion process. The corrosion usually takes place around coating breaks and has cathodic disbondment characteristics. Tests have shown that loss of adhesion for ECR occurs in NaOH solutions free of chloride ions, and in solutions containing adequate concentrations of sodium and potassium ions [14].

1.3 Scope of the Study

The objective of this research was to test the behavior of ECR in simulated concrete pore water solutions. Adhesion of the epoxy-coating to the steel surface, blister formation, and development of the corrosion process for ECR was studied and compared to bare steel tested under the same conditions.

Bare steel performance was also evaluated in pore solutions with three different corrosion inhibitors. The purpose was to evaluate other corrosion protection systems for reinforcing steel in concrete and to compare their performance to ECR.

Chapter 2. BACKGROUND

2.1 Corrosion Protection Methods

Several parameters, oxygen, moisture content, and chloride concentration, will influence the development and rate of corrosion of reinforcing steel in concrete. It is known that corrosion will take place only if there is enough oxygen and water available at the bar depth for the corrosion process to occur. The presence of chloride ions will initiate the corrosion of steel in concrete and the rate of corrosion increases with increasing chloride concentration.

Based on these well known facts of corrosion science various methods for corrosion protection of reinforcing steel in concrete structures were proposed. First of all a high quality, low permeable concrete plays an important role in corrosion prevention. Low permeability and a sufficient cover depth will delay reinforcing steel corrosion by reducing the rate of chloride penetration into the concrete and extending the time to corrosion initiation. Protective coatings and sealers, and overlays are also used on concrete surfaces to prevent rapid chloride ingress into concrete. An important tool in corrosion protection is use of corrosion inhibitors admixed into concrete as well as protective coatings on reinforcing steel. Corrosion inhibitor admixtures elevate the chloride corrosion initiation concentration. Epoxy and zinc-galvanized coatings are currently the most popular protective coatings used on reinforcing steel.

Two types of corrosion protection methods were analyzed in this study: epoxy-coated reinforcing steel and corrosion inhibitors. ECR from three different manufacturers from the United States and one from Canada were evaluated during this research. Corrosion inhibitors from three manufacturers were also tested in this study.

2.1.1. Epoxy-Coated Reinforcing Steel

Epoxy-coatings for reinforcing steel were introduced as one of methods for corrosion protection of reinforcing steel in early 1970s. Presently ECR is used primarily in the USA, Canada, and Europe. The process for manufacturing of ECR was based on the coating of small diameter pipes used by the petroleum industry and utility companies. First step in this procedure is removing the millscale by grit or shot blasting. Then the bar is heated to about 230°C and dry epoxy powder is applied by an electrostatic spray. The powder melts, flows, and covers the bar surface. The last step is quenching in a water spray bath and holiday detection [15].

Laboratory research conducted on ECR through the last 20 years and more recently field investigations of existing bridge structures have presented mixed results concerning the protective properties of epoxy-coating against the chloride induced corrosion.

A FHWA study performed in 1980-1982 showed a reduction in corrosion for laboratory outdoor specimens with ECR in comparison to bare steel specimens. No cracking was developed for the ECR slabs even though some corrosion at holidays and bare areas on the ECR was observed. The bare steel specimens on the other hand cracked and the bars were corroding [15].

Research conducted for C-SHRP in 1990 by Kenneth C. Clear Inc. demonstrated a failure mechanism for ECR involving loss of adhesion and underfilm corrosion. It was also stated that the use of the ECR will extend the time to corrosion damage for bridge structures exposed to marine or deicing salt environments by only three to six years in comparison to bare steel [15].

A field investigation performed by CRSI on bridges located in Virginia, Wisconsin, Pennsylvania, New York, and Ohio showed no signs of progressive deterioration for the ECR [10].

Corrosion of ECR in the areas between 0.61 m and 1.83 m above high tide was observed in the Florida Keys bridges. It was found that ECR used in substructure elements, exposed to the marine environment, will corrode faster than bare steel [10].

2.1.2. Corrosion Inhibitors

Corrosion inhibitors are widely used to delay corrosion of reinforcing steel in concrete. There are three general groups into which corrosion inhibitors can be classified: anodic, cathodic, and adsorption inhibitors.

Anodic inhibitors react with the ions of the corroding metals increasing the polarization of the anode and producing thin passive film or salt layers which coat the anode. Two types of anodic corrosion inhibitors are important for steel, those which are oxidizing agents (nitrates, nitrites, and chromates), and those which require dissolved oxygen to be effective (silicates, phosphates, molybdates and borates) [16]. Anodic inhibitors are said to be dangerous because the corrosion rate will increase if too little inhibitor is used.

Cathodic inhibitors affect cathodic reactions. They react with the hydroxyl ions to precipitate insoluble compounds on the cathode site and prevent access of oxygen (salts of zinc and magnesium, calcium) or form a layer of adsorbed hydrogen on the cathode surface (arsenic, bismuth, antimony and some organic compounds) [16]. They are said to be safe because the active cathode area is reduced even if too little inhibitor is added.

From the two corrosion inhibitor groups, anodic inhibitors were found to be more efficient than cathodic corrosion inhibitors. Presently a combination of both is being used to provide the most corrosion protection (chromate/polyphosphate/zinc system) [16].

Adsorption inhibitors are adsorbed and desorbed from the metal surface. These are long organic molecules with side chains which can limit the diffusion of oxygen to the surface, trap the metal ions on the surface, and reduce the rate of dissolution or stabilize the double layer [16].

2.2 Pore Solution in Concrete

Concrete is a porous material containing several classes of pores in the cement paste. The internal pore system retains a significant amount of pore fluid called concrete pore water. Chemistry of the pore water is important for the understanding of migration processes in cement paste and trace elements mobility, including chloride in connection with corrosion of reinforcing steel in concrete. The composition of the concrete pore water solution can be determined by expressing the pore solution from concrete cores using a special high pressure device. It was found that potassium and sodium hydroxide are the primary components of the pore solution [17].

In an experiment performed by Diamond a pressure of 170 MPa was applied repeatedly to express 5 to 10 ml of pore solution from specimens. The steady state condition of the ion concentration in pore solution was reached after four days. The following ions and their concentrations were found for the 174 day old portland-cement specimens: 0.4 M Na^+, 0.2 M K^+, and 0.6 M OH^-. Ion concentration of calcium was equal to 0.004 M after one day of curing and decreased in time. The calculated pH level for the pore solution after four days was 13.75 and will be maintained indefinitely [18].

In a study performed by Andersson et al. a pressure of 375 MPa was applied on prepared specimens, and 4 to 10 ml of pore solution was obtained. The following ion concentrations were obtained in this study from 10 month old portland-cement paste: 1500 mg/l Na^+, 6300 mg/l K^+, and 90 mg/l Ca^{2+}. The measured pH was 13.4 [19].

Chapter 3. METHODS & MATERIALS

3.1 Test Methods

An accelerated corrosion protection evaluation of epoxy-coated reinforcement (ECR) was performed in this study. The behavior of ECR in comparison to bare steel (BS) was tested through an immersion test in various solutions. Following the immersion test period all specimens were evaluated by a series of corrosion performance test indicators.

3.1.1 Test Procedure

BS specimens and ECR specimens were tested through the immersion test at 40 °C in a simulated concrete pore water solution (PS). BS and ECR specimens were immersed into PS and PS containing additional ingredients, sodium chloride (NaCl) and/or a corrosion inhibitor (CI), which were aerated at the initiation of the pretreatment period. NaCl was added to the desired solutions after a 7-day PS pretreatment period. During pretreatment specimens were kept in PS or PS with CI. After pretreatment NaCl was added and the solutions were aerated with compressed oxygen (O_2) or breathing air (air) for one minute. Subsequently the solutions were aerated with O_2 or air once a week throughout the 90-day test period. The immersion test configuration is presented in Table 1.

After four weeks of immersion the test specimens were visually examined. Afterwards, visual examination was performed every two weeks for the remaining 90-day immersion period. BS specimens were examined for the initiation and progress of the corrosion process. ECR specimens were checked for blister formation and the presence of the corrosion products.

3.1.2 Solutions

Once a week the polypropylene containers with the specimens were taken out 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.

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.

3.1.3 ECR

After 90 days of immersion ECR specimens were taken out of the solutions. They were examined visually. 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 a development of corrosion on the steel under the blister was performed. Hardness of the epoxy coating was tested according to ASTM D 3363 - 92a "Film Hardness by Pencil Test". The knife peel test according to MTO - Draft 93 10 27 "Hot Water Test for Epoxy-Coated Reinforcing Bars" was also performed to determine the adhesion of the epoxy coating to steel. Results of the adhesion and hardness tests were compared with the before immersion test results.

3.1.4 Bare Steel

BS specimens were also examined visually for the development of the corrosion process after the 90-day immersion test. The corrosion area on each bar was estimated and the percent corroded area was calculated.

3.2 Test Solutions

The PS chosen for this study was determined to be the most suitable to simulate the concrete environment. NaCl was added to the PS in various quantities to produce the corrosive environment for tested BS and ECR specimens. Three different corrosion inhibitors were added to the PS to evaluate their protective properties against corrosion due to chloride ions present in the solutions.

3.2.1 PS Selection

PS used in this experiment was based on work of Diamond [18]. The basic PS composition is as follows: 0.4 M KOH, 0.2 M NaOH and 0.004 M $Ca(OH)_2$.

3.2.2 Solution Concentration

Four different amounts of NaCl were added to the PS 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 % by weight [20]. Considering drying effects and the low w/c concrete (0.45) used in Virginia, the 3 % weight was selected and used in this study. Equivalent chloride content in one 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.

Corrosion inhibitors from three sources were used according to the manufacturers' recommendations for addition to concrete. It was assumed that all of corrosion inhibitors, DCI, R222 and A2000, would be dissolved in the concrete pore water. Only one of the corrosion inhibitors (DCI) was used to produce PS for the testing of ECR specimens with 1 % damage. Other solutions with all types of corrosion inhibitors were used for the BS specimen testing only. Composition of the different PS are presented in Table 2.

3.2.3 Air & Oxygen Saturation

During the immersion test the solutions were aerated once a week with pure compressed oxygen or breathing air. Time of the aeration equal to one minute was determined through the oxygen saturation testing using an oxygen meter.

3.2.4 Temperature Selection

The test temperature of 40 °C used in this experiment was determined from a series of measurements taken in concrete at reinforcing steel depths of 25 and 51 mm in Blacksburg, Virginia. Slabs used in this study were kept outdoors, and the temperature was measured throughout the whole year. The near highest summer temperature at the depth of the reinforcing steel was 40 °C.

3.3 Materials

3.3.1 ECR

ECR, # 5 bars, from four different sources were evaluated in this study. Three of them were from the US manufacturers (FS, LNE and FSC) and one was from a Canadian manufacturer (CGN). ECR from the United States were collected at the construction site and stored outside without being covered for a total exposure period of 30 days, before being brought into the laboratory and stored under a black plastic cover until used. Thus, the US bars were exposed to the natural environment and had some surface damage due to the transportation to the job site and handling at the job site. ECR from Canada were in perfect condition. Each bar was packed separately and shipped directly from the manufacturer.

ECR were cut into the 152 mm ECR specimens using a hand-held bandsaw. Plastic caps were attached to the cut ends of ECR using a hot melt glue and a glue gun. The purpose of this was to protect the bare ends of ECR specimens from corrosion during the immersion test.

Damage evaluation was performed on each ECR specimen. Visual observations of ECR specimens having any cracks in coating, holes, and mashed, scraped or dent areas were recorded. The Tinker & Rasor Model M/1 holiday detector was used according to ASTM G 62 - 87

"Holiday Detection in Pipeline Coatings" to detect any flaws (holidays) in the coating not visible with the unaided eye. Coating thickness of the prepared ECR specimens was measured according to ASTM G 12 - 83 "Nondestructive Measurement of Thickness of Pipeline Coatings on Steel" using the coating thickness gauge Minitest 500 produced by Elektro-Phisik (Germany).

Percent damage was calculated and specimens were divided into 0 % and 1 % damage groups within each specimen type except for the Canadian bars. The Canadian specimens had only minor defects compared to the US specimens, and single holidays present, so the coating surface was assumed to be perfect with 0 % damage for the whole group. Each percent damage group was then divided into test groups of three specimens each, and were exposed to the same solution types. A total of 120 ECR specimens were prepared for this study.

3.3.2 Bare Steel

BS used in this study was manufactured by Resco Steel from Roanoke, Virginia. All bars were #5 bars (d = 16 mm), Grade 60, Tensile Strength = 645-703 MPa, Yield Point = 425-473 MPa, Elongation (200 mm) = 10 %. The chemical composition of BS was as follows: C = 0.38-0.43 %, Mn = 0.83-1.00 %, S = 0.03-0.05 %, P = 0.01 %. They were stored indoors, in the laboratory, before they were prepared for the experiment.

Bare steel reinforcement was cut into the 152 mm long BS specimens using a hand-held bandsaw. They were soaked in the hexane for 24 hours to remove any grease and dirt collected on the surface. Specimens were divided in the test groups of two and placed into the selected solutions. A total of 80 BS specimens were prepared for this experiment.

3.3.3 Corrosion Inhibitors

Three corrosion inhibitors were evaluated in this study: DCI, R222 and A2000. They are produced by three different manufacturers, two from the United States and one from Europe. Chemical compositions of tested corrosion inhibitors were not determined. The main difference among three corrosion inhibitors was that two of them: R222 and A2000 are organic based inhibitors. Whereas DCI is a non-organic inhibitor. According to the manufacturers, DCI contains 30 % calcium nitrite and 70 % water, R222 is an aqueous mixture of amines and esters, and A2000 is a mixture of alcohol and amine.

3.4 Immersion Test

Prepared and pretreated specimens were tested through the immersion test. The immersion test period was 90 days. Specimens were placed into the closed polypropylene containers, covered with the various PS, and kept in the oven at 40 °C. The number and the type of specimens used in the immersion test, and various environments they were exposed to, are presented in Table 3.

Chapter 4. RESULTS

4.1 Bare Steel

Bare steel tested in this experiment was visually examined after the 90-day immersion period. The specimen condition was evaluated with the unaided eye and later microphotographs were taken to document the type of corrosion damage present on the steel surface. The corrosion area was estimated for each specimen and the percent surface corrosion was calculated.

4.1.1 Visual Examination

The corrosion type 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 BS specimens tested in the PS with no corrosion inhibitors, aerated with oxygen, developed the larger areas of corrosion on the steel surface in comparison to the specimens evaluated in PS aerated with air, see Figure 1.

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 PS.

The corrosion area on the specimens' surface for the BS specimens tested in solutions with all three corrosion inhibitors increased with the increasing concentrations of Cl^- ions for the oxygen and air aeration, Figures 2 and 3.

Typical corrosion observed for BS specimens tested in various PS is illustrated in the microphotographs presented in Figures 4 through 7.

4.2 ECR

Before the ECR specimens were immersed into the chosen PS the thickness of the coating was measured and the holiday detection test was performed. After the 90-day immersion period the ECR specimens were examined visually, the hardness of the coating and the coating adhesion to the steel surface was also tested. The detailed description of the above procedures is given in the Methods and Materials section.

4.2.1 Thickness Determination

Three specimens from each manufacturer were tested. The coating thickness was measured in three locations: on the radial ribs, longitudinal ribs, and between ribs. The mean, standard deviation, and coefficient of variation were determined for the each set of measurements, and for the whole specimen (bar). The results of the coating thickness measurements are presented in Tables 5 to 8.

The average coating thickness for the bar was about 300 microns for the FS specimens, 200 microns for the LNE specimens, 250 microns for the FSC specimens, and 270 microns for the CGN specimens. Coating thickness also varied depending on the measurement location. For the FS specimens the average thickness on radial ribs was close to 400 microns, between ribs close to 300 microns, and on longitudinal-ribs close to 250 microns, Figure 8. The average coating thicknesses for the LNE specimens were as follows: radial ribs close to 250 microns, between ribs close to 150 microns, and longitudinal-ribs close to 150 microns, Figure 9. For the FSC specimens the average coating thicknesses were close to 300 microns for the radial ribs, close to 170 microns between ribs, and close to 270 microns for the longitudinal-ribs, Figure 10. The last group of the ECR specimens, CGN, had the following coating thickness measurements: radial ribs close to 300 microns, between ribs close to 200 microns, and longitudinal ribs close to 250 microns, Figure 11.

4.2.2 Holiday Detection

The average number of holidays for the tested ECR specimen types was as follows: CGN - 0.14 holidays per 152 mm, FSC - 0.19 holidays per 152 mm, FS - 0.22 holidays per 152 mm, and LNE - 10 holidays per 152 mm. The value of 10 holidays per 152 mm was assigned to the LNE specimens because of the continuous holidays in the epoxy coating, Figure 12.

4.2.3 Visual Examination

After the 90 day immersion test, ECR specimens were examined visually. 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 the percent blister area was calculated for each ECR specimen. Visual examination for the corrosion development on the steel surface under the blister was performed. The results of the visual examination are presented in Tables 9 to 12.

For the specimens with assumed 0 % damage only CGN specimens did not developed any blisters in the epoxy coating throughout the immersion in PS test. Blisters in the coating for the FSC specimens were present only for the solution with the Cl^- ion concentration equal to 0.59 mole. The percent blister area was about 0.10 %. The FS specimens developed blisters for the solutions with the three highest Cl^- ion concentrations, 0.59, 1.16, and 2.3 moles. The largest percent blister area for the FS specimens was calculated for the specimens immersed in the PS with the Cl^- ion concentration equal to 0.59 mole , and was about 0.50 %. The percent blister area of about 0.10 % was characteristic for the FS specimens immersed in the PS with 1.16 and 2.3 moles of Cl^- ion. The largest percent blister area was determined for LNE specimens immersed in the PS with the three Cl^- ion concentrations, 0.28, 1.16 and 2.3 moles, and were 0.70 %, 0.95 % and 1.05 %, respectively. For the solution with the 0.59 mole Cl^- ion concentration the percent blister area for the LNE specimens was about 0.50 %.

For the specimens with about 1 % damage the FS specimens immersed in the PS with the DCI corrosion inhibitor in it developed blisters for the PS with the 0.59 and 2.10 mole Cl^- ion concentrations. Blister areas were about 0.15 % and 0.05 %, respectively. The percent blister areas equal to 0.05 %, 0.20 %, and 0.20 % were characteristic for the FS specimens immersed into the PS with 0.28, 0.59, and 1.16 moles of the Cl^- ion. The FSC specimens developed blisters for the solutions with the 0.28, 0.59, 1.16, and 2.30 mole Cl^- ion concentrations. They were about 0.40 %, 0.55 %, 0.35 %, and 0.15 %, respectively. The largest percent blister area was determined for the LNE specimens immersed in the PS with the 0.28, 0.59, 1.16, and 2.30 mole Cl^- ion, and the results were: 1.10 %, 0.80 %, 0.95 %, and 0.80 %, respectively.

Blisters in the epoxy coating were not present after the 90 day test period neither for the specimens with the 0 % damage nor for the specimens with the 1 % damage immersed into the PS with no sodium chloride (NaCl).

The pH of the solution inside the blister was determined using pH paper. The lowest pH measurements were 5 and 6, the highest pH measurements were about 11 and 12. There were a few measurements with a pH 8. It was observed that 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 to 12.

After striping the coating from the specimens in the blister area various corrosion states were observed on the steel surface. There were cases were steel looked as a white metal surface. On the other occasions different stages of the corrosion process were taking place underneath the coating, see microphotographs presented in Figures 13 through 17.

4.2.4 Adhesion Testing

The knife peel test was performed to determine the adhesion of the epoxy coating to steel. The adhesion rating used in this test 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.

The adhesion test was performed on all four types of ECR specimens before the 90 day immersion test. The adhesion rating of FS, FSC, and CGN specimens was 1. The LNE specimens had an adhesion rating of 2.

After the immersion test period the adhesion was tested on each specimen. The results of the knife peel test are presented in Tables 13 to 16. For the specimens with the 0 % damage the adhesion rating of the CGN specimens was equal to 1 except the solution with the 2.30 mole Cl^- ion concentration. For this solution the adhesion value had changed from 1 to 2. The adhesion of the FSC specimens was equal to 2 for all specimens except for the specimens immersed in the PS of 0.28 mole Cl^- ion, which had an adhesion rating of 3. The FS specimens had an adhesion rating equal to 2 for the solutions with the Cl^- ion concentrations of 0.28 and 1.16 moles. For the PS with no sodium chloride (NaCl) in it and the solutions with the 0.59 and 2.30 mole Cl^- ion concentrations the adhesion was 4. The LNE specimens had an adhesion value equal to 3 only for the specimens tested in the PS with no Cl^- ions in it. For all four solutions with NaCl, the adhesion of the LNE specimens was 5.

In the group of specimens with the 1 % damage the adhesion rating of the FS specimens immersed in the PS with DCI was constant at 1 except for the solution with no NaCl in it where the adhesion had changed from 1 to 2. For the solutions without admixed DCI the adhesion of 1 was observed only for the FS specimens tested in the PS with no Cl^- ions in it. The FS specimens from the solutions with the 0.59 and 2.30 mole Cl^- ion concentrations had an adhesion equal to 3. The adhesion values of 4 and 5 were determined for the FS specimens immersed in the solutions with the Cl^- ion concentrations of 1.16 and 0.28 moles, respectively. The FSC specimens had an adhesion value of 1 only for the solution with no NaCl in it. For the FSC specimens tested in the solutions with the 0.28 and 0.59 mole Cl^- ion the adhesion was equal to 4. The adhesion values of 3 were determined for the FSC specimens immersed in the PS with the Cl^- ion concentrations of 1.16 and 2.30 moles. The LNE specimens had the adhesion equal to 1 for the PS without NaCl in it, and the adhesion of 5 for the four other solutions containing various amounts of NaCl.

4.2.5 Hardness Test

Hardness of the epoxy coating was tested according to ASTM D 3363 - 92a "Film Hardness by Pencil Test". The results of the hardness test for all four specimen types were always equal to "B", before and after the immersion test, see Tables 17 to 20.

4.3 Test Solutions

Before the immersion test, selected PS had been tested to determine the time for saturation by oxygen and breathing air.

Throughout the immersion test pH for all solutions was measured biweekly. After the 90-day immersion test, chosen solutions were titrated to determine their pH and compared to the pH measured with the pH probe.

Chloride content of all solutions was titrated after the immersion test period.

4.3.1 Air & Oxygen

During the immersion test the solutions were aerated once a week with pure compressed oxygen or breathing air. Time of the aeration equal to one minute was determined through the oxygen saturation testing using an oxygen meter. The results of the testing are presented in Table 21. The PS with the various chloride content and the PS with admixed DCI and NaCl were evaluated for the oxygen saturation. The temperature of tested solutions was about 40 °C, and their measured pH was about 12. Oxygen level was measured first for the solutions before the aeration, and then after the four different aeration periods of 30, 60, 120, and 240 seconds, for the same solutions. The oxygen content in solutions was determined for the solutions aerated with compressed oxygen and breathing air. In both cases 60 seconds was a sufficient time period for the solutions to become saturated with oxygen.

4.3.2 Chloride Titration

Chloride concentration of the supernatant for all solution types was also determined by the titration against silver nitrate ($AgNO_3$). The results of the chloride titration are presented in Table 22. Average chloride concentrations in all solution types, starting from the PS with the smallest amount of NaCl, were as follows: 0.3 mole, 0.6 mole, 1.1 mole, and 2.2 mole. The expected chloride concentrations from the solution calculation were equal to 0.3 mole, 0.6 mole, 1.2 mole, and 2.4 mole for the same solution types respectively.

4.3.3 pH Testing

The pH for each solution was measured biweekly using the pH probe. Measured values of pH decreased with increasing NaCl content within each solution test series, Table 23. The measured PS pH decreased from 12.8 at zero chloride content to 12.4 at the highest chloride content. The highest and the lowest measured pH for PS with the R222 and A2000 corrosion inhibitors were equal to 13.0 and 12.5, respectively. However, the PS with DCI had a pH lower than all other PS. The probe measured pH for these solutions ranged between 11.4 and 11.8.

The pH titration was also performed to evaluate the pH values measured with the pH probe and the results are presented in Table 23. The pH of the titrated PS containing various chloride concentrations was equal to 13.6. The titrated pH values for the PS with R222, A2000, and DCI were as follows: 13.6, 13.8, and 13.8, which are approximately equal to the calculated pH of 13.8 considering 100 % dissolution of the hydroxide compounds.

The pH values of the supernatants (solution in the contact with the bar) were also determined and are presented in Table 23. The results of the supernatant titration for the solutions with the smallest and the highest Cl^- ion concentrations were equal to 13.6 for PS, 13.5 for PS with R222, 13.8 and 13.7 for PS with A2000, and to 12.6 and 12.5 for PS with DCI, respectively.

Chapter 5. DISCUSSION

5.1 Bare Steel

The area of corrosion was influenced by the solution type, chloride content and method of aeration. For every group of specimens pitting corrosion progressed rapidly at the highest solution chloride ion content. The area covered with corrosion products was larger and the corrosion pits were deeper, Table 4. The PS with no corrosion inhibitor, aerated with oxygen, produced a more corrosive environment than solutions aerated with air, Figure 1. The corrosion process was influenced by the rate of oxygen diffusion in solution to the bar surface. As the concentration of chloride increased in the solution, the corrosion rate increased until the process was controlled by the oxygen concentration at the bar, as illustrated by the reduction in the corrosion area with increasing chloride content, Figures 1,2 and 3.

For the three corrosion inhibitors tested in this study : R222, A2000, and DCI, neither R222 nor A2000 provided any corrosion protection for the BS, only DCI was able to protect BS samples from corrosion, Figures 2 and 3. Specimens tested in the PS and the PS with R222 or A2000 behaved almost identically to the BS with no corrosion inhibitor. The corrosion area on the specimen's surface increased with increasing Cl^- ion content. This was observed for both types of aeration: oxygen and air, Figures 2 and 3.

5.2 ECR

According to ASTM A 775 - 95, ECR coating thickness is to be between 175 and 300 μm. Coating thickness of tested ECR specimens varied depending on the location of the thickness measurement, see Figures 4 to 7. The average coating thickness for each ECR type was within the specification limits. The observed tendency for FS specimens was that the average coating thickness seemed to be slightly higher than the upper limit of 300 μm. Whereas the average coating thickness of LNE specimens was close to the lower limit of 175 μm.

Holiday detection testing showed that FS, FSC and CGN specimens were within the specification limits according to ASTM A 775 - 95. The number of holidays detected for these specimens was smaller than 1 holiday per 152 mm. Continuous holidays were observed for LNE specimens. During the holiday detection it was not possible to distinguish the exact number of holidays for the LNE specimens. LNE specimens were the only ECR type which did not meet the holiday specification limit, see Figure 12.

Coating hardness for all specimens types was equal to B before and after the immersion test, see Tables 17 to 20. Therefore this particular hardness test does not seem to be a proper method for the evaluation of the short term exposure of ECR specimens.

The change in adhesion was observed for all ECR specimen types. The best adhesion performance was determined for the CGN specimens with 0 % damage, immersed into the PS with the various chloride content, and for the FS specimens with 1 % damage, immersed into the PS with DCI at the various chloride content, see Figures 18 and 19. For the CGN specimens a reduction in the adhesion rating from 1 to 2 was observed only for the PS with the highest chloride concentration. The adhesion for FS specimens changed from 1 to 2 only for the PS containing DCI and no NaCl. The worst performance according to the adhesion testing was observed for the LNE specimens with 0 % and 1 % damage. The decrease in adhesion rating from 2 to 3 was determined for the PS with no NaCl. For the PS with chloride, total loss of adhesion was observed, all adhesion ratings were equal to 5. The adhesion rating decrease was also determined for the FS and FSC specimens with 0 % and 1 % damage. The change in the adhesion rating varied from 2 to 5 with no general detectable trends.

Blisters in the epoxy coating were not observed throughout the immersion test for only the CGN specimens with 0 % damage. The FSC specimens with 0 % damage developed blisters in the PS with 0.59 mole chloride concentration only, see Figure 20. For the specimens with 1 % damage the best performance was observed for the FS specimen type immersed in the PS with DCI at various chloride content. Blisters were present for only the FS specimens immersed in the PS with DCI and 0.59 mole and 2.1 mole chloride concentrations, see Figure 21. The largest area on the epoxy coating covered with blisters was determined for the LNE specimens with 0 % and 1 % damage.

Visual examination of steel surface under the blister and pH measurements of the solution inside the blister would suggest the following mechanism for the corrosion of the steel underneath the epoxy coating. First, PS 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 is about 12. The steel surface does not corrode at this stage of the deterioration process. The next step is the arrival of chloride ions at the clean steel surface at a sufficient concentration to initiate corrosion, the pH decreases to 5 as the corrosion process proceeds. Corrosion products accumulate underneath the coating and their expansion causes the coating to crack. PS mixes with the solution inside the blister and the new pH under the coating goes back to the previous value of about 12 as more PS enters the blister. The corrosion mechanism observed in this study of ECR was first observed and proposed by Sagues [21].

5.3 Test Solutions

Chloride concentrations in test solutions determined through the titration are equal or very close to the expected values, see Table 22.

The results of the pH titration for the PS, and PS 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 13.8, see Table 23.

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 PS. It is known that the high concentrations of alkali metal ions will cause an alkaline error for glass electrodes [22].

Chapter 6. CONCLUSIONS

The only corrosion inhibitor that performed well under the experimental conditions was DCI. BS specimens immersed into the PS with DCI aerated with O_2 had no signs of corrosion for the chloride concentration in solution below 0.6 mole. For the two other corrosion inhibitors, R222 and A2000, BS specimens demonstrated similar behavior as the BS specimens tested in PS with NaCl containing no corrosion inhibitor.

The study performed on ECR specimens showed that coating thickness and damage present in the coating will influence the adhesion loss between the coating and steel surface, and blister formation.

The best results from the immersion test were observed for the CGN specimens within the group of specimens with 0 % damage and for the FS specimens with 1 % damage immersed in the solutions with the DCI corrosion inhibitor. The FS and FSC specimens immersed into the PS with the various chloride contents showed only some corrosion protection. The worst overall performance was determined for the LNE specimens.

The results of this study suggest that ECR as a corrosion protection method may perform well in a PS environment if the ECR has a perfect epoxy coating, with no damage, no holidays, good adhesion and the thickness within the specification limits. Any damage present in the coating will cause ECR to perform 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.

Chapter 7. RECOMMENDATIONS FOR FURTHER RESEARCH

Based on the limited time and scope of this study, the following recommendations can be made for further research:

1. To more accurately predict the satisfactory performance of corrosion inhibitors, long term testing of those inhibitors in concrete, where chloride diffusion and corrosion initiation levels could be elevated, should be conducted.
2. The mechanism of blister formation on ECR specimens should be examined carefully including testing of the blister solution for pH values and different ion concentrations with special attention given to the Cl^- ion concentration.
3. Electrochemical techniques like Electrochemical Impedance Spectroscopy (EIS) and Polarization Resistance should be employed into the epoxy-coating and corrosion inhibitor performance evaluation in simulated pore water solutions and in concrete
4. Dual corrosion protection systems consisting of epoxy-coatings and corrosion inhibitors should be evaluated in a simulated concrete pore water solution and in concrete.

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Table 1. Immersion Test Exposure Conditions

Solution Type	Aeration Type	Specimen Type				
		BS	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	---	---	---	---

Table 2. 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	------	0.5
PS + NaCl	1.47	------	1
PS + NaCl	2.93	------	2
PS + NaCl	5.86	------	4
PS* + DCI	0.00	20	------
PS* + DCI + NaCl	0.73	20	0.5
PS* + DCI + NaCl	1.47	20	1
PS* + DCI + NaCl	2.93	20	2
PS* + DCI + NaCl	5.86	20	4
PS + R222	0.00	5	------
PS + R222 +NaCl	0.73	5	0.5
PS + R222 +NaCl	1.47	5	1
PS + R222 +NaCl	2.93	5	2
PS + R222 +NaCl	5.86	5	4
PS + A2000	0.00	2.5	------
PS + A2000 + NaCl	0.73	2.5	0.5
PS + A2000 + NaCl	1.47	2.5	1
PS + A2000 + NaCl	2.93	2.5	2
PS + A2000 + NaCl	5.86	2.5	4

Note: PS* - pore solution with smaller water quantity, because of the water present in the corrosion inhibitor (DCI = 30% solids + 70 % water)

Table 3. Immersion Test Matrix

			SpecimenType										
solution	temp.	aeration	BS				ECR-FS			ECR-LNE		ECR-FSC		ECR-CGN
			DCI	R222	A2000	---	0%	1%	1%+DCI	0%	1%	0%	1%	0%
PS	40C	air				2								
	40C	O2				2	3	3		3	3	3	3	3
PS + CI	40C	air	2	2	2									
	40C	O2	2	2	2				3					
PS + NaCl	40C	air				2								
0.73	40C	O2				2	3	3		3	3	3	3	3
PS + CI + NaCl	40C	air	2	2	2									
0.73	40C	O2	2	2	2				3					
PS + NaCl	40C	air				2								
1.47	40C	O2				2	3	3		3	3	3	3	3
PS + CI + NaCl	40C	air	2	2	2									
1.47	40C	O2	2	2	2				3					
PS + NaCl	40C	air				2								
2.93	40C	O2				2	3	3		3	3	3	3	3
PS + CI + NaCl	40C	air	2	2	2									
2.93	40C	O2	2	2	2				3					
PS + NaCl	40C	air				2								
5.86	40C	O2				2	3	3		3	3	3	3	3
PS + CI + NaCl	40C	air	2	2	2									
5.86	40C	O2	2	2	2				3					
Sum:			80				45			30		30		15

Total: 200

Table 4. Visual Examination of BS Specimens

specimen type	titrated Cl concentration in moles	corrosion type *	corrosion area [mm2] specimen 1	specimen 2	% corrosion
BS 1 O2	0	------	0	0	0
BS 2 O2	0.3	pitting corrosion	71	46	1.07
BS 3 O2	0.6	deeper pitting corrosion	141	142	2.58
BS 4 O2	1.2	deeper pitting corrosion	180	212	3.57
BS 5 O2	2.3	deepest pitting corrosion	219	215	3.96
BS 1 (R) O2	0	------	0	0	0
BS 2 (R) O2	0.3	pitting corrosion	115	103	1.99
BS 3 (R) O2	0.6	deeper pitting corrosion	163	190	3.22
BS 4 (R) O2	1.1	deeper pitting corrosion	180	170	3.19
BS 5 (R) O2	2.2	deepest pitting corrosion	192	230	3.85
BS 1 (R) air	0	------	0	0	0
BS 2 (R) air	0.3	pitting corrosion	104	112	1.97
BS 3 (R) air	0.6	deeper pitting corrosion	110	115	2.05
BS 4 (R) air	1.1	deeper pitting corrosion	162	120	2.57
BS 5 (R) air	2.2	deepest pitting corrosion	230	239	4.27
BS 1 (A) O2	0	------	0	0	0
BS 2 (A) O2	0.3	pitting corrosion	43	60	0.94
BS 3 (A) O2	0.5	deeper pitting corrosion	130	143	2.49
BS 4 (A) O2	1.1	deeper pitting corrosion	148	140	2.62
BS 5 (A) O2	2.1	deepest pitting corrosion	170	154	2.95
BS 1 (A) air	0	------	0	0	0
BS 2 (A) air	0.3	pitting corrosion	72	80	1.39
BS 3 (A) air	0.5	deeper pitting corrosion	110	140	2.28
BS 4 (A) air	1.1	deeper pitting corrosion	153	150	2.76
BS 5 (A) air	2.1	deepest pitting corrosion	150	170	2.92

Table 4. Visual Examination of BS Specimens (cont.)

specimen type	titrated Cl concentration in moles	corrosion type *	corrosion area [mm2] specimen 1	corrosion area [mm2] specimen 2	% corrosion
BS 1 (DCI) O2	0	------	0	0	0
BS 2 (DCI) O2	0.3	------	0	0	0
BS 3 (DCI) O2	0.6	pitting corrosion	65	70	1.23
BS 4 (DCI) O2	0.9	deeper pitting corrosion	89	100	1.72
BS 5 (DCI) O2	2.1	deepest pitting corrosion	140	132	2.48
BS 1 (DCI) air	0	------	0	0	0
BS 2 (DCI) air	0.3	pitting corrosion	30	50	0.73
BS 3 (DCI) air	0.6	deeper pitting corrosion	72	67	1.27
BS 4 (DCI) air	0.9	deeper pitting corrosion	88	102	1.73
BS 5 (DCI) air	2.1	deepest pitting corrosion	102	105	1.89

Note: R = R222
A = A2000
* Comparison of depth of pitting is relative to those specimens within each above group not between groups. Thus no comparison between test groups on pit depths is inferred.

Table 5. Coating Thickness, ECR-FS Specimens

steel	coating thickness [micrometer]			
type	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
std. dev.	26.55	40.72	28.18	70.39
c.o.v.	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
std. dev.	24.67	31.01	37.81	87.94
c.o.v.	0.06	0.11	0.16	0.27

Table 5. Coating Thickness, ECR-FS Specimens (cont.)

steel	coating thickness [micrometer]			
type	radial ribs	between ribs	longitudinal ribs	bar
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
std. dev.	44.95	69.35	36.82	85.82
c.o.v.	0.11	0.26	0.14	0.28

Table 6. Coating Thickness, ECR-LNE Specimens

steel	coating thickness [micrometer]			
type	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
std. dev.	46.04	28.24	24.98	54.58
c.o.v.	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
std. dev.	47.69	29.28	14	66.29
c.o.v.	0.18	0.19	0.1	0.36

Table 6. Coating Thickness, ECR-LNE Specimens (cont.)

steel	coating thickness [micrometer]			
type	radial ribs	between ribs	longitudinal ribs	bar
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
std. dev.	40.98	30.54	41.59	52.28
c.o.v.	0.17	0.2	0.19	0.26

Table 7. Coating Thickness, ECR-FSC Specimens

steel type	coating thickness [micrometer] radial ribs	between ribs	longitudinal ribs	bar
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
std. dev.	29.56	25.11	30.61	58.51
c.o.v.	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
std. dev.	21.41	36.37	22.24	61.33
c.o.v.	0.07	0.19	0.07	0.23

Table 7. Coating Thickness, ECR-FSC Specimens (cont.)

steel	coating thickness [micrometer]			
type	radial ribs	between ribs	longitudinal ribs	bar
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
std. dev.	42.66	24.2	17.83	68.43
c.o.v.	0.14	0.14	0.1	0.32

Table 8. Coating Thickness, ECR-CGN Specimens

steel	coating thickness [micrometer]			
type	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
std. dev.	25.62	20.42	31.62	48.61
c.o.v.	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
std. dev.	20.69	20.84	18.84	57.16
c.o.v.	0.05	0.08	0.06	0.18

Table 8. Coating Thickness, ECR-CGN Specimens (cont.)

steel type	coating thickness [micrometer] radial ribs	 between ribs	 longitudinal ribs	 bar
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
std. dev.	22.03	29.72	28.59	43.56
c.o.v.	0.08	0.15	0.12	0.18

Table 9. Visual Examination of ECR-FS Specimens

specimen type	specimen symbol	corr	visual observation blisters			% area of blisters
			#	pH	area [mm2]	
ECR-FS 0%	2Q	---	---	---	---	
0.00, O2	2K	---	---	---	---	
	2R	---	---	---	---	
average						0
ECR-FS 0%	3O	---	---	---	---	
0.73, O2	3L	---	---	---	---	
	3S	---	---	---	---	
average						0
ECR-FS 0%	3K *	---	2	12	12	
1.47, O2	3J *	---	2	5 &12	46	
	3F *	+	1	---	18	
average					25.33	0.5
ECR-FS 0%	4G	---	---	---	---	
2.93, O2	4O	---	---	---	---	
	4S *	+	2	11	10	
average					3.33	0.1
ECR-FS 0%	4H	+	---	---	---	
5.86, O2	4A *	---	2	12	20	
	4P	---	---	---	---	
average					6.67	0.1
ECR-FS 1%	1C	---	---	---	---	
0.0, O2	1G	---	---	---	---	
	1N	---	---	---	---	
average						0
ECR-FS 1%	2P	+	---	---	---	
0.73, O2	2D	+	---	---	---	
	2F *	+	1	12	10	
average					3.33	0.1

Table 9. Visual Examination of ECR-FS Specimens (cont.)

specimen type	specimen symbol	corr	visual observation blisters #	pH	area [mm2]	% area of blisters
ECR-FS 1%	3N	+	1	12	20	
1.47, O2	3E *	+	1	12	15	
	3B	---	---	---	---	
average					11.67	0.2
ECR-FS 1%	4D *	+	1	5	25	
2.93, O2	4C	+	---	---	---	
	4L *	+	1	5	12	
average					12.33	0.2
ECR-FS 1%	5N	+	---	---	---	
5.86, O2	5J	---	---	---	---	
	5K	---	---	---	---	
average						0
ECR-FS 1%	7K	---	---	---	---	
DCI, 0.00, O2	7B	---	---	---	---	
	7P	---	---	---	---	
average						0
ECR-FS 1%	11	---	---	---	---	
DCI, 0.73, O2	11O	---	---	---	---	
	11J	---	---	---	---	
average						0
ECR-FS 1%	7I	---	---	---	---	
DCI, 1.47, O2	7L	---	---	---	---	
	7G *	---	5	---	25	
average					8.33	0.2
ECR-FS 1%	9I	---	---	---	---	
DCI, 2.93, O2	9K	---	---	---	---	
	9A	---	---	---	---	
average						0

Table 9. Visual Examination of ECR-FS Specimens (cont.)

specimen type	specimen symbol	visual observation corr	blisters #	pH	area [mm2]	% area of blisters
ECR-FS 1%	5S	---	---	---	---	
DCI, 5.86, O2	5A	---	---	---	---	
	5M *	---	1	---	10	
average					3.33	0.1

Note: 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	corr	visual observation blisters #	pH	area [mm2]	% area of blisters
ECR-LNE 0%	1Q	---	---	---	---	
0.00, O2	1O	---	---	---	---	
	1R	---	---	---	---	
average						0
ECR-LNE 0%	1N *	+	7	12	49	
0.73, O2	1S *	+	4	12	12	
	1A *	+	8	5 & 12	58	
average					39.67	0.72
ECR-LNE 0%	1H *	+	4	12	17	
1.47, O2	1P *	+	5	12	32	
	1G *	+	8	12	34	
average					27.67	0.5
ECR-LNE 0%	2E *	+	4	12	40	
2.93, O2	2D *	+	5	12	69	
	2R *	+	4	12	47	
average					52	0.95
ECR-LNE 0%	2F *	+	3	12	55	
5.86, O2	2Q *	+	9	12	66	
	2O *	+	5	12	52	
average					57.67	1.05
ECR-LNE 1%	2K	---	---	---	---	
0.00, O2	2I	---	---	---	---	
	2L	---	---	---	---	
average						0
ECR-LNE 1%	1L *	+	9	12	60	
0.73, O2	1B *	+	3	12	60	
	1C *	+	6	12	64	
average					61.33	1.12

Table 10. Visual Examination of ECR-LNE Specimens (cont.)

specimen type	specimen symbol	corr	visual observation blisters #	pH	area [mm2]	% area of blisters
ECR-LNE 1%	1J *	+	8	12	35	
1.47, O2	1E *	+	3	12	11	
	1I *	+	5	12	80	
average					42	0.77
ECR-LNE 1%	3K *	+	6	12	58	
2.93, O2	3F *	+	5	12 & 5	58	
	3G *	+	5	12	40	
average					52	0.95
ECR-LNE 1%	3J *	+	5	12	40	
5.86, O2	3E *	+	3	12	34	
	3I *	+	4	12	60	
average					44.67	0.81

Note: 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	corr	visual observation blisters #	pH	area [mm2]	% area of blisters
ECR-FSC 0%	21F	---	---	---	---	
0.00, O2	21Q	---	---	---	---	
	21S	---	---	---	---	
average						0
ECR-FSC 0%	21G	---	---	---	---	
0.73, O2	21O	---	---	---	---	
	21J	---	---	---	---	
average						0
ECR-FSC 0%	21D	---	---	---	---	
1.47, O2	21P	---	---	---	---	
	21E *	+	1	6	15	
average					5	0.1
ECR-FSC 0%	23M	+	---	---	---	
2.93, O2	32R	---	---	---	---	
	23Q	+	---	---	---	
average						0
ECR-FSC 0%	23	---	---	---	---	
5.86, O2	23P	---	---	---	---	
	23O	---	---	---	---	
average						0
ECR-FSC 1%	21C	---	---	---	---	
0.00, O2	21N	---	---	---	---	
	21M	---	---	---	---	
average						0
ECR-FSC 1%	22D	---	2	12	18	
0.73, O2	22N	---	---	---	---	
	22K *	+	1	12	45	
average					21	0.4

Table 11. Visual Examination of ECR-FSC Specimens (cont.)

specimen type	specimen symbol	corr	visual observation blisters #	pH	area [mm2]	% area of blisters
ECR-FSC 1%	22H *	+	11	12	71	
1.47, O2	22O	---	---	---	---	
	22S *	---	2	6	20	
average					30.33	0.6
ECR-FSC 1%	23N *	+	4	6 & 12	42	
2.93, O2	23H	+	---	---	---	
	23J *	+	2	6 & 8	16	
average					19.33	0.4
ECR-FSC 1%	23S *	+	1	8	20	
5.86, O2	23B	---	---	---	---	
	23L	---	---	---	---	
average					6.67	0.1

Note: 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 12. Visual Examination of ECR-CGN Specimens

specimen type	specimen symbol	corr	visual observation blisters #	pH	area [mm2]	% area of blisters
ECR-CGN 0%	2A	---	---	---	---	
0.00, O2	2B	---	---	---	---	
	2C	---	---	---	---	
average						0.0
ECR-CGN 0%	4B	---	---	---	---	
0.73, O2	4C	---	---	---	---	
	4D	---	---	---	---	
average						0.0
ECR-CGN 0%	4E	---	---	---	---	
1.47, O2	4F	---	---	---	---	
	4A	---	---	---	---	
average						0.0
ECR-CGN 0%	6F	---	---	---	---	
2.93, O2	6E	---	---	---	---	
	6C	---	---	---	---	
average						0.0
ECR-CGN 0%	8C	---	---	---	---	
5.86, O2	8B	---	---	---	---	
	8A	---	---	---	---	
average						0.0

Note: ECR-CGN 0% - ECR specimen from CGN manufacturer with 0 % damage

Table 13. Adhesion Test for ECR-FS Specimens

specimen type	specimen symbol	knife peel test (adhesion)			knife peel test group average
ECR-FS 0%	2Q	4	4	4	
0.00, O2	2K	4	4	4	
	2R	4	4	4	
average		4	4	4	4
ECR-FS 0%	3O	2	4	4	
0.73, O2	3L	1	1	2	
	3S	1	2	3	
average		1	2	3	2
ECR-FS 0%	3K	2	4	4	
1.47, O2	3J	3	4	4	
	3F	4	4	4	
average		3	4	4	4
ECR-FS 0%	4G	1	1	1	
2.93, O2	4O	1	2	3	
	4S	4	4	4	
average		2	2	3	2
ECR-FS 0%	4H	5	4	4	
5.86, O2	4A	4	4	5	
	4P	1	1	4	
average		3	3	4	4
ECR-FS 1%	1C	1	1	1	
0.0, O2	1G	1	1	2	
	1N	1	1	2	
average		1	1	2	1
ECR-FS 1%	2P	5	5	5	
0.73, O2	2D	5	5	5	
	2F	5	5	5	
average		5	5	5	5

Table 13. Adhesion Test for ECR-FS Specimens (cont.)

specimen type	specimen symbol	knife peel test (adhesion)			knife peel test group average
	3N	1	2	4	
ECR-FS 1%					
1.47, O2	3	2	4	4	
	3B	1	2	3	
average		1	3	4	3
ECR-FS 1%	4D	4	5	5	
2.93, O2	4C	4	4	5	
	4L	1	4	4	
average		3	4	5	4
ECR-FS 1%	5N	2	2	4	
5.86, O2	5J	4	4	3	
	5K	1	1	2	
average		2	2	3	3
ECR-FS 1%	7K	2	2	2	
DCI, 0.0, O2	7B	2	2	2	
	7P	2	2	2	
average		2	2	2	2
ECR-FS 1%	11	1	1	1	
DCI, 0.73, O2	11O	1	1	1	
	11J	1	1	1	
average		1	1	1	1
ECR-FS 1%	7I	1	1	1	
DCI, 1.47, O2	7L	1	1	1	
	7G	1	1	2	
average		1	1	1	1
ECR-FS 1%	9I	1	1	1	
DCI, 2.93, O2	9K	1	1	1	
	9A	1	1	1	
average		1	1	1	1

Table 13. Adhesion Test for ECR-FS Specimens (cont.)

specimen type	specimen symbol	knife peel test (adhesion)			knife peel test group average
ECR-FS 1% DCI, 5.86, O2	5S	1	1	1	
	5A	1	1	1	
	5M	1	1	1	
average		1	1	1	1

Table 14. Adhesion Test for ECR-LNE Specimens

specimen type	specimen symbol	knife peel test (adhesion)			knife peel test group average
ECR-LNE 0%	1Q	2	2	5	
0.00, O2	1O	5	5	5	
	1R	2	2	2	
average		3	3	4	3
ECR-LNE 0%	1N	5	5	5	
0.73, O2	1S	5	5	5	
	1A	5	5	5	
average		5	5	5	5
ECR-LNE 0%	1H	5	5	5	
1.47, O2	1P	5	5	5	
	1G	5	5	5	
average		5	5	5	5
ECR-LNE 0%	2E	5	5	5	
2.93, O2	2D	5	5	5	
	2R	5	5	5	
average		5	5	5	5
ECR-LNE 0%	2F	5	5	5	
5.86, O2	2Q	5	5	5	
	2O	5	5	5	
average		5	5	5	5
ECR-LNE 1%	2K	1	2	2	
0.00, O2	2I	5	5	5	
	2L	1	2	3	
average		2	3	3	3
ECR-LNE 1%	1L	5	5	5	
0.73, O2	1B	5	5	5	
	1C	5	5	5	
average		5	5	5	5

Table 14. Adhesion Test for ECR-LNE Specimens (cont.)

specimen type	specimen symbol	knife peel test (adhesion)			knife peel test group average
ECR-LNE 1%	1J	5	5	5	
1.47, O2	1E	5	5	5	
	1I	5	5	5	
average		5	5	5	5
ECR-LNE 1%	3K	5	5	5	
2.93, O2	3F	5	5	5	
	3G	5	5	5	
average		5	5	5	5
ECR-LNE 1%	3J	5	5	5	
5.86, O2	3E	5	5	5	
	3I	5	5	5	
average		5	5	5	5

Table 15. Adhesion Test for ECR-FSC Specimens

specimen type	specimen symbol	knife peel test (adhesion)			knife peel test group average
ECR-FSC 0%	21F	1	1	1	
0.00, O2	21Q	2	2	5	
	21S	1	1	1	
average		1	1	2	2
ECR-FSC 0%	21G	1	1	1	
0.73, O2	21O	1	1	5	
	21J	5	5	3	
average		2	2	3	3
ECR-FSC 0%	21D	1	1	1	
1.47, O2	21P	5	5	3	
	21E	1	1	4	
average		2	2	3	2
ECR-FSC 0%	23M	2	2	2	
2.93, O2	32R	2	2	2	
	23Q	2	2	5	
average		2	2	3	2
ECR-FSC 0%	23E	2	2	2	
5.86, O2	23P	2	2	2	
	23O	2	2	2	
average		2	2	2	2
ECR-FSC 1%	21C	1	1	1	
0.00, O2	21N	1	1	1	
	21M	1	1	1	
average		1	1	1	1
ECR-FSC 1%	22D	5	5	5	
0.73, O2	22N	2	2	2	
	22K	5	5	5	
average		4	4	4	4

Table 15. Adhesion Test for ECR-FSC Specimens (cont.)

specimen type	specimen symbol		knife peel test (adhesion)		knife peel test group average
ECR-FSC 1%	22H	5	5	5	
1.47, O2	22O	3	3	4	
	22S	5	5	5	
average		4	4	5	4
ECR-FSC 1%	23N	2	2	5	
2.93, O2	23H	2	2	2	
	23J	2	2	5	
average		2	2	4	3
ECR-FSC 1%	23S	2	5	5	
5.86, O2	23B	2	2	2	
	23L	2	2	2	
average		2	3	3	3

Table 16. Adhesion Test for ECR-CGN Specimens

specimen type	specimen symbol	knife peel test (adhesion)			knife peel test group average
ECR-CGN 0%	2A	1	1	1	
0.00, O2	2B	1	1	1	
	2C	1	1	1	
average		1	1	1	1
ECR-CGN 0%	4B	1	1	1	
0.73, O2	4C	1	1	1	
	4D	1	1	1	
average		1	1	1	1
ECR-CGN 0%	4E	1	1	1	
1.47, O2	4F	1	1	1	
	4A	1	1	1	
average		1	1	1	1
ECR-CGN 0%	6F	1	1	1	
2.93, O2	6E	1	1	1	
	6C	1	1	1	
average		1	1	1	1
ECR-CGN 0%	8C	2	2	2	
5.86, O2	8B	2	2	2	
	8A	2	2	2	
average		2	2	2	2

Table 17. Hardness Test for ECR-FS Specimens

specimen type	specimen symbol	hardness test		
ECR-FS 0% 0.00, O2	2Q	B	B	B
	2K	B	B	B
	2R	B	B	B
ECR-FS 0% 0.73, O2	3O	B	B	B
	3L	B	B	B
	3S	B	B	B
ECR-FS 0% 1.47, O2	3K	B	B	B
	3J	B	B	B
	3F	B	B	B
ECR-FS 0% 2.93, O2	4G	B	B	B
	4O	B	B	B
	4S	B	B	B
ECR-FS 0% 5.86, O2	4H	B	B	B
	4A	B	B	B
	4P	B	B	B
ECR-FS 1% 0.0, O2	1C	B	B	B
	1G	B	B	B
	1N	B	B	B
ECR-FS 1% 0.73, O2	2P	B	B	B
	2D	B	B	B
	2F	B	B	B
ECR-FS 1% 1.47, O2	3N	B	B	B
	3E	B	B	B
	3B	B	B	B
ECR-FS 1% 2.93, O2	4D	B	B	B
	4C	B	B	B
	4L	B	B	B
ECR-FS 1% 5.86, O2	5N	B	B	B
	5J	B	B	B
	5K	B	B	B

Table 17. Hardness Test for ECR-FS Specimens (cont.)

specimen type	specimen symbol		hardness test	
ECR-FS 1%	7K	B	B	B
0.0, O2	7B	B	B	B
DCI	7P	B	B	B
ECR-FS 1%	11E	B	B	B
0.73, O2	11O	B	B	B
DCI	11J	B	B	B
ECR-FS 1%	7I	B	B	B
1.47, O2	7L	B	B	B
DCI	7G	B	B	B
ECR-FS 1%	9I	B	B	B
2.93, O2	9K	B	B	B
DCI	9A	B	B	B
ECR-FS 1%	5S	B	B	B
5.86, O2	5A	B	B	B
DCI	5M	B	B	B

Table 18. Hardness Test for ECR-LNE Specimens

specimen type	specimen symbol		hardness test	
ECR-LNE 0% 0.00, O2	1Q	B	B	B
	1O	B	B	B
	1R	B	B	B
ECR-LNE 0% 0.73, O2	1N	B	B	B
	1S	B	B	B
	1A	B	B	B
ECR-LNE 0% 1.47, O2	1H	B	B	B
	1P	B	B	B
	1G	B	B	B
ECR-LNE 0% 2.93, O2	2E	B	B	B
	2D	B	B	B
	2R	B	B	B
ECR-LNE 0% 5.86, O2	2F	B	B	B
	2Q	B	B	B
	2O	B	B	B
ECR-LNE 1% 0.00, O2	2K	B	B	B
	2I	B	B	B
	2L	B	B	B
ECR-LNE 1% 0.73, O2	1L	B	B	B
	1B	B	B	B
	1C	B	B	B
ECR-LNE 1% 1.47, O2	1J	B	B	B
	1E	B	B	B
	1I	B	B	B
ECR-LNE 1% 2.93, O2	3K	B	B	B
	3F	B	B	B
	3G	B	B	B
ECR-LNE 1% 5.86, O2	3J	B	B	B
	3E	B	B	B
	3I	B	B	B

Table 19. Hardness Test for ECR-FSC Specimens

specimen type	specimen symbol		hardness test	
ECR-FSC 0%	21F	B	B	B
0.00, O2	21Q	B	B	B
	21S	B	B	B
ECR-FSC 0%	21G	B	B	B
0.73, O2	21O	B	B	B
	21J	B	B	B
ECR-FSC 0%	21D	B	B	B
1.47, O2	21P	B	B	B
	21E	B	B	B
ECR-FSC 0%	23M	B	B	B
2.93, O2	32R	B	B	B
	23Q	B	B	B
ECR-FSC 0%	23E	B	B	B
5.86, O2	23P	B	B	B
	23O	B	B	B
ECR-FSC 1%	21C	B	B	B
0.00, O2	21N	B	B	B
	21M	B	B	B
ECR-FSC 1%	22D	B	B	B
0.73, O2	22N	B	B	B
	22K	B	B	B
ECR-FSC 1%	22H	B	B	B
1.47, O2	22O	B	B	B
	22S	B	B	B
ECR-FSC 1%	23N	B	B	B
2.93, O2	23H	B	B	B
	23J	B	B	B
ECR-FSC 1%	23S	B	B	B
5.86, O2	23B	B	B	B
	23L	B	B	B

Table 20. Hardness Test for ECR-CGN Specimens

specimen type	specimen symbol	hardness test		
ECR-CGN 0% 0.00, O2	2A	B	B	B
	2B	B	B	B
	2C	B	B	B
ECR-CGN 0% 0.73, O2	4B	B	B	B
	4C	B	B	B
	4D	B	B	B
ECR-CGN 0% 1.47, O2	4E	B	B	B
	4F	B	B	B
	4A	B	B	B
ECR-CGN 0% 2.93, O2	6F	B	B	B
	6E	B	B	B
	6C	B	B	B
ECR-CGN 0% 5.86, O2	8C	B	B	B
	8B	B	B	B
	8A	B	B	B

Table 21. Oxygen Saturation Test

solution	chlorides	aeration	weight	temp.	salinity	oxygen content (ppm) after aeration				
type	kg/m3	type	[g]	[C]	[ppt]	0 s	30 s	60 s	120 s	240 s
PS	0.00	O2	945	44	12	3.50	14.60	15.40	16.00	15.80
PS	0.73	O2	945	41	29	3.00	13.20	13.40	13.80	14.00
PS	1.47	O2	945	41	40	2.90	11.40	12.10	12.10	12.60
PS	2.93	O2	945	40	40	2.60	10.60	11.60	11.60	11.80
PS	5.86	O2	945	40	40	2.30	9.00	10.00	10.20	10.20
PS + DCI	0.00	O2	945	43	40	2.35	10.60	10.40	10.80	11.00
PS + DCI	0.73	O2	945	43	40	2.40	9.10	10.10	10.60	10.70
PS + DCI	1.47	O2	945	43	40	2.50	9.80	9.70	10.10	10.00
PS + DCI	2.93	O2	945	44	40	2.10	10.20	9.40	10.20	11.40
PS + DCI	5.86	O2	945	42	40	1.95	9.60	9.80	9.80	10.00
PS	0.00	air	945	40	12	4.50	4.50	4.90	5.00	5.20
PS	0.73	air	945	39	29	3.75	3.90	4.20	4.30	4.40
PS	1.47	air	945	43	40	3.40	3.10	3.40	3.55	3.75
PS	2.93	air	945	43	40	3.00	2.80	3.30	3.10	3.25
PS	5.86	air	945	44	40	2.80	2.45	2.75	2.35	2.35
PS + DCI	0.00	air	945	43	40	2.25	3.40	3.40	3.45	3.55
PS + DCI	0.73	air	945	43	40	2.05	2.95	3.10	3.00	3.10
PS + DCI	1.47	air	945	43	40	2.15	2.60	2.60	2.80	2.90
PS + DCI	2.93	air	945	43	40	1.90	2.10	2.25	2.30	2.30
PS + DCI	5.86	air	945	43	40	1.80	2.05	2.10	2.15	2.25

Table 22. Chloride Titration Results

solution type	calculated mole Cl	chlorides kg/m3	titrated chlorides mole	titrated chlorides kg/m3
PS	0.00	0.00	0.00	0.00
PS	0.30	0.73	0.28	0.69
PS	0.60	1.47	0.59	1.43
PS	1.20	2.93	1.16	2.82
PS	2.40	5.86	2.30	5.60
PS + R222	0.00	0.00	0.00	0.00
PS + R222	0.30	0.73	0.30	0.73
PS + R222	0.60	1.47	0.56	1.37
PS + R222	1.20	2.93	1.05	2.57
PS + R222	2.40	5.86	2.21	5.39
PS + A2000	0.00	0.00	0.00	0.00
PS + A2000	0.30	0.73	0.29	0.71
PS + A2000	0.60	1.47	0.54	1.33
PS + A2000	1.20	2.93	1.10	2.68
PS + A2000	2.40	5.86	2.07	5.05
PS + DCI	0.00	0.00	0.00	0.00
PS + DCI	0.30	0.73	0.30	0.73
PS + DCI	0.60	1.47	0.59	1.44
PS + DCI	1.20	2.93	0.93	2.26
PS + DCI	2.40	5.86	2.10	5.11

Table 23. Test Solution Cl/OH and pH

solution type	Cl/OH ratio 100% dissolution	pH calculated 100% dissolution	titrated solution Cl/OH	titrated solution pH	titrated supernatant *Cl/OH	titrated supernatant pH	probe pH
PS	0.00	13.8	0.00	13.6			12.8
PS	0.50	13.8	0.70	13.6	0.70	13.6	12.7
PS	1.00	13.8					12.6
PS	2.00	13.8					12.5
PS	4.00	13.8	5.74	13.6	5.99	13.6	12.4
PS + R222	0.00	13.8					13.0
PS + R222	0.50	13.8	0.75	13.6	0.86	13.5	12.9
PS + R222	1.00	13.8					12.8
PS + R222	2.00	13.8					12.7
PS + R222	4.00	13.8			6.55	13.5	12.6
PS + A2000	0.00	13.8					13.0
PS + A2000	0.50	13.8	0.49	13.8	0.51	13.8	12.9
PS + A2000	1.00	13.8					12.8
PS + A2000	2.00	13.8					12.6
PS + A2000	4.00	13.8			3.79	13.7	12.5
PS + DCI	0.00	13.8					11.8
PS + DCI	0.50	13.8	0.50	13.8	7.05	12.6	11.7
PS + DCI	1.00	13.8					11.6
PS + DCI	2.00	13.8					11.5
PS + DCI	4.00	13.8			64.49	12.5	11.4

Note: * - chloride and hydroxide present in supernatant

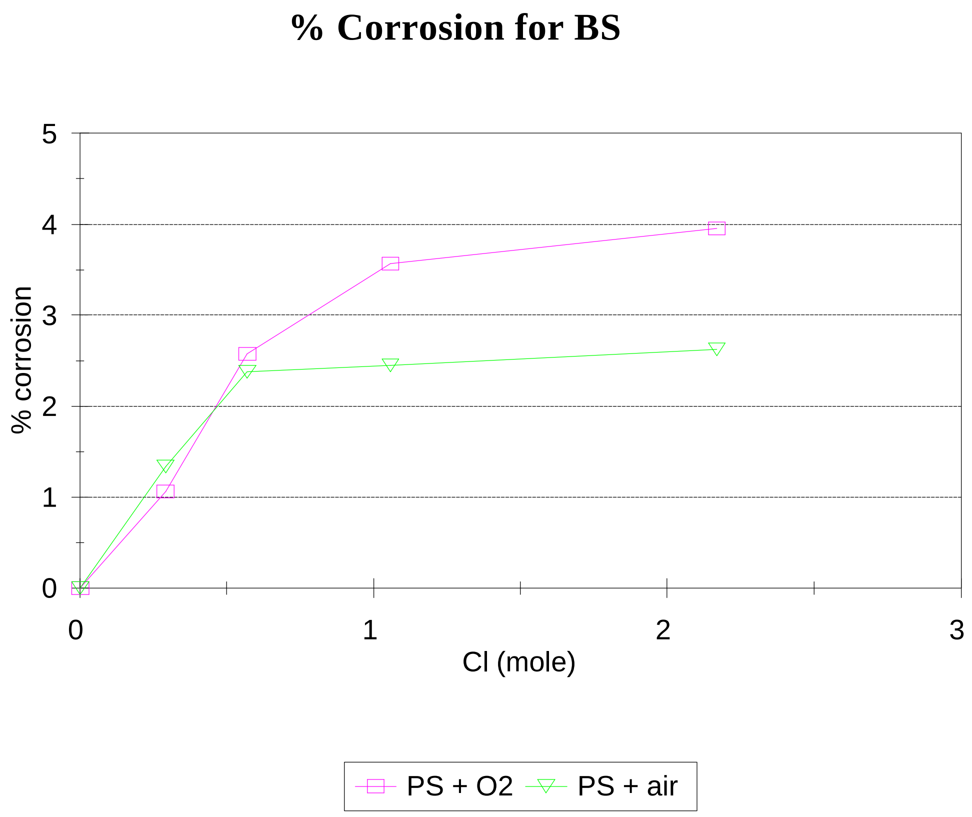


Figure 1. % Corrosion for BS Specimens Tested in PS; O2 and Air Aeration.

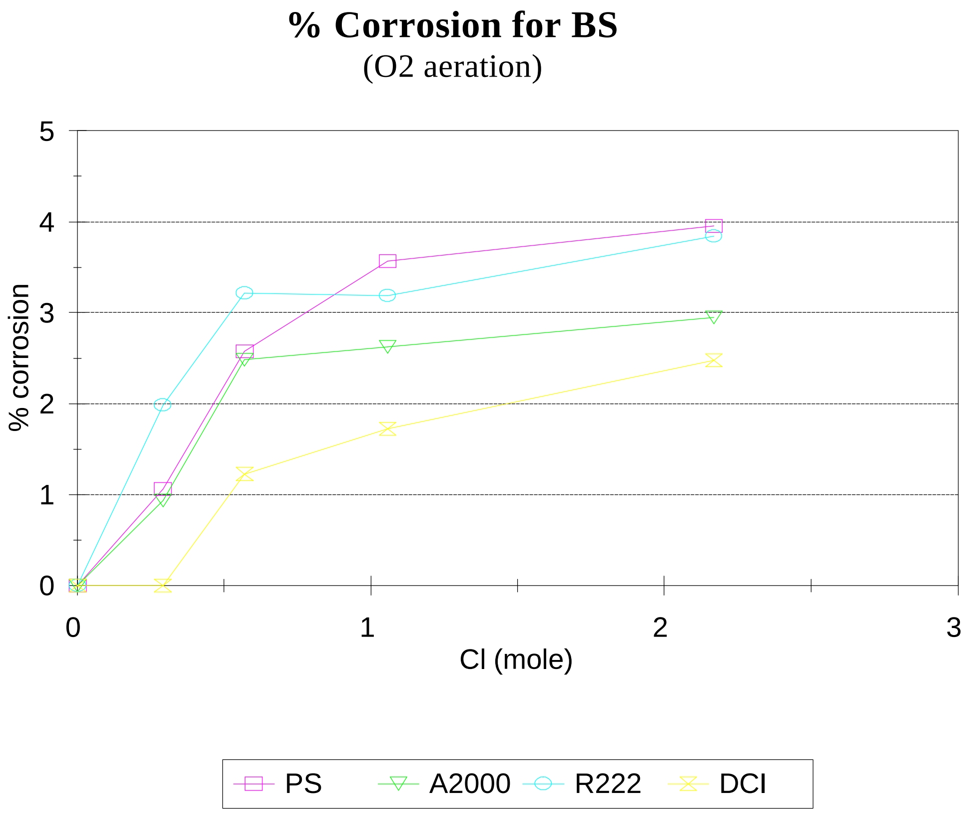


Figure 2. % Corrosion for BS Specimens Tested in PS and PS+Corrosion Inhibitor; O2 Aeration.

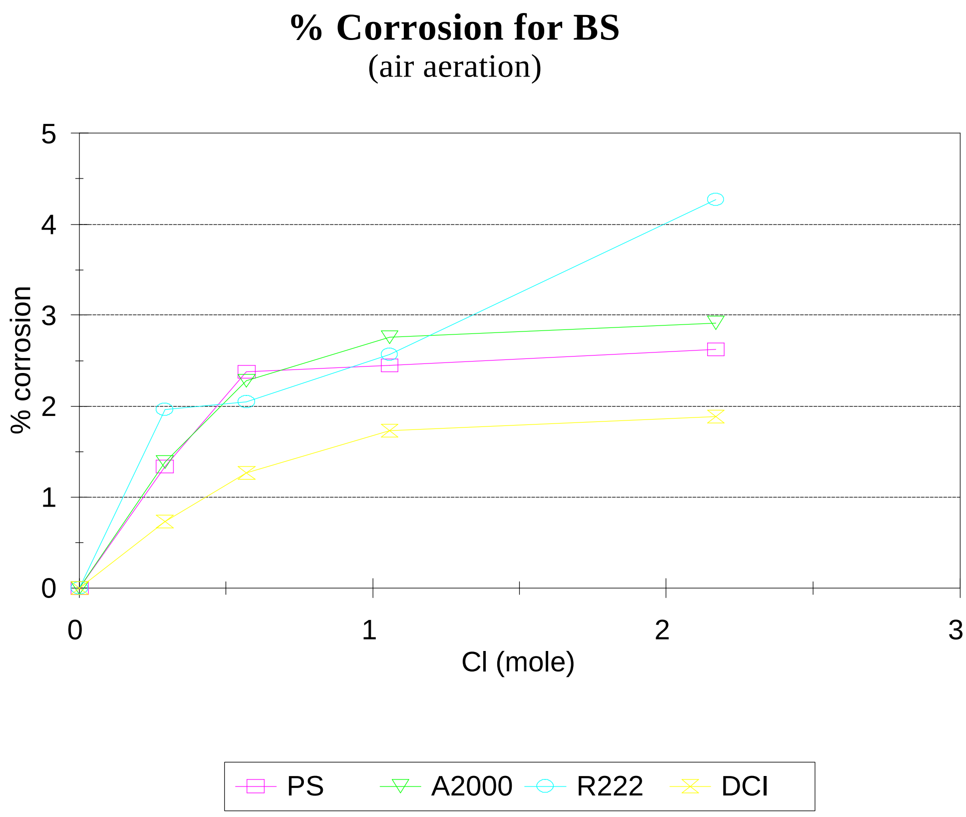


Figure 3. % Corrosion for BS Specimens Tested in PS and PS+Corrosion Inhibitor; Air Aeration.

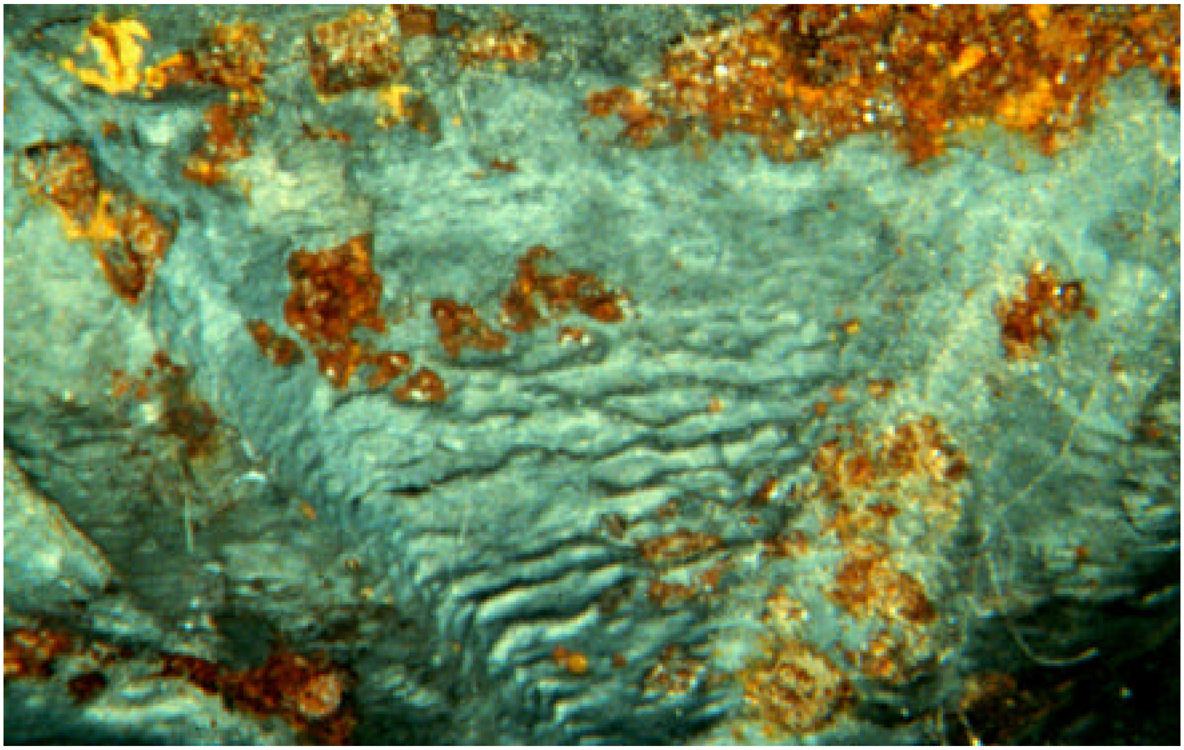


Figure 4. BS specimen with pitting corrosion; PS + NaCl: Cl = 0.28 mole, O_2 aeration.

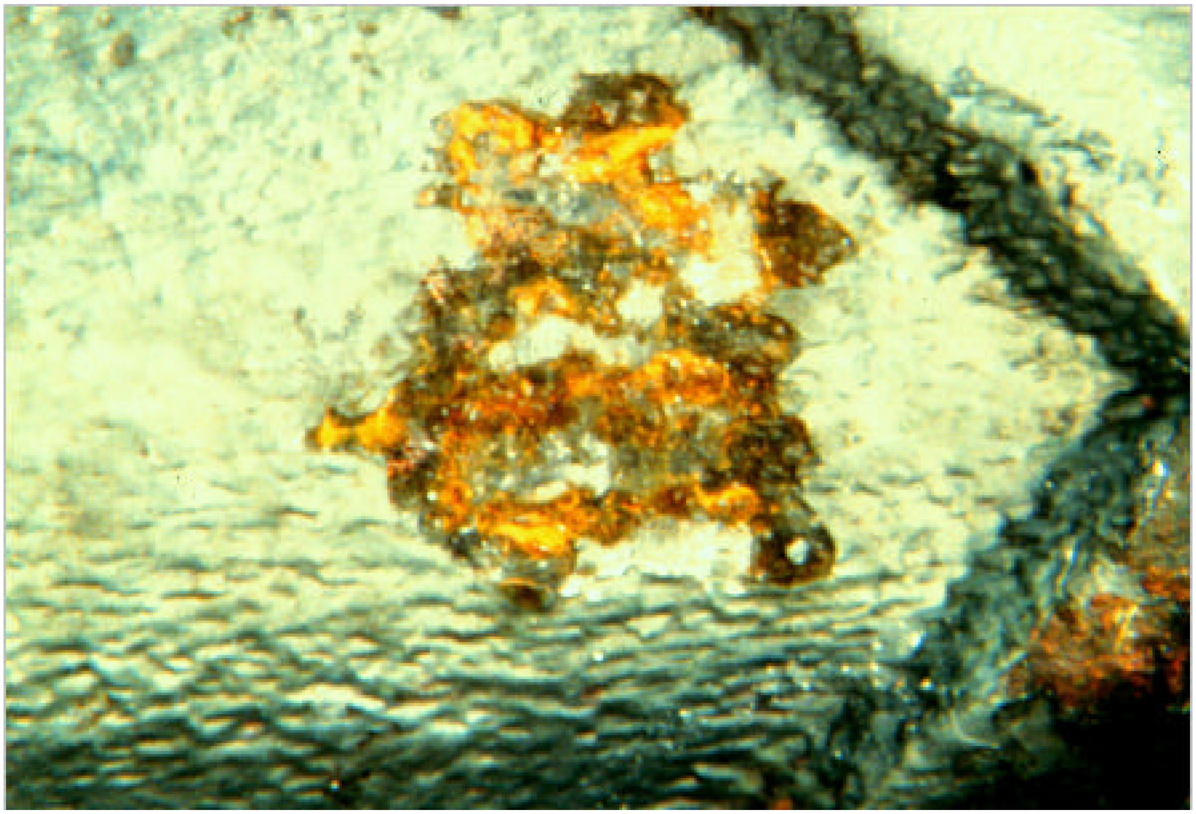


Figure 5. BS specimen with pitting corrosion; PS + R222 + NaCl: Cl = 0.30 mole, O_2 aeration.

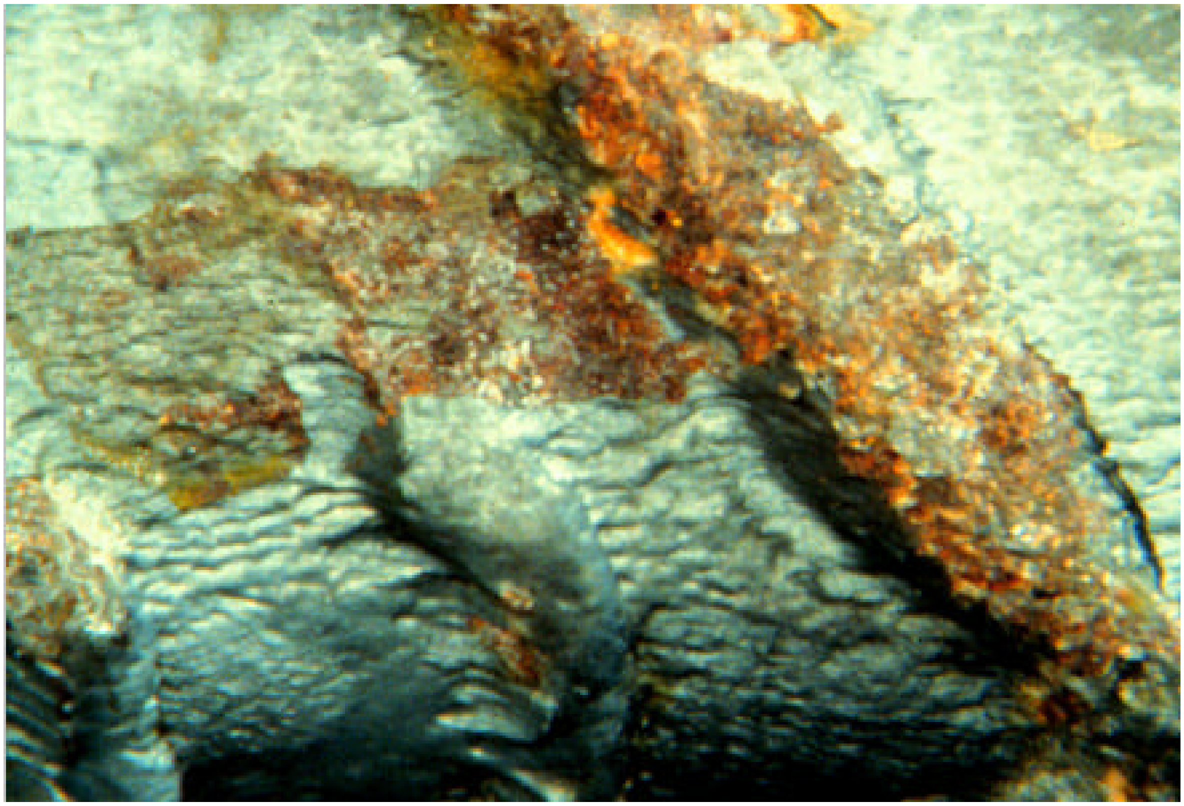


Figure 6. BS specimen with pitting corrosion; PS + A2000 + NaCl: Cl = 0.29 mole, O_2 aeration.

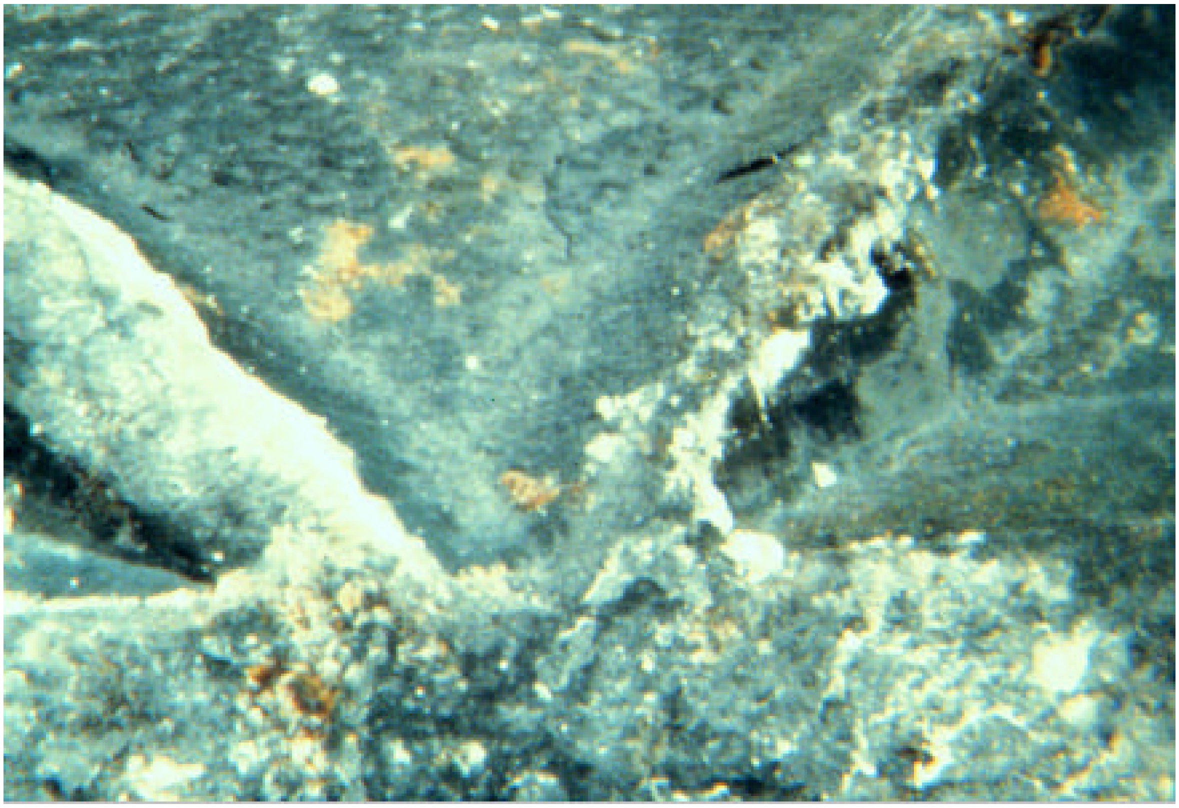
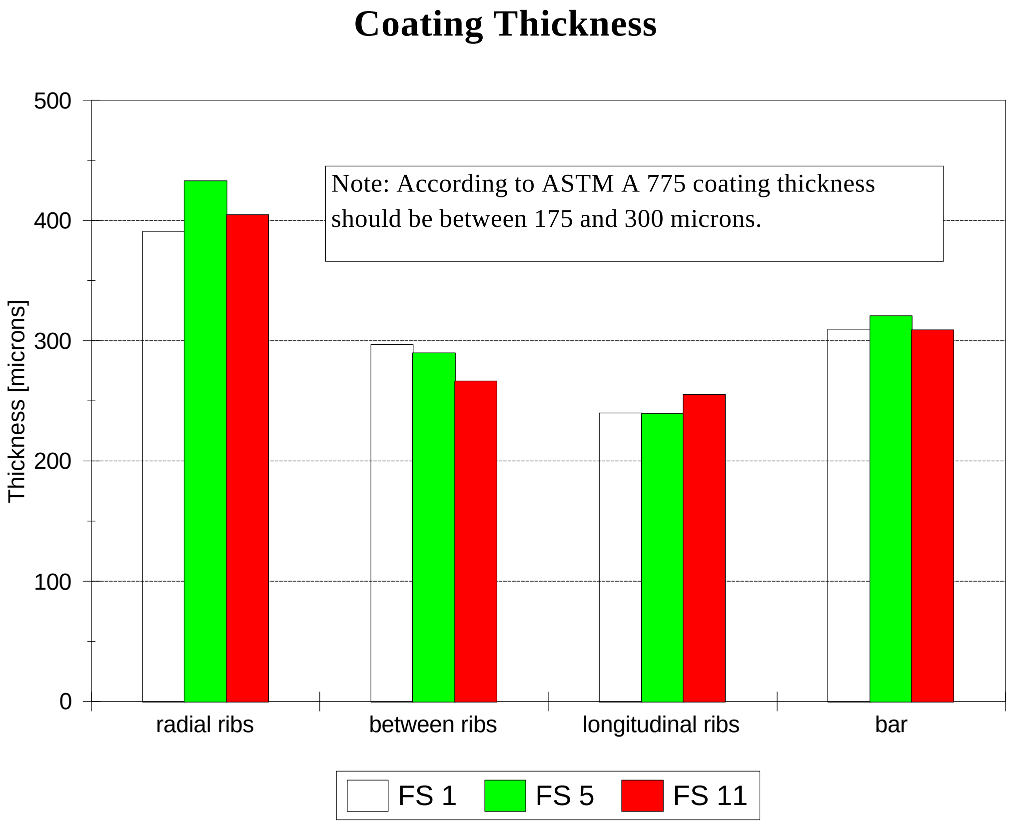


Figure 7. BS specimen with no corrosion; PS + DCI + NaCl: Cl = 0.30 mole, O_2 aeration.



Note: According to ASTM A 775 coating thickness should be between 175 and 300 microns.

Figure 8. Coating Thickness, ECR-FS Specimens.

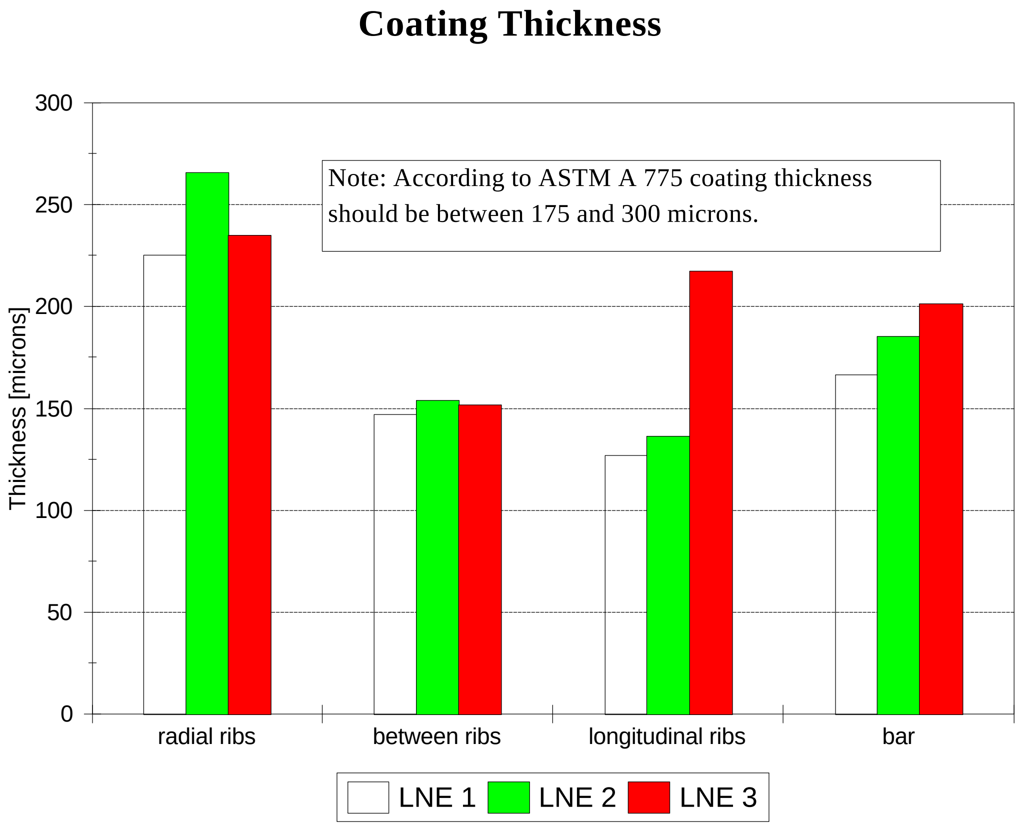
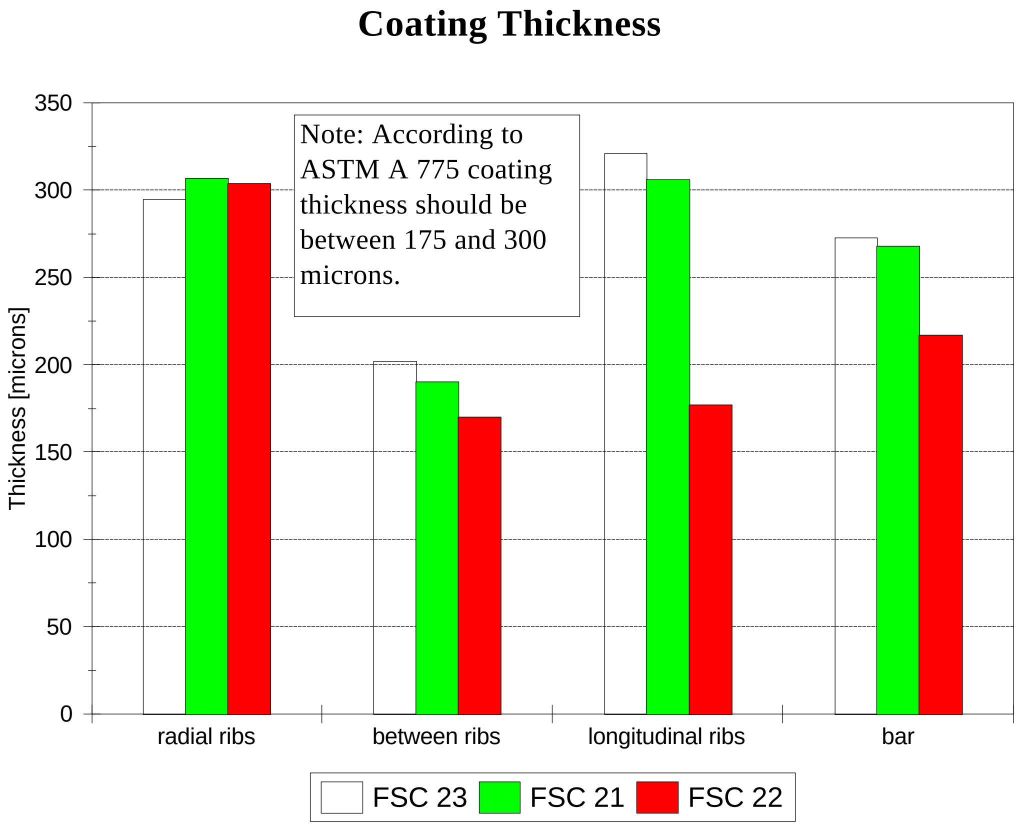


Figure 9. Coating Thickness, ECR-LNE Specimens.



Note: According to ASTM A 775 coating thickness should be between 175 and 300 microns.

Figure 10. Coating Thickness, ECR-FSC Specimens.

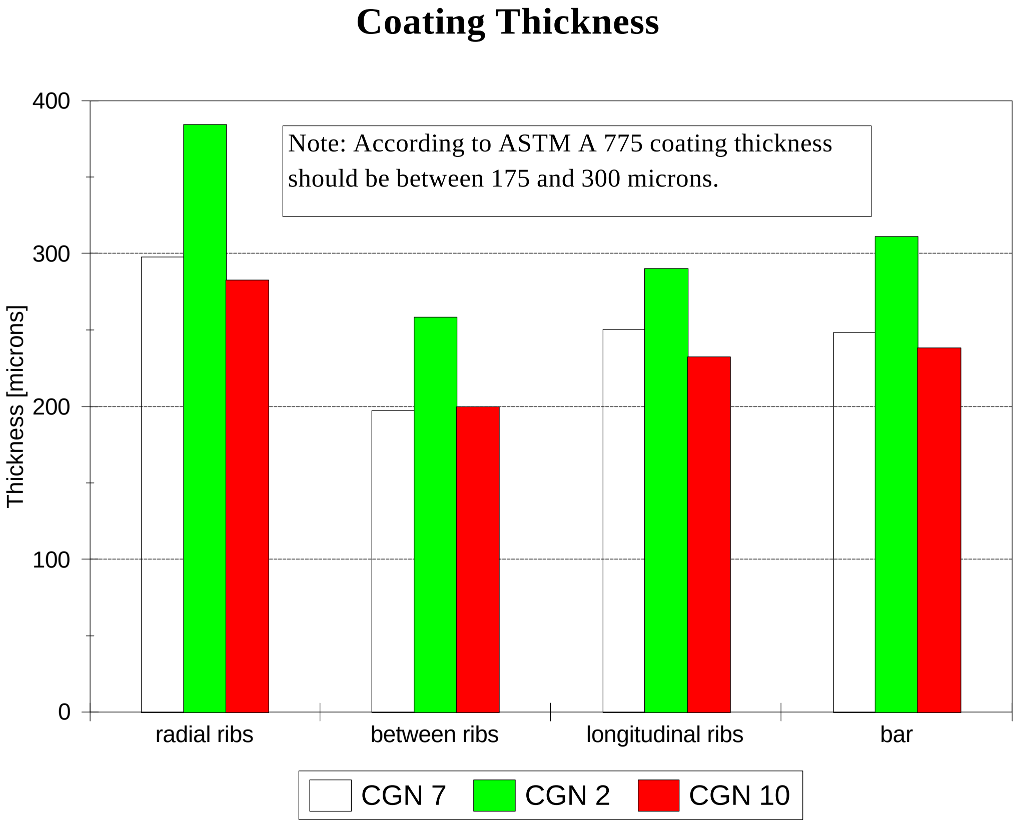


Figure 11. Coating Thickness, ECR-CGN Specimens.

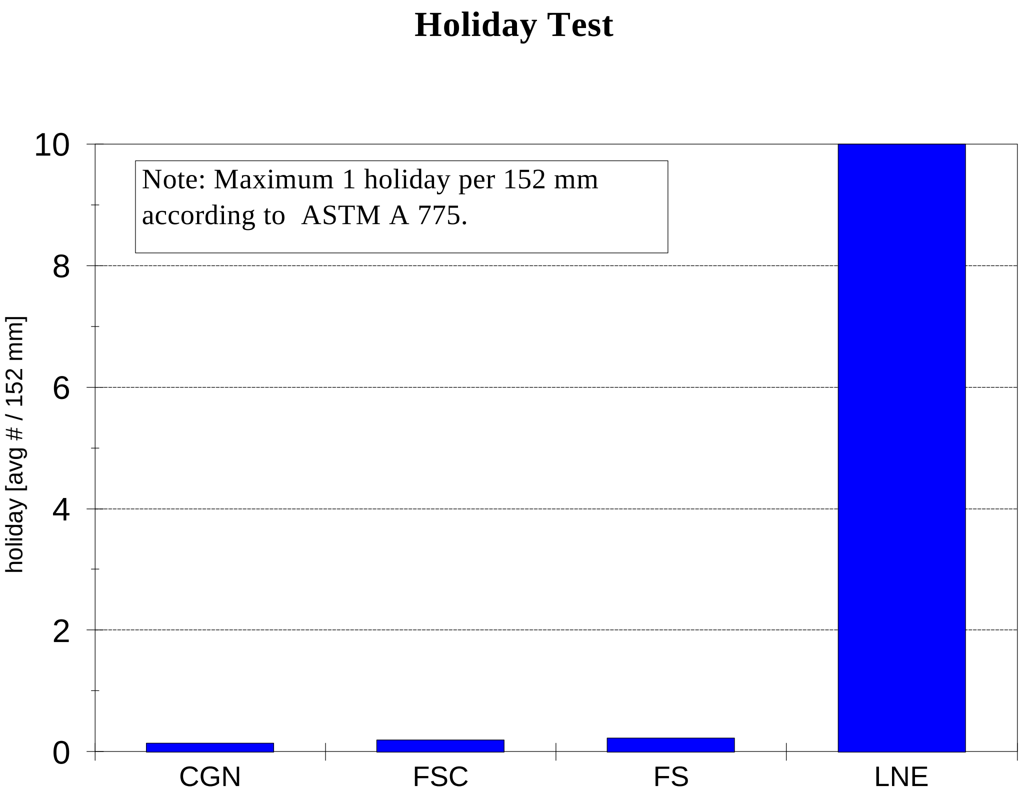


Figure 12. Holiday Detection of ECR Specimens.

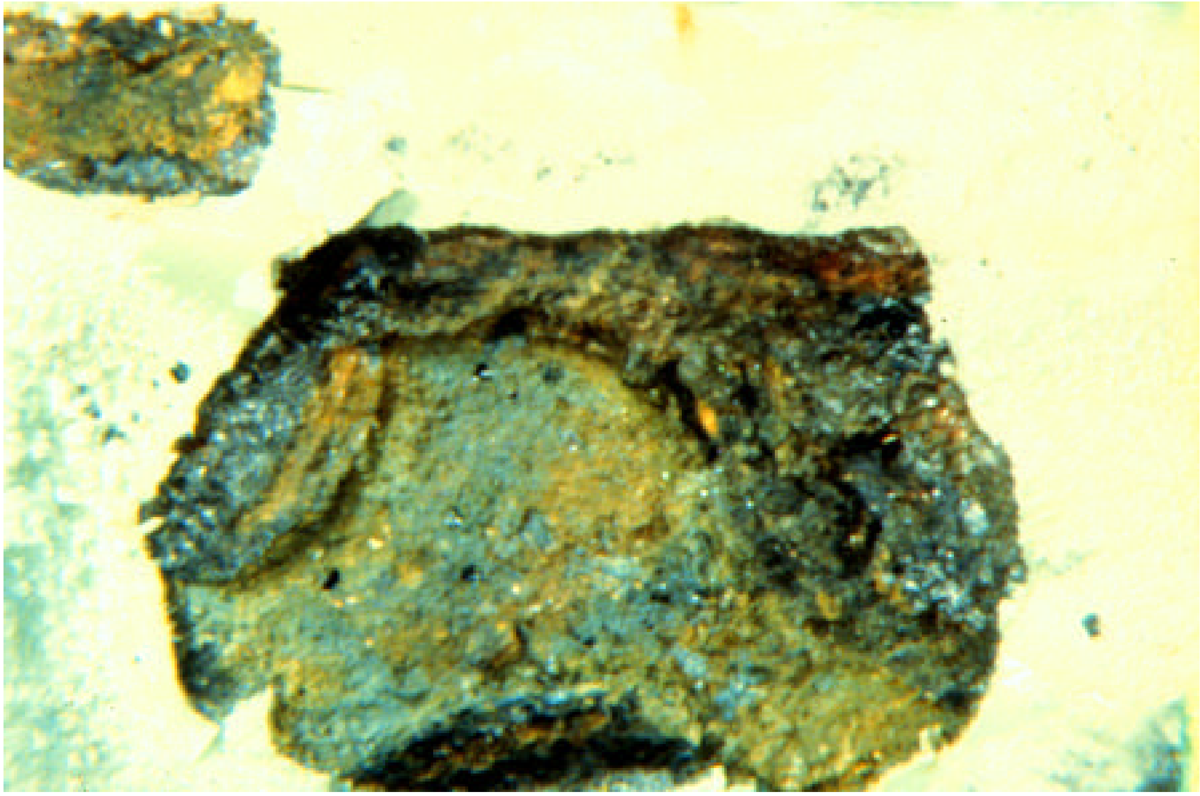


Figure 13. Steel surface under a blister for ECR-FS specimen with 0% damage; pH 5 of blister solution; PS + NaCl: Cl = 0.59 mole, O_2 aeration.

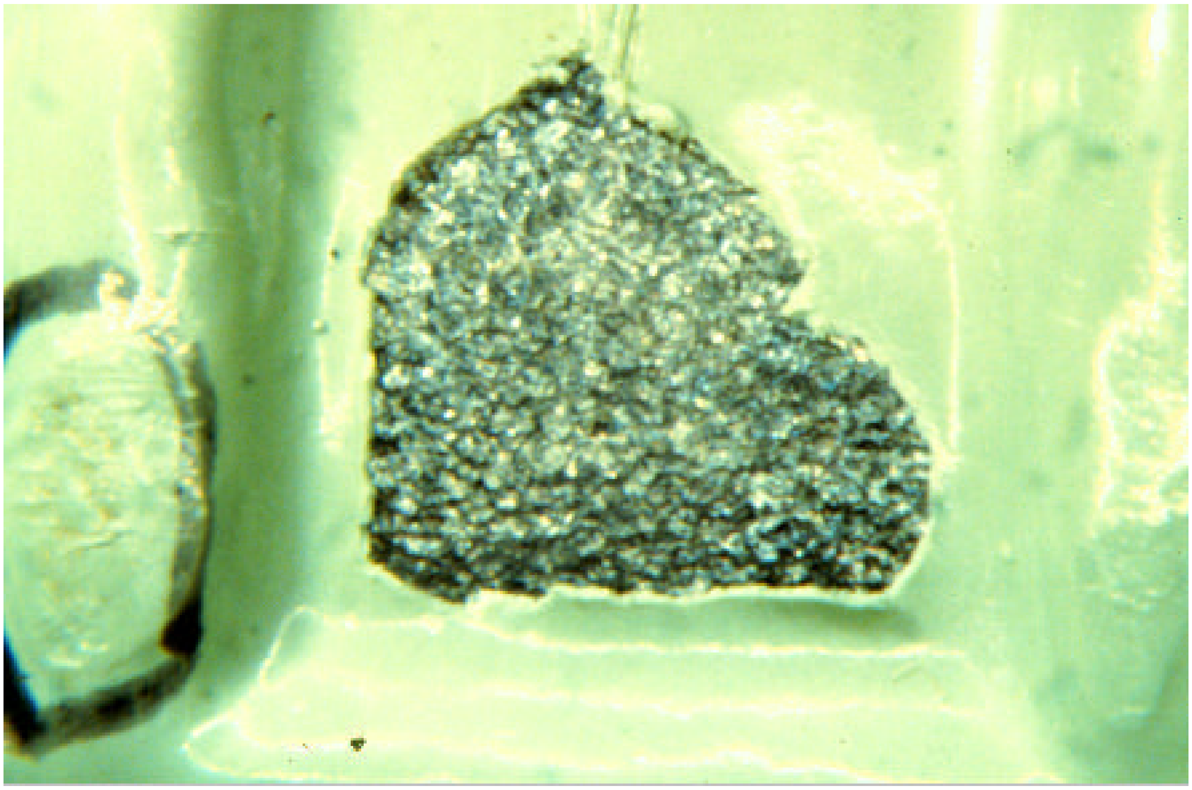


Figure 14. Steel surface under a blister for ECR-FS specimen with 1% damage; pH 12 of blister solution; PS + NaCl: Cl = 0.59 mole, O_2 aeration.

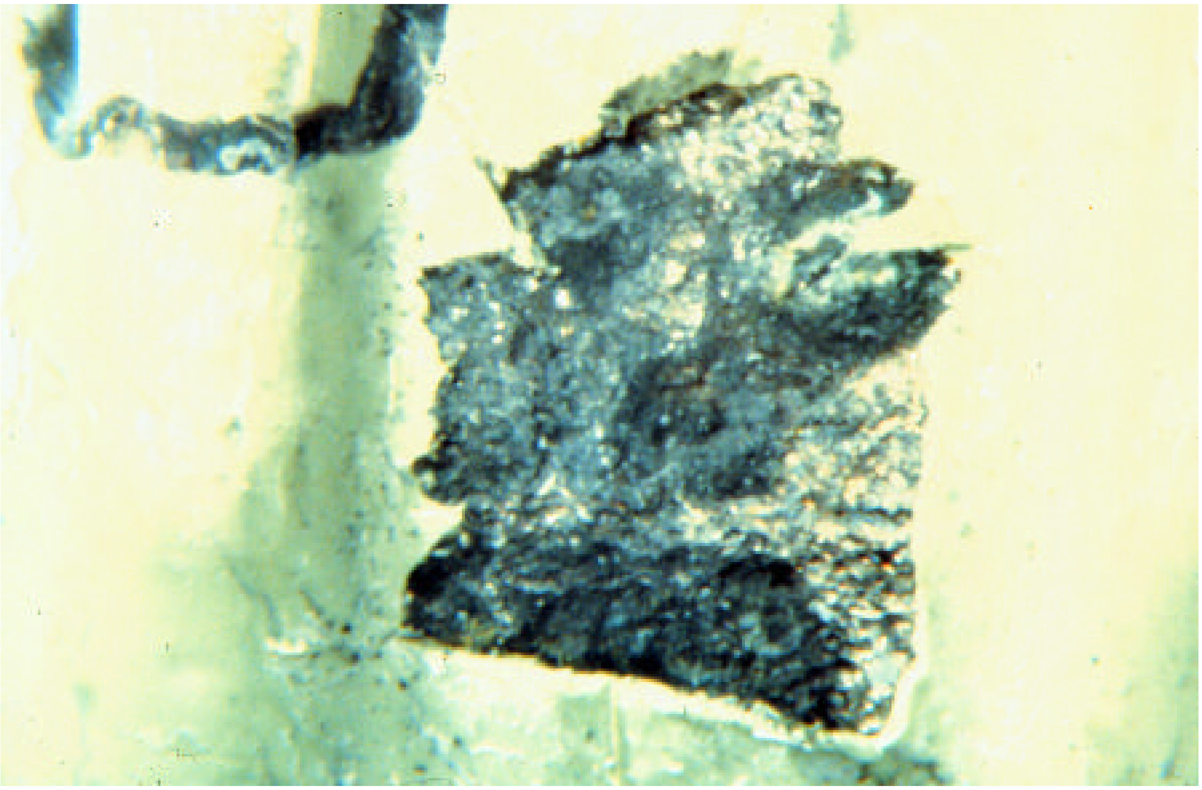


Figure 15. Steel surface under a blister for ECR-FS specimen with 1% damage; no blister solution present - pH not possible to determine; PS + DCI + NaCl: Cl = 0.59 mole, O_2 aeration.

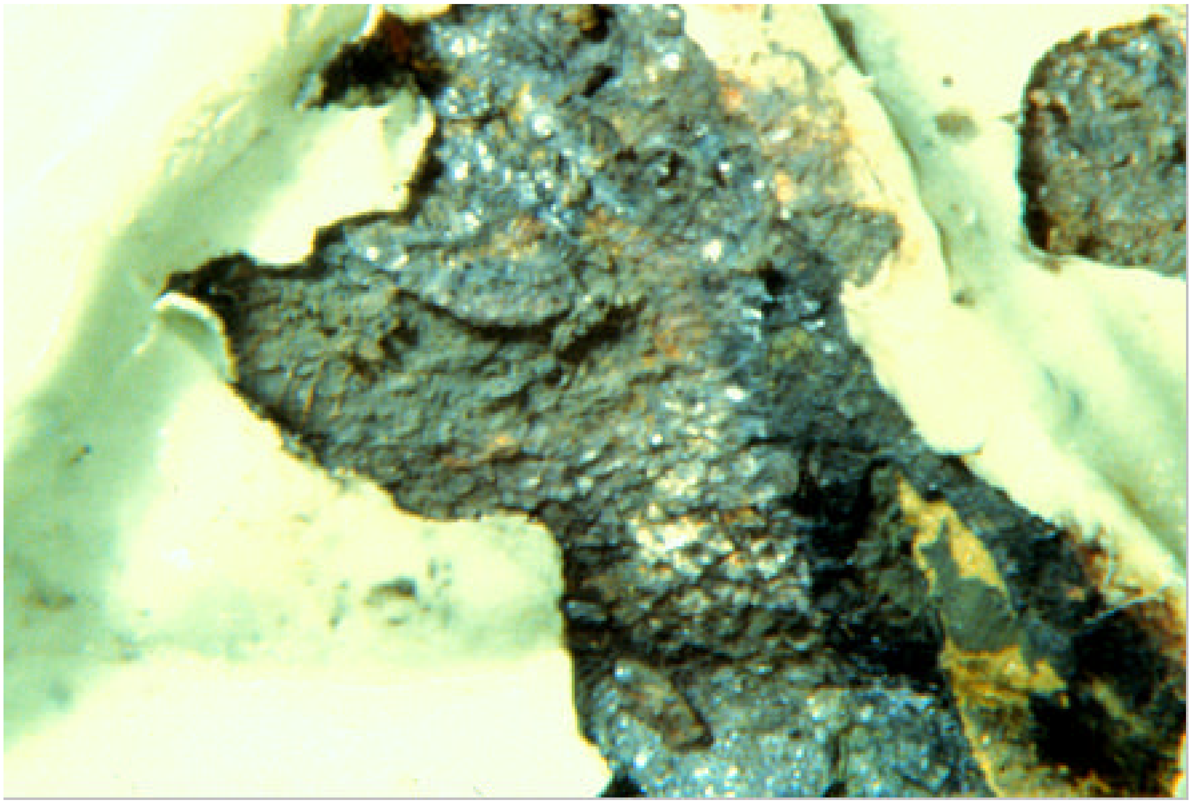


Figure 16. Steel surface under a blister for ECR-LNE specimen with 1% damage; pH 12 of blister solution; PS + NaCl: Cl = 0.59 mole, O_2 aeration.

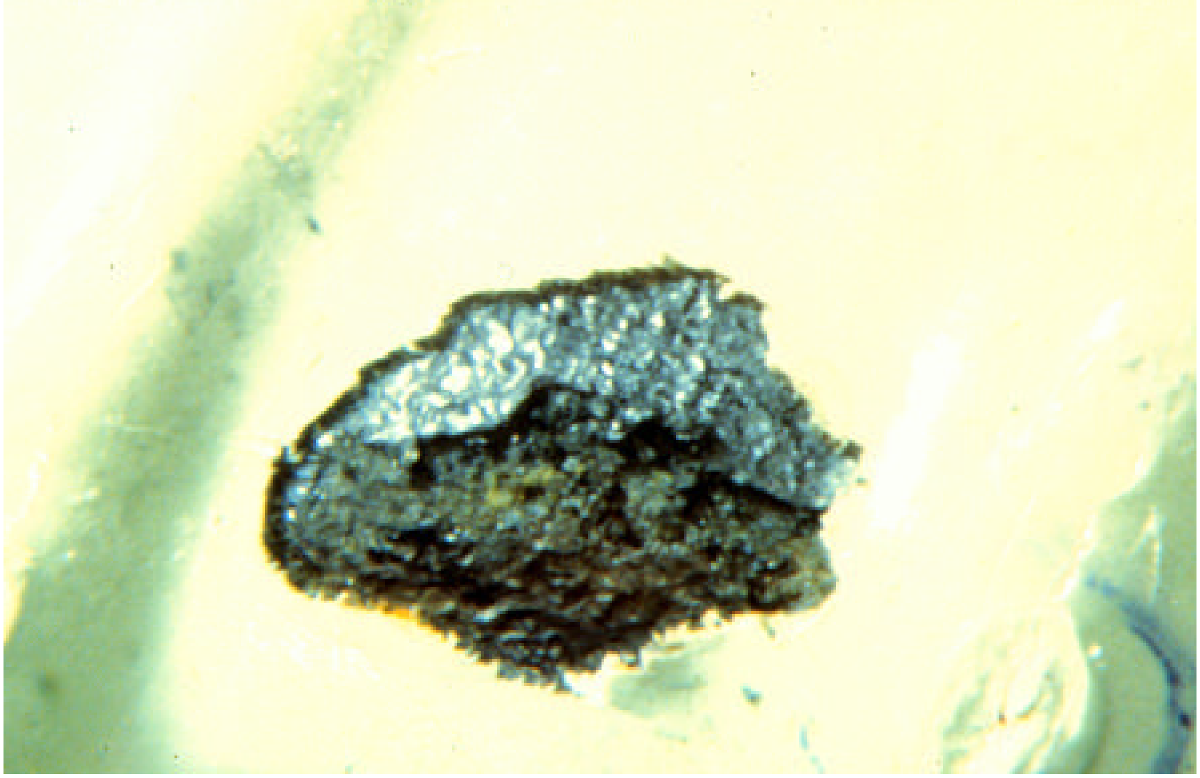


Figure 17. Steel surface under a blister for ECR-FSC specimen with 0% damage; pH 6 of blister solution; PS + NaCl: Cl = 0.59 mole, O_2 aeration.

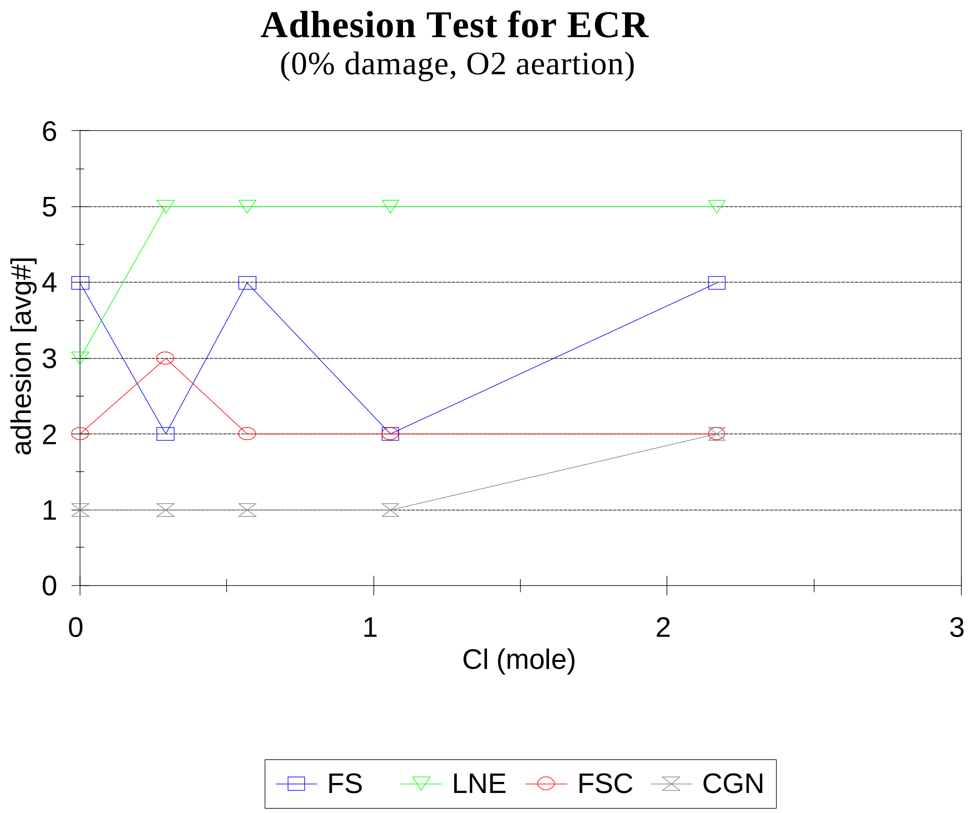


Figure 18. Adhesion Test for ECR Specimens with 0% Damage; O2 Aeration.

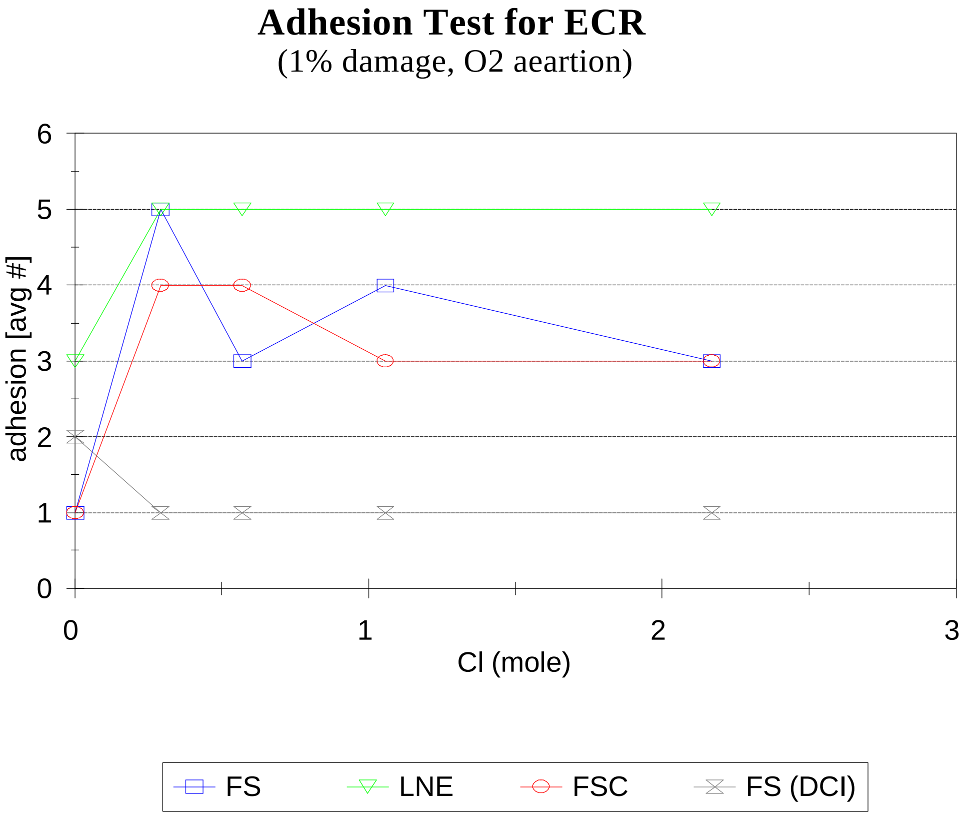


Figure 19. Adhesion Test for ECR Specimens with 1% Damage; O2 Aeration.

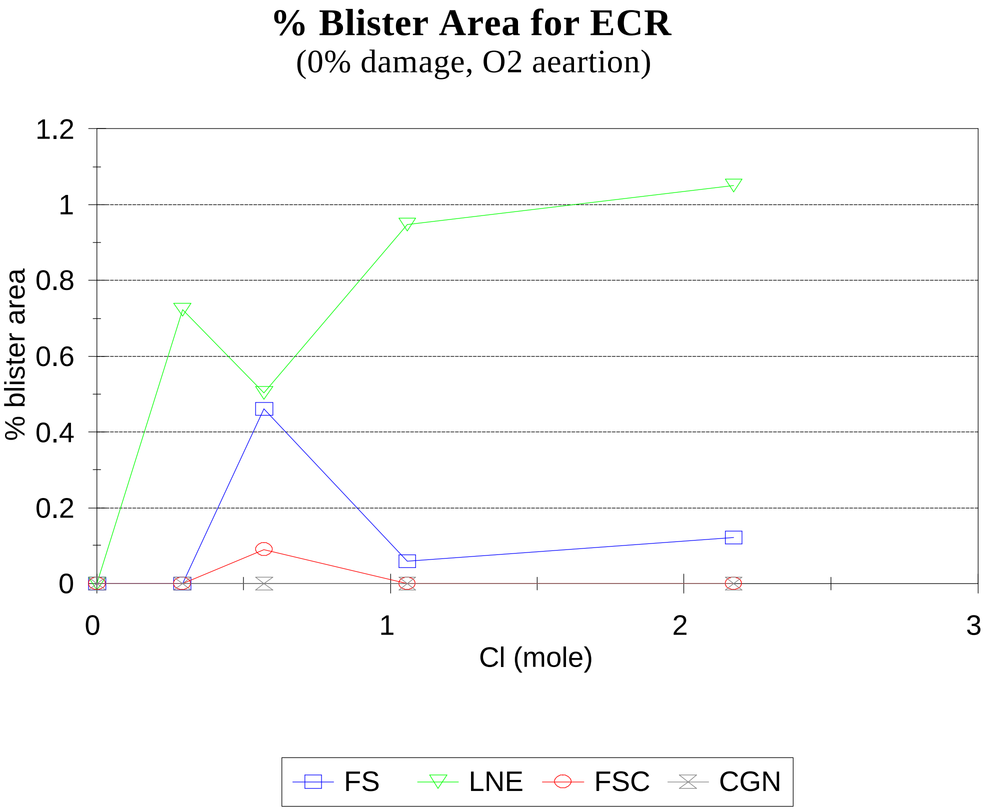


Figure 20. % Blister Area for ECR Specimens with 0% Damage; O2 Aeration.

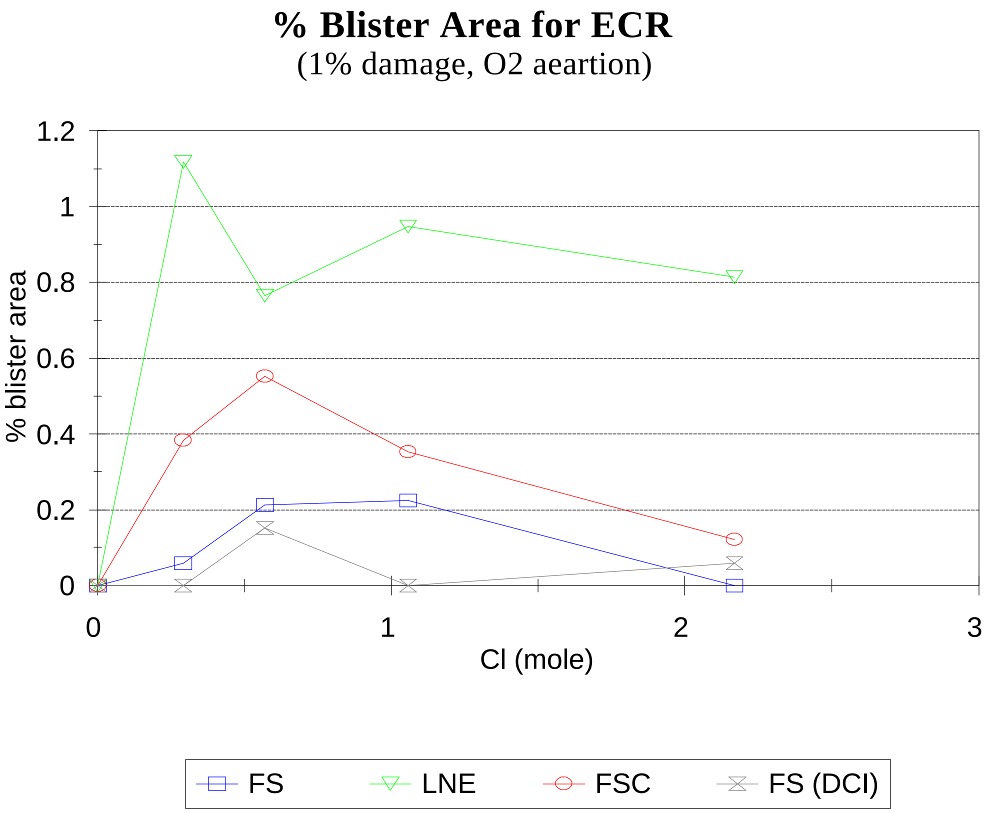


Figure 21. % Blister Area for ECR Specimens with 1% Damage; O2 Aeration.

APPENDIX A:

STANDARD TEST METHOD FOR EVALUATION OF CORROSION INHIBITORS
IN
PORE SOLUTION

Standard Test Method for Evaluation of Corrosion Inhibitors in Concrete Pore Water Solutions

1. Scope

1.1 This test method is intended for use as 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 The values stated in SI units are to be regarded as the standard.

1.3 This standard may involve hazardous materials, operation, 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

2.1 The results obtained by this method should serve as a guide in, but not as the sole basis for, the selection of 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 into 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 Bandsaw --- A hand-held bandsaw 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 in order 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 the form of pellets.

4.3 Potassium Hydroxide --- Standard grade solid in the 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 %.

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 $Ca(OH)_2$. In order to produce 1000 g of pore solution the following amount of all ingredients should be used:

- 8 g NaOH
- 14 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 into the pore solution based on dosage for one cubic meter of concrete which has 3 % by weight of pore water.

NOTE: If corrosion inhibitor contains large amount of water, the water content in the pore solution should be decreased based on the water present in corrosion inhibitor.

5.2 Pore Solution with Corrosion Inhibitor and Sodium Chloride --- Sodium chloride is added into 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 any 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.

5.3 Temperature --- The temperature should be 40°C ± 5°C.

6. Sample Preparation

6.1 Using the hand-held bandsaw 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 they should be cleaned in hexane.

7. Procedure

7.1 Place the three reinforcing specimens in clean plastic polypropylene container.

7.2 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.

7.3 Saturate the solution with compressed oxygen for 1 minute.

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

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

7.6 Saturate the solutions with compressed oxygen for 1 minute.

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

7.8 Twice a week, at day one and four, 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.

7.9 After the 90 days immersion test ends, take the specimens out of the solution and perform a visual examination.

8. Visual Examination

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

8.2 Estimate the corrosion area for each specimen.

9. Calculation

9.1 Calculate a percent area corrosion for each specimen.

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

9.3 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 The report should include the following:

10.1.1 Corrosion inhibitor and solution concentrations,

10.1.2 Conditioning procedure,

10.1.3 Test conditions,

10.1.4 Surface appearance of specimens before testing,

10.1.5 Total duration of the test and the examination periods in days,

10.1.6 Average percent corrosion of three specimens tested in the same solution,

10.1.7 Graph showing average percent corrosion plotted against increasing chloride concentrations in the tested solution.

10.2 For each examination period the following data are required:

10.2.1 Appearance of the specimens,

10.2.2 Measured pH value of the tested solution.

11. Precision and Bias

11.1 All test specimens values must be considered.

12. Significance of Results

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

Vita

Wioleta A. Pyc

Wioleta Agata Pyc was born on August 10, 1965 in Miastko, Poland. She graduated from Adam Mickiewicz High School in Miastko, Poland, in June 1984. In November 1989 she received a B.S./ M.S. degree in Civil Engineering from the Technical University of Gdansk, Poland. After that she worked for a year as an assistant designer in Gdansk Roads and Bridges Design Office.

She entered graduate school in the Materials Division of the Department of Civil Engineering at Virginia Polytechnic Institute and State University in January 1994. While attending graduate school she worked as a graduate teaching assistant and research assistant at the Structures and Materials Laboratory.