CORROSION BEHAVIOR OF BURIED PIPELINE IN PRESENCE OF AC STRAY CURRENT IN CONTROLLED ENVIRONMENT

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ABSTRACT

Cathodic protection (CP) and other corrosion mitigation strategies to preserve the integrity of pipelines are reported have failed in the presence of AC. This type of failure is a threat for catastrophic failure and there is a lack of well-agreed mitigation criteria for it. AC grounding systems as well as "consensus" standards that recommend limits on the maximum allowable AC current density and critical ratios of AC and CP currents are the only available techniques for preventing AC corrosion. Unclear mechanism of AC corrosion is the main reason for the uncertainty on the CP criteria in the presence of AC interference. AC interference can occur by conduction or induction mechanism where pipelines share right of way with some interference sources such as a high-voltage transmission line typically fed by a high voltage line at 50 or 16.7 Hz frequency. The goal of this work is to understand the mechanism of AC induced corrosion by studying the effects of AC interference on steel at different DC potentials.

This work consists of two phases. In the first phase, the influence of simultaneous presence of different AC and DC potentials on corrosion rate of API grade X65 pipeline steel by performing both electrochemical techniques and weight loss analysis in sodium chloride solution was studied. Experimental test results showed that the effect of AC is most pronounced near the open circuit potential; at more positive potentials the rates approach those of the ohmic drop/mass transport-limited DC rates. Correspondingly, at negative potentials the rates decrease. Surprisingly, at all potentials, it was found that the
AC corrosion rate was equal to the average AC current in the system. The data generated from weight loss experiments were compared with the results from a model for AC corrosion that was developed using a modified Butler-Volmer approach. The model considers the anodic and cathodic Tafel slopes, diffusion limited oxygen transport, interfacial capacitance and solution resistance. The model was used to explain the observation that the AC corrosion rate was equal to the average AC current in the system. Both experimental and model results showed the importance of the solution resistance and interfacial capacitance on the rate of AC corrosion, especially at the frequency of 60Hz or higher.

As it relates to the pipeline, one of the factors that influences this interfacial capacitance is the composition of the soil around the pipeline. For example, alkaline earth mineral content of the soil such as calcium or magnesium base minerals produce calcareous deposits on the coating fault. In the second phase of this project, the influence of the solution resistance and interfacial capacitance on the rate of AC corrosion was investigated in more detail. This was done by performing AC experiments in both extracted soil environment and soil simulated solution. Additionally, artificial scales were grown on X65 pipeline steel, which were then exposed to different AC and DC potentials in a soil-simulating solution. These films were meant to simulate those that might deposit on the surface of the steel in calcium and carbonate rich soils during long-term exposure to cathodic protection (CP). In these experiments films in the order of 2µm were deposited onto X65 carbon steel. After the deposition process, the properties of these films were characterized extensively including film capacitance. Results showed that the interfacial capacitance is one of the key parameters that ties together different factors
controlling the magnitude of AC induced corrosion, such as the magnitude of AC voltage, AC current density, AC frequency and soil properties. In the light of the developed model and the experimental results, some misconceptions about AC corrosion were discussed. For example, it was shown that the current density is not a good candidate as a basis of AC mitigation criteria.

Keywords: AC interference on pipelines, corrosion, carbon steel, scale formation, interfacial capacitance
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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>LIST OF TABLES</th>
<th>xiii</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIST OF FIGURES</td>
<td>xv</td>
</tr>
</tbody>
</table>

## CHAPTER

### I INTRODUCTION

1.1 Overview ................................................................................................................ 1

1.2 Cathodic Protection .................................................................................................. 2

1.3 AC Corrosion .......................................................................................................... 3

1.3.1 Level of CP Protection, AC Potential and AC Current ..................................... 4

1.4 Proposed AC Corrosion Mechanisms ..................................................................... 12

1.5 Objectives and Goals ............................................................................................. 14

### II PHASE I: STUDIES OF THE MECHANISM OF AC CORROSION OF API GRADE X65 PIPELINE STEEL

2.1 Theoretical Models for AC Corrosion ................................................................. 16

### III PHASE I: EXPERIMENTAL PROCEDURES AND TECHNIQUES

3.1 Materials ................................................................................................................ 21

3.2 Testing Solution ..................................................................................................... 21
3.3 Electrochemical Set-up ........................................................................................................ 22
3.4 Weight Loss Testing ........................................................................................................... 24

IV PHASE I: RESULTS AND DISCUSSION ........................................................................... 25

4.1 Electrochemical Experiments on X65 in NaCl Solution .................................................. 25

4.1.1 Effect of Solution Composition on Corrosion Rate ................................................... 25
4.1.2 Influence of Combined AC and DC Potentials on Corrosion Rate ......................... 27
4.1.3 AC Potentials and Faradaic Currents ........................................................................ 32

4.2 AC Corrosion Model Development .................................................................................. 38

4.2.1 Model Results of Experiments in NaCl Solution ......................................................... 40
4.2.2 Relationship between Average Current and Mass Loss ........................................... 40
4.2.3 Influence of Frequency and Capacitance on Corrosion Rate with AC .................... 43

V PHASE I: CONCLUSION .................................................................................................. 50

VI PHASE II: INFLUENCE OF SOIL PROPERTIES ON AC CORROSION RATE .......... 52

6.1 Influence of Soil Resistivity on Corrosion Behavior: .................................................... 53

6.1.1 Parameters Influencing the Soil Resistivity ............................................................... 54

6.2 Calcareous Deposits ........................................................................................................ 57

6.2.1 Influence of Calcareous Deposits on Cathodic Protection and DC Corrosion Rate ........................................................................................................... 61
6.2.2 Influence of Calcareous Deposits on AC Corrosion Rate ....................................... 64

6.3 Iron Carbonate Deposits ................................................................................................. 65
6.3.1 Mechanism of CO2 Corrosion

6.3.2 Influence of FeCO₃ Scale Formation on Corrosion Rate

VII PHASE II: EXPERIMENTAL PROCEDURES AND TECHNIQUES

7.1 AC Corrosion in Extracted Soil Environment

7.1.1 Soil Resistivity Measurement

7.1.2 AC corrosion Initiation Tests in Extracted Soil Environment

7.2 AC Corrosion in Simulated Soil Environment

7.2.1 Materials and Electrochemical Set Up

7.2.2 AC Corrosion Prorogation Tests in Simulated Soil Environment

7.3 CaCO₃ Scale Formation

7.3.1 Materials

7.3.2 Testing Solution

7.3.3 Electrochemical Set-up

7.3.4 Surface Analysis

7.4 FeCO₃ Scale Formation

7.4.1 Materials

7.4.2 Testing Solution

7.4.3 Electrochemical Set-up

7.4.4 Surface Analysis

VIII PHASE II: RESULTS AND DISCUSSION
8.1 Electrochemical Experiments on API X65 Carbon Steel in Soil Extracted .......... 85
8.1.1 Parameters Influencing the Soil Resistivity .................................................. 85
8.1.2 AC Experiments in Soil Environment .......................................................... 88
8.2 Electrochemical Experiments on API X65 carbon steel in NS4 Solution .......... 92
8.2.1 AC and DC influence on Corrosion Rate of X65 in NS4 Solution ............ 92
8.2.2 Influence of IR Drop on AC Corrosion Rate of X65 Carbon Steel ......... 94
8.2.3 Influence of CP and RMS Current on AC Corrosion Rate of X65 Carbon Steel ................................................................. 102
8.3 Calcareous Deposition on X65 Coupons ...................................................... 105
8.3.1 Determination of Calcareous Deposition Potential Using Cathodic Polarization Experiment ....................................................... 105
8.3.2 Influence of Rotation Speed and Applied Potential on Calcareous Deposits 107
8.3.3 Progressive Nucleation and Growth of the Calcareous Layer ............... 111
8.3.4 EIS Analysis on Calcite Films ................................................................. 116
8.3.5 The Analysis of EIS Results Using Equivalent Circuit Modeling .......... 120
8.4 Iron Carbonate Deposition on X65 Coupons .............................................. 126
8.4.1 Self-Passivation of X65 Carbon Steel in CO₂ Atmosphere .................... 126
8.4.2 Progressive Coverage of the Surface by FeCO₃ .................................... 130
8.4.3 EDS Analysis of the FeCO₃ Layer .......................................................... 133
8.4.4 FIB Cross-Sectional Morphology of the FeCO₃ Layer ....................... 136
8.4.5  EIS Analysis on Siderite Films: ................................................................. 139

8.4.6  Analysis of EIS Results Using Equivalent Circuit Modeling .................. 145

8.5  Electrochemical Experiments on X65 with Interfacial Scales in NS4 Solution .... 151

8.5.1  EIS Analysis Prior to the AC Experiments ............................................. 151

8.5.2  Application of the Proposed Model on AC Corrosion of Scaled Metal ...... 153

8.5.3  Scale Formation Influence on AC Corrosion Behavior of X65 Carbon Steel in NS4 Solution .................................................................................................................. 158

IX  PHASE II: CONCLUSION .................................................................................... 167

X  FUTURE STUDIES .................................................................................................. 169

BIBLIOGRAPHY ......................................................................................................... 170

APPENDIX .................................................................................................................. 179
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Fixed input parameters obtained from polarization curve without AC in 0.1 M NaCl solution.</td>
<td>40</td>
</tr>
<tr>
<td>2. Experimental data and input variables in solving Equation (15) to obtain Figures 19 and 20.</td>
<td>42</td>
</tr>
<tr>
<td>3. Effect of frequency and capacitance on faradaic and non-faradaic current at 0.6 V RMS and DC biases of -0.5 V and -0.7 for Rs= 48 Ω.cm² (Table 1 used as Input values (Equation [15])).</td>
<td>44</td>
</tr>
<tr>
<td>4. Input variables for solving Equation (15) that used to obtain Figure 21 through Figure 23.</td>
<td>47</td>
</tr>
<tr>
<td>5. Conductivity of ions in soil.</td>
<td>55</td>
</tr>
<tr>
<td>6. Chemical composition and characteristic of the extracted soil.</td>
<td>75</td>
</tr>
<tr>
<td>7. Composition of simulated soil solution.</td>
<td>77</td>
</tr>
<tr>
<td>8. Chemical composition of artificial sea water according to the ASTM D1141.</td>
<td>79</td>
</tr>
<tr>
<td>9. Input variables for solving Equation (15) that used to obtain Figure 48(b).</td>
<td>96</td>
</tr>
<tr>
<td>10. The mean and RMS values of the potential drop across the working electrode obtained from Equation (15).</td>
<td>100</td>
</tr>
<tr>
<td>11. Measured particle size and blocked area from SEM observation at different I/I₀ values.</td>
<td>112</td>
</tr>
<tr>
<td>12. Fit results for equivalent circuit elements at -0.8VSC and 600rpm.</td>
<td>124</td>
</tr>
<tr>
<td>13. Measured particle size and blocked area from SEM observation at different deposition time.</td>
<td>132</td>
</tr>
</tbody>
</table>
14. Quantitative EDS analysis of point (A) in Figure 76 (a). ......................... 135

15. Quantitative EDS analysis of point (B) in Figure 76 (a). ......................... 135

16. Equivalent circuit elements in Figure 84 obtained to fit the impedance spectra of Figure 80 through Figure 83. ................................................................. 150

17. Fitted values from EIS spectrum before AC experiments at OCP. ............ 152

18. Input parameters used to obtain Figure 88, Figure 89 and Figure 90 respectively. .................................................................................................................... 154

19. Effect of variation of C, Rs and βa on faradaic and non-faradaic currents, RMS current and the peak value of the potential drop in the system at 0.6 V RMS and DC biases of -0.67 V (Table 1 used as Input values for Equation[15]). ......................... 157

20. The uncovered active area percentage before AC experiment. ............... 160

21. Uncovered surface area of X65/CaCO3 samples after CaCO3 deposition obtained from Figure 70................................................................................. 161

22. The uncovered active area percentage after AC experiment with 3V RMS at 60 Hz........................................................................................................... 161

23. The uncovered active area percentage of X65/CaCO3 before and after AC experiment with 3V RMS at 60 Hz................................................................. 162

24. The uncovered active area percentage of X65/FeCO3 before and after AC experiment with 3V RMS at 60 Hz................................................................. 163
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Corrosion rate of corrosion coupons in CP condition as a function of AC current density.</td>
<td>5</td>
</tr>
<tr>
<td>2.</td>
<td>Study of the Steel coupons in simulated soil solution a) AC corrosion rate by weight loss analysis at different AC current densities and CP potentials after 48 h of immersion. b) variation of DC potential due to 200 A.m-2 AC current density</td>
<td>6</td>
</tr>
<tr>
<td>3.</td>
<td>CP criteria for AC mitigation in carbonate/bicarbonate solution.</td>
<td>6</td>
</tr>
<tr>
<td>4.</td>
<td>AC corrosion rate at as a function of AC current density and CP potentials.</td>
<td>7</td>
</tr>
<tr>
<td>5.</td>
<td>AC corrosion risk diagram.</td>
<td>8</td>
</tr>
<tr>
<td>6.</td>
<td>a) AC corrosion rate data point at various CP On potential and AC potential. b) AC corrosion rate data point at various CP and AC current densities.</td>
<td>10</td>
</tr>
<tr>
<td>7.</td>
<td>Schematic representation of the proposed mechanism by Bucher et al. in which the AC corrosion happens on the steel surface at different CP currents: a) high CP current, b) very high CP current, c) low CP current.</td>
<td>13</td>
</tr>
<tr>
<td>8.</td>
<td>Schematic of Pourbaix diagram showing unsafe region with respect to AC corrosion.</td>
<td>14</td>
</tr>
<tr>
<td>9.</td>
<td>Diagram of Experimental set-up used for AC experiments.</td>
<td>23</td>
</tr>
<tr>
<td>10.</td>
<td>Effect of solution replenishment and stirring on current density in 0.1 M NaCl.</td>
<td>26</td>
</tr>
<tr>
<td>11.</td>
<td>Effect of solution replenishment and stirring on: (a) Fe content of the electrolyte at DC=-500 mV vs. SCE; (b) pH of the electrolyte at DC=0 V vs. SCE in 0.1 M NaCl solution.</td>
<td>27</td>
</tr>
</tbody>
</table>
12. Effect of AC potential on corrosion rate of carbon steel at different DC biases in 0.1 M NaCl solution .......................................................................................................................................................................................... 28

13. Effect of AC potential on current density of carbon steel at different DC biases in 0.1 M NaCl solution ........................................................................................................................................................................................................... 30

14. Effect of different RMS values on the ratio of corrosion rate with AC to the corrosion rate without AC at different DC potentials in 0.1 M NaCl solution ........................................... 31

15. a) Schematic of sinusoidal AC current density from potentiostatic test, b) Comparison of current density with 60 Hz AC (RMS=600mV at different DC biases) from weight loss and AC(+), AC(-) and AC(average) in 0.1 M NaCl solution ........................................... 32

16. A schematic illustration of the proposed equivalent circuit .......................................................... 34

17. Comparison of current density with 60 Hz AC (RMS=600mV and DC=-500mV) from weight loss and AC(+), AC(-) and AC(average) at different frequencies in 0.1 M NaCl solution ........................................................................................................................................................................................................ 35

18. Snapshots of the surfaces of working and counter electrode (a-f), (g) i-t curve and (h) E-t curve during the experiment with AC (at OCP, RMS=600 mV) in one cycle at 0.01Hz along with (i) schematic of the polarization curve without AC ........................................... 36

19. Comparison of experimental mass loss data at 60Hz and the solution of the Equation (15) for two different capacitance values (0.001 and 0.0001 F) ........................................... 42

20. Model Results for 60 Hz AC and 0.6 V RMS for AC(+), AC(-), AC(average) and io (Equation [15]) ........................................................................................................................................................................................................... 43

21. Comparison of the faradaic and non-faradaic currents at two different frequencies from the model. a) anodic current, b) cathodic current and c) capacitive current at 60 Hz and d) anodic current, e) cathodic current and f) capacitive current at 0.01 Hz ........................................................................................................................................................................................................... 46

22. Comparison of the total current from the experiment at 60, and 0.01 Hz (a& b respectively) and corresponding calculated current from the model (c & d respectively) ........................................................................................................................................................................................................... 48

23. Comparison of the applied potential at 60, and 0.01 Hz (a & b respectively) and corresponding calculated potential across the faradaic resistance obtained from solving Equation 15 (c & d respectively) ........................................................................................................................................................................................................... 49
24. Conceptual model of the pH value distribution and possible reaction regions at a fault location.  72
25. Schematic of the pH profile in the electrolyte adjacent to a cathodically protected metal surface.  75
26: Interfacial pH-potential curves for cathodic reactions with different Reynolds number in artificial seawater without Mg salt.  76
27: pH titration curves of both (FeCl3) and (MgCl2) with 0.01M sodium hydroxide (NaOH) solution.  82
28: Schematic of the time dependency of the polarization curve for carbon steel in seawater.  83
29. CP current density vs time for A710/no. 600 steel at –900 mV CP potential in seawater at a flow rate of 100 mL/min.  84
30. Schematic of calcareous film on mild steel surface during cathodic protection in artificial seawater.  82
31. Dependency of FeCO3 solubility on CFe2+ and pH in 1 wt% NaCl at 80°C and pCO2 of 0.53 bar.  100
32. Influence of pH on the self-passivation of C1018 steel in 1%wt NaCl at T=80°C and pCO2=0.53 bar.  97
33. Influence of PCO2 on the self-passivation of C1018 steel in 1%wt NaCl at T=80°C and pH=8.97.  97
34. Influence of temperature on the self-passivation of C1018 steel in 1%wt NaCl at pH=7.5 and pCO2=0.53 bar.  97
35. Soil preparation steps: a) grinding, b) sieving, c) homogenizing and mixing with water and salt and d) compacting in the soil box.  75
36: Electrochemical set up for precipitation of calcareous layer.  80
37. Schematic of the electrochemical set up for FeCO3 formation.  83
38. Influence of the soil volume on the soil resistance.  86
39. Influence of soil volume on its resistance.  86
40. Influence of adding ions and water on the soil resistance in 20 L soil............. 87

41. a) Schematic of sinusoidal AC current density from potentiostatic test with the marked max and min current densities. b) The maximum and minimum values of the total current during AC experiments in soil and NaCl solution at CP of -0.85VCSE......... 89

42. Experimental results recorded during the experiment in 20 L, 15wt% water soil with 0.84 g. L-1 CaCl2.2H2O and 2.34 g. L-1 MgSO4.7H2O with -0.85 VCSE CP and 3 V RMS at 60Hz and a) i-t curve, b) E-t curve. ................................................................. 90

43. Variation of the soil resistance during the experiment over time.................. 90

44. Dry soil near the coupon after the experiment with AC.............................. 91

45. Effect of AC potential on current density of carbon steel at different DC biases in NS4 solution. ................................................................................................................ 93

46. Comparison of current density with AC on X65 in different solutions. .......... 94

47. Comparison of solution resistance in different solutions by EIS analysis before experiment at OCP................................................................. 95

48. The total applied potential at 60 (a) and corresponding calculated potential across the faradaic resistance obtained from solving Equation 15 (b)....................... 96

49. Comparison of current density with 60 Hz AC (RMS=600mV at different DC biases) from weight loss and AC(+), AC(-) and AC(avg) in NS4 solution. ................. 98

50. Comparison of current densities of X65 carbon steel at IR corrected DC biases in 0.1 M NaCl and NS4 solution................................................................. 100

51. Comparison of the influence of NS4 and NaCl solution on the ratio of the AC corrosion current density to DC corrosion current density at different DC biases at 600mVRMS. .................................................................................. 101

52. Postmortem corrosion rate measured by mass loss along with AC RMS current densities recorded by oscilloscope during AC experiment of X65carbon steel in NS4 solution at different DC biases with 3V AC RMS at 60 Hz.............................. 103

53. Influence of CP on current densities measured by mass loss after AC experiment of X65carbon steel in NS4 solution at different DC biases with 4.2V AC RMS at 60 HZ.............................................................................. 104

XVIII
54. Current-potential curve for X65 in artificial seawater without Mg in cathodic region at different rotation speeds................................................................. 106

55. Results from potentiostatic tests showing the influence of rotation rate on the CaCO3 deposition a) DC=-1VSCE, b)-0.8VSCE. ......................................................... 109

56. Relationship between Ln(-Ln(I/I0)) and Ln(t) obtained from Figure 55 at 600rpm at two different DC potentials of -1 and -0.8VSCE. ........................................ 110

57. SEM photographs of the deposits formed at 600 rpm on a steel substrate at: (a) -0.8 (b) -1VSCE. ................................................................................................. 110

58. Potentiostatic result at DC=-0.8 VSCE and 600 rpm................................. 112

59. SEM photographs of the nucleation and growth process of CaCO3 formed at 600 rpm on X65 carbon steel polarized at -0.8VSCE at different time of percoipitation, a)1700s b) 3300 c)5700s d)8900s and e) 9500s.............................................................. 113

60. Covered area versus deposition time.......................................................... 114

61. XRD analysis (λ-Co-Kα1 radiation) of the deposits. ............................... 114

62. FIB cross section of calcite layer after the experiment a) 20 hours and b) 70 hours.......................................................................................................................... 116

63. AC impedance diagram during calcite deposition at -0.8 VSCE ad 600 rpm. a& b) Nyquist and Bode plot respectively for I/I0>0.3, c& d) Nyquist and Bode plot respectively when I/I0<0.15. .............................................................. 118

64. AC impedance diagram during calcite deposition at -0.8 VSCE and 600 rpm for 70 hours of experiment. a) Bode magnitude plot and b) Bode phase plot. ......... 119

65. Equivalent circuit of the interface of the carbon steel in NaCl solution, proposed by Deslouis et al................................................................. 121

66. Schematic of the equivalent circuits used for EIS interpretation, a) partly covered and b) fully covered interface with CaCO3. ........................................ 121

67. EIS measurements and model fits of Nyquist plots (a) and corresponding Bode plots (b) and (c) of X65 electrodes after 1 hour calcite deposition at -0.8 VSCE at 600 rpm (I/I0>0.3). Inset in (a): the equivalent circuit. ........................................ 122
68. EIS measurements and model fits of Nyquist plots (a) and corresponding Bode plots (b) and (c) of X65 electrodes after 3 hours calcite deposition at -0.8 VSCE at 600 rpm (I/I0<0.15). Inset in (a): the equivalent circuit. ....................................................... 123

69. Summary of the fitted values from EIS analysis (Table 12), variation of a) Rc, b) Rf, c) covered area, d) CPEf-P. ................................................................. 125

70. Covered area estimation versus I/I0 during formation of calcite layer at -0.8 VSCE and 600 rpm. ................................................................. 126

71. The open circuit potential (OCP) evolution of X65 carbon steel immersed in 10wt% NaCl solution in CO2 atmosphere for 70 hours. ................................................ 127

72. Schematic diagram of the transition from active state to passive state. 98 .... 128

73. Schematic of the Pourbaix diagram of Fe-C-H2O system, that shows the influence of the increasing of the pH on the steel passivation. 98 ................................... 129

74. Open circuit potential trend of X65 carbon steel in 10%wt NaCl solution in CO2 atmosphere ................................................................................. 131

75. SEM photographs of the formation process of FaCO3 on X65 carbon steel immersed in 10wt% NaCl solution in CO2 atmosphere at different precipitation time, a) 1.5 h b) 3h c) 5h and d)8h. ................................................................. 132

76. EDS analysis on the surface of the sample immersed in 10wt% NaCl solution in CO2 atmosphere after 1.5 hours of immersion a) SEM image of the serface b) EDS analysis of point (A) c) EDS analysis of point (B). ................................................................. 135

77. XRD phase analysis of the FeCO3 layer. ..................................................... 135

78. FIB cross section of siderite layer after the experiment a) 20 hours and b) 70 hours.............................................................................................................. 137

79. FIB cross section of siderite layer showing formation FeCO3 between narrow gap of Fe3C. ................................................................................ 138

80. Impedance results obtained for a X65 carbon steel at different exposure times (first 1.15 hr) in 10 wt.% NaCl solution saturated with CO2: Nyquist (a) and Bode plots (b and c) representations. ....................................................... 139

81. Impedance results obtained for a X65 carbon steel at different exposure times in 10 wt.% NaCl solution saturated with CO2: Nyquist (a) and Bode plots (b and c) representations. ................................................................. 141
82. Impedance results obtained for a X65 carbon steel at different exposure times in 10 wt.% NaCl solution saturated with CO2: Nyquist (a) and Bode plots (b and c) representations. ............................................................................................................................ 143

83. Impedance results obtained for a X65 carbon steel after 20 hours of exposure in 10 wt.% NaCl solution saturated with CO2: Nyquist (a) and Bode plots (b and c) representations. ............................................................................................................................ 144

84. Schematic of the equivalent circuits used for EIS interpretation, a) partly covered and b) fully covered interface with FeCO3. ............................................................................................................. 146

85. EIS measurements and model fits of Nyquist plots (a) and corresponding Bode plots (b) and (c) of X65 electrodes after 2 hours immersion in 10wt% NaCl solutions in CO2 atmosphere. Inset in (a): the equivalent circuit. ........................................... 147

86. EIS measurements and model fits of Nyquist plots (a) and corresponding Bode plots (b) and (c) of X65 electrodes after 20 hours immersion in 10wt% NaCl solutions in CO2 atmosphere. Inset in (a): the equivalent circuit. .................................................... 148

87. Simplified equivalent circuit of X65/CaCO3 considering only when the Ceff,f<<Ceff,dl. .............................................................................................................. 152

88. Influence of the variation of the Rp on a) polarization current, b) total current, c) capacitive current and d) interfacial potential across the capacitor in the Randles circuit. ............................................................................................................................. 155

89. Influence of the variation of the C on a) polarization current, b) total current, c) capacitive current and d) interfacial potential across the capacitor in the Randle’s circuit. ............................................................................................................................. 156

90. Influence of the variation of the Rs on a) polarization current, b) total current, c) capacitive current and d) interfacial potential across the capacitor in the Randle’s circuit. ............................................................................................................................. 156

91. Comparison of current densities obtained by mass loss analysis and considering of apparent area on X65, X65/CaCO3 and X65/FeCO3 in NS4 solution with 3V applied AC. ............................................................................................................................ 159

92. Current densities obtained by mass loss analysis and considering the uncovered area of scaled samples in NS4 solution with 3V applied AC at 60 Hz. ........ 163
93. The surface area of the X65/CaCO3 sample a) Samples after 30 days of exposure to 3V AC at CP=-0.77VSCE in NS4 solution b) during the experiment with AC at DC=-0.65VSCE. ........................................................................................................................................... 164

94. SEM micrographs after AC experiments at DC=-0.6VSCE with 3V RMS at 60 Hz, (a)&(b) X65, (c)&(d) X65/CaCO3 (e)&(f) X65/FeCO3. .................................................................................. 166
CHAPTER I
INTRODUCTION

1.1 Overview

Unprotected buried pipelines would be subject to failure due to environment interactions such as corrosion. Therefore, pipelines are equipped with corrosion prevention systems, including insulating coatings and cathodic protection (CP). However, these mitigation strategies are reported to have failed in the case of AC corrosion. This type of failure is a threat to the integrity of the pipeline and there is a lack of well-agreed mitigation criteria for it. AC grounding systems as well as "consensus" standards that recommend limits on the maximum allowable AC current density and critical ratios of AC and CP currents are the only available techniques for preventing AC corrosion. Unclear mechanism of AC corrosion is the main reason for the uncertainty on the CP criteria in the presence of AC interference. AC interference can occur by conduction or induction mechanism where pipelines share right of way with some interference sources such as a high-voltage transmission line typically fed by a high voltage line at 50 or 16.7 Hz frequency. The goal of this work is to understand the mechanism of AC induced corrosion by studying the effects of AC interference on steel at different DC potentials.
1.2 Cathodic Protection

Cathodic protection (CP), usually combined with insulating coatings is the most effective way for controlling the corrosion of underground or submerged metallic structures. Utilizing the external potential or current sources (impressed current) and sacrificial anodes are two ways for applying CP and reducing the corrosion rate to a safe level.

Although the concept of cathodic protection is based on the experiment by Sir Humphry Davy as early as 1824, it was not until 1983 when Hoar and Mears et al. using Evans diagrams, offered the following description for cathodic protection$^{1-4}$:

\[ \ldots \text{in cases where corrosion is entirely electrochemical in nature it is necessary to polarize the cathodes in the corrosion cell to the open circuit potential of the local anodes in order to obtain complete cathodic protection.} \]

The recent CP criteria is still based on guidelines that issued by NACE in 1969 with some modification in 2007 which is the most accepted set of CP standards. The current version of NACE CP standard contains three primary criteria for steel exposed to soil environments.

- $-850 \text{ mV}_{\text{CSE}}$ potential criterion with current applied
- $-850 \text{ mV}_{\text{CSE}}$ polarized potential
- $100 \text{ mV}$ polarization criterion$^{5}$

As regards CP criteria in the presence of AC interference conditions, there are some sets of standards that are not consensus so far and will be discussed in further detailed in section 1.3.1.
1.3 AC Corrosion

Increased corrosion rate in the presence of alternating current (AC) has been known to occur for quite some time. About 100 years ago, investigators from the National Institute of Science and Technology described the “Influence of Frequency of Alternating or Infrequently Reversed Current on Electrolytic Corrosion”.\(^6\) However, it was not until an accident on a pipeline in Germany in 1986 that it became a widespread industry topic and a safety concern. The mentioned failure occurred on a polyethylene coated pipe installed parallel to a 16.6 Hz powered railway. The pipeline was cathodically protected with instant off-potential of -1V vs. copper-copper sulfate electrode (CSE) using an impressed current system, typical of European industry standards of the time.\(^7\) It was concluded that a low soil resistivity of 1900 ohm.cm from de-icing salts was a contributing factor in the failure. Since then, there have been numerous field cases of AC induced failures in pipelines with otherwise adequate cathodic protection (CP).\(^8\) AC corrosion failures in France with CP On-potentials of -2 and -2.5 V\text{CSE} and also five cases of failure in North America due to AC are only a few case histories of AC corrosion failures in CP condition.\(^9\) As a result, international and US standards as well as “best practices” have been published detailing corrosion protection criteria to mitigate AC-induced corrosion on buried pipelines.\(^8,10\text{–}12\) In addition to pipelines, the prospect of AC induced corrosion has prompted the oil and gas industry to develop mitigation strategies for its subsea operations.\(^13,14\) In that application, AC is used for autonomous operations as well as to heat pipelines coming from the well to reduce the formation of hydrates and waxes.
To contribute to the development of standards, a large number of field studies along with laboratory experiments have been carried out to characterize the variables that contribute to AC induced corrosion on pipelines, such as: AC potential (or AC current), level of cathodic protection and soil resistivity.\textsuperscript{15-20} In the following section, a brief literature review of the parameters that influence the AC corrosion rate will be discussed.

1.3.1 Level of CP Protection, AC Potential and AC Current

This section explains controversy about AC corrosion rate as a function of CP levels, AC potential and AC current density. There are various criteria for AC corrosion mitigation and none of them have reached a consensus. This may be due to an incomplete understanding of the mechanism of AC corrosion.

In 1998, Ragault performed on-site experiments on coupons in field condition. Coupons were installed close to the failure spots of a polyethylene coated steel pipeline, protected with CP, which was parallel to a high voltage transmission line. After 18 months, their measurement results showed no correlation between the value of AC current density and the corrosion rate except that high level of AC current density might result in high AC corrosion risk.\textsuperscript{21} On the other hand, Song et al stated that there is a linear relationship between the level of applied AC current density and corrosion rate. They did their study on both corrosion coupons and electrical resistivity probes (ER) in CP condition (Figure 1).\textsuperscript{22} In this project, it will be shown that AC current density is not the sole parameter controlling AC corrosion rate.
In the study by Xu et al., the effect of CP on AC corrosion rate of steel in a simulated soil solution containing Cl\(^-\), SO\(_4^{2-}\) and HCO\(_3^-\) salts was examined and they reported a relationship between CP potentials and corrosion rate. While some protection was afforded at -0.85 V saturated calomel reference electrode (SCE), it was not until the CP potential is reduced to -1.0 V vs. SCE that the effects of AC can be sufficiently mitigated even when the AC current density is up to 400 A.m\(^{-2}\) (Figure 2[a]). They stated that applied AC current would shift the CP potential from designated value and the amount of this change depends on the value of the applied CP potential (Figure 2[b]). In another study by Fu et al. it was shown that by increasing the CP level to -1.25V\(_{\text{CSE}}\), AC induced current densities as high as 100 A.m\(^{-2}\) would be mitigated. Based on their results they proposed a CP criteria for AC corrosion mitigation which is shown in Figure 3.
Figure 2. Study of the Steel coupons in simulated soil solution a) AC corrosion rate by weight loss analysis at different AC current densities and CP potentials after 48 h of immersion. b) Variation of DC potential due to 200 A.m⁻² AC current density.

Figure 3. CP criteria for AC mitigation in carbonate/bicarbonate solution.

Effect of additional CP values on AC corrosion is not clear, there are some other literatures that proposed that at lower CP potentials with an impressed AC,
overprotection of pipelines may occur. In laboratory experiments by Yunovich et al. two different AC current densities (20 and 500 A.m$^{-2}$) in different CP potentials were examined, the results are shown in Figure 4. They stated that for higher AC current densities, applying higher CP results in higher corrosion rates compared to the condition with lower CP values or even without CP. They also showed that low AC current density of 20 A.m$^{-2}$ without applied CP results in significant corrosion rate. Field experimental results on ER coupons at two different CP on-potentials (-1.25 and -1.5 V$_{\text{CSE}}$) in the presence of AC current density by Nielson et al. showed higher corrosion rate for lower CP potentials. Brenna et al. proposed an AC corrosion risk diagram (Figure 5) for carbon steel samples in simulated soil solution and showed that by increasing the CP level lower than -1.1 V$_{\text{CSE}}$ not only AC corrosion wouldn’t be stopped but also there is a more dangerous condition with respect to the AC corrosion risk.

![Figure 4. AC corrosion rate as a function of AC current density and CP potentials.](image)
Buchler et al. stated that the corrosion rate with AC depends strongly on the level of CP on-potential. They reported that at high CP current densities obtained from high CP on-potentials, AC corrosion rate is higher than 0.1mm/year and also the effect of AC voltage level at this point is negligible. Even high corrosion rate with low AC voltages at this point is possible. Buchler et al., based on field and laboratory investigations, proposed new criteria for mitigation of AC corrosion which is shown in Figure 6. This figure shows high AC corrosion rate data points shown by larger circles above the dashed line. They stated that for lowering AC corrosion rate, one should remain outside of this dashed line area which is provided by satisfying one of these options, 1) keeping the average AC current density lower than 30 A.m$^{-2}$, 2) keeping the average cathodic current density lower than 1 A.m$^{-2}$ and 3) keeping the ratio between AC current density and DC current density less than 3. In our project, it was concluded that decrease of CP values decreases the faradic current that would provide better protection of the substrate in
presence of AC. Although at really low CP values, the possible formation of the protective passive layer or scales on the metal surface in soil environment might be hindered. This is due to the hydrogen evolution at low potential values.

The European standard CEN/TS 15280 uses current density criteria for mitigation of AC corrosion: 1) maintaining the AC current density lower than 30 A.m$^{-2}$ (RMS) on a 1cm$^2$ coupon or probe, 2) maintaining the average cathodic current density on a 1cm$^2$ coupon or probe lower than 1 A.m$^{-2}$ if the average AC current density is more than 30 A.m$^{-2}$ or 3) maintaining a ratio between AC current density and DC current density less than 5.$^{30}$

While there seems to be some evidence that maintaining the AC current density lower than 30 A.m$^{-2}$ lowers susceptibility to AC induced corrosion, the magnitude of 30 A.m$^{-2}$ threshold is being debated. Pourbaix et al. showed that there is not a relationship between AC corrosion rate and any particular AC current density.$^{31}$ Also the work done by Yunovich, which discussed earlier in this section, showed that there is not a safe theoretical AC current density threshold.$^{25}$ This was similar to the conclusion made by Goidanich, in which she suggested that even AC current density as low as 10 A.m$^{-2}$ might be hazardous. She performed weight loss analysis on carbon steel samples in both de-aerated and aerated condition in soil simulated solution without CP and showed that at 10 A.m$^{-2}$ AC current density, corrosion rate is almost twice of the value that measured at the same condition without AC. She also stated that AC current densities higher than 30 A.m$^{-2}$ leads to the high and an unacceptable corrosion rate.$^{32}$
Although the European standard CEN/TS 15280 and the NACE standard both use the AC current density as guidance for AC mitigation, both elude to the importance of alternating voltage (AV) of an interfered structure. The European standard CEN/TS
15280 explains that, in order to reduce AC corrosion risk, the AC potential on the pipeline should not at any time, exceed 10 V where the local soil resistivity is greater than 25 Ω.m and 4 V where the local soil resistivity is lower than 25 Ω.m. However these limits may sometime be overly restrictive for many pipelines with overhead power transmission lines without any history of failure and results in extensive and expensive mitigation.\textsuperscript{8,30}

As we will show in this project AC current density is unreliable to be considered as a parameter for AC corrosion threshold because AC current consists of both in-phase (real) and out of phase (imaginary) parts and only the in-phase part of the current contributes to corrosion. While the magnitude of the AC current density is important, we will demonstrate that the critical parameters in AC induced corrosion are the AC pipe to soil potential ($R_s$), the time constant formed by the polarization resistance ($R_p$) at a holiday (proportional to corrosion rate) and the capacitance of the interface ($C_{dl}$). When a DC potential is applied across the pipeline, all of the current (I) at steady state is passed across $R_p$. This current is the corrosion current. As it relates to AC, one might think of this DC potential as a very low AC frequency ($<<0.1$ Hz). As frequency is increased a portion of the AC current is passed across $C_{dl}$ and a portion across $R_p$. It is the portion of the AC current passed across $R_p$ that contributes to the increased corrosion rates associated with AC induced corrosion of pipelines. The portion of AC current passing across $R_p$ is determined by the magnitudes of the frequency, $C_{dl}$ and $R_s$. Thus, the AC current itself is not the sole determining factor in assessing the magnitude of the induced corrosion rate. More details will be further discussed in sections 4.1 and 8.2.3 by analyzing AC corrosion data.
1.4 Proposed AC Corrosion Mechanisms

Although there are different proposed mechanisms of AC corrosion, no one has been able to fully explain this phenomenon. In this section, some of these proposed mechanisms will be discussed.

Bucher et al. proposed an AC corrosion mechanism based on the potential oscillation of the metal in the presence of AC interference. They stated that the continuous formation and dissolution of the passive film during positive half wave (metal oxidation) and negative half wave (reduction of passive film to iron hydroxide) in presence of AC, results in the corrosion of the metal. Based on this model, in very high CP values, since the formation of the passive layer is entirely prevented, AC corrosion could be stopped. Similarly they concluded that AC corrosion can be decreased if the dissolution of the once formed passive film is decreased, which is possible by decreasing the cathodic protection current. Based on their observations and proposed mechanism, they claimed a significant decrease in AC corrosion rate if the off-potential is more negative than -850 V\textsubscript{CSE} and the on-potential is in the range of -1.2 V\textsubscript{SCE}. Figure 7 shows a schematic presentation of their model.\textsuperscript{33} In this model they assumed that all of the positive current results in dissolution of the metal while in our work, it will be shown that at 60 Hz, most of the AC current is passing through the interfacial capacitance and only small portion of the current is the faradaic current.

Nielson et al. also proposed the alkalization theory. Their model, like Bucher’s model, was based on potential oscillations in the presence of AC interference but this time between the passivity and the immunity state of the metal due to the high pH values (Figure 8). This high pH in the vicinity of the coating fault is the result of cathodic...
protection and consequent electrochemical reaction. They stated that by adding more CP, AC corrosion doesn’t stop. Unlike their model, AC corrosion mechanism proposed in this project considers the fluctuation of the potential between the metal dissolution and cathodic reactions. As a result, decreasing CP leads to mitigation of AC corrosion.

Conversely, Carpentiers, et al. claimed the necessity of the existence of very high pH values in order to provide the immunity potential. They proposed that because the AC superimposed potential could destroy the formed passive film, the maximum true potentials should be always kept lower than $-1.22 \, \text{V}_{\text{CSE}}$. 

Figure 7. Schematic representation of the proposed mechanism by Bucher et al. in which the AC corrosion happens on the steel surface at different CP currents: a) high CP current, b) very high CP current, c) low CP current.
This brief overview shows that there is a high degree of uncertainty about the current proposed mechanisms of AC corrosion on steel in CP condition along with mitigation criteria. It should also be noted that most of these researches focused on the relationship between applied AC potential and current response of the system, without characterizing the current and its correlation to the actual rate of material degradation.

1.5 Objectives and Goals

This project has two goals. The first goal is to develop a theoretical model for AC corrosion. The second goal of this project is to examine the relationship between soil properties and corrosion rate. Therefore, the research plan consists of two phases. In the first phase, the influence of simultaneous presence of different AC and DC potentials on
corrosion rate of API grade X65 pipeline steel by performing both electrochemical techniques and weight loss analysis in sodium chloride solution was studied. The data generated from weight loss experiments were compared with the results from a model for AC corrosion that was developed using a modified Butler-Volmer approach. The model considers the anodic and cathodic Tafel slopes, diffusion limited oxygen transport, interfacial capacitance and solution resistance.

In the second phase of this project, the influence of the soil resistivity and the scale formation and interfacial capacitance on the rate of AC corrosion were investigated in more detail. This was done by growing an artificial calcareous and siderite scale on X65 pipeline steel, which was then exposed to different AC and DC potentials in a soil-simulating solution.
CHAPTER II

PHASE I: STUDIES OF THE MECHANISM OF AC CORROSION OF API GRADE X65 PIPELINE STEEL

2.1 Theoretical Models for AC Corrosion

There are also some theoretical approaches developed trying to explain the way that AC produces and enhances corrosion. Gellings was among the first researchers to model AC corrosion rates of metals.\(^\text{17}\) In that work, the influence of parameters such as Tafel slope (i.e. activation vs. transport control) were used to develop a generalized expression to estimate weight loss. However, no data or model validation was presented. Chin et al. proposed a preliminary theoretical approach to explain the polarization behavior of mild steel in a sodium sulfate solution with a superimposed AC potential.\(^\text{16}\) In their model, a Butler-Volmer (B-V) style equation was used. While the comparison between the calculated polarization curves and the experimental results was limited at best, they reported oscillograms of the AC current response (current vs. time) as a function of frequency that showed a distortion in peak shape away from the "sinusoidal form." The magnitude of this distortion was a function of frequency, however, the frequency dependence was not explained by the authors. We will show in section 4.1 that it may be attributed to the juxtaposition of the reactions occurring at the double layer, namely oxidation rate, reduction rate and interfacial capacitance.
Other theoretical investigations worth mentioning include the work of Bertocci and later by Bosch, both of which used a B-V style expressions of the form: \(15, 36\)

\[
i = i_{\text{corr}} \left[ e^{\frac{(E_{\text{DC}} + E_0 \sin(\omega t))}{\beta_a}} - e^{\frac{(E_{\text{DC}} - E_0 \sin(\omega t))}{\beta_c}} \right]
\]

(1)

where: \(i\) is current density passing through the system, \(i_{\text{corr}}\) is the corrosion current density in the absence of applied alternating voltage, \(E_{\text{DC}}\) is the applied DC potential, \(\beta_a\) and \(\beta_c\) are anodic and cathodic Tafel slopes, \(E_0\) is the peak potential and \(\omega\) is the angular frequency of the AC signal.

Equation (1) assumes activation control and does not consider potential-drop across the solution resistance or the effect of double layer capacitance. Bosch et al. were among a few researchers who considered the effect of diffusion phenomena on corrosion rate with applied AC potential.\(^{15}\) In their analysis, they assumed that AC and DC polarizations do not influence each other and as a result, concentration of oxidants at the electrode surface consists of two separate DC and AC parts. However, the authors did not consider the effect of the solution resistance and double layer capacitance in their model. Based on their model, Bosch et al. concluded that the increase in the corrosion rate was limited by the diffusion-limited current density. This conclusion will be rebutted by the model proposed in this work in section 4.2.

In comparison, Lalvani et al. proposed a model that considered both potential-drop across the solution resistance and the effect of double layer capacitance.\(^{37}\) In that model a simple Randles' circuit was assumed, where the total potential drop in the system \((E_T)\), was the sum of DC and AC potentials:
\[ E_T = E_{DC} + E_0 \sin \omega t \]  

(2)

In this model \( E_T \) was equal to the sum of the potential drop across the electrochemical interface (\( E \)) plus the potential drop across the solution resistance (\( R_s \)):

\[ E_T = E + i_T R_s \]  

(3)

The total current flow (\( i_T \)) across the interface was defined as the sum of the capacitive current (\( i_c \)) and the faradaic current (\( i_F \)):

\[ i_T = i_c + i_F \]  

(4)

where \( i_F \) is the sum of the anodic (\( i_o \)) and the cathodic (\( i_r \)) currents:

\[ i_F = i_o + i_r \]  

(5)

The current flow through the interfacial capacitance (\( C_i \)) was defined as:

\[ i_c = C_i \frac{dE}{dt} \]  

(6)

Substituting Equations (6) and (5) into Equation (4) and further combination of result with Equations (2) and (3), yielded a general expression for the potential drop across the interface:

\[ \frac{dE}{dt} + \frac{E}{C_i R_s} + \frac{i_o + i_r}{C_i} = \frac{E_{DC} + E_0 \sin \omega t}{C_i R_s} \]  

(7)

Lalvani et al. also considered both anodic and cathodic reactions under activation control. In their model, the values of \( i_o \) and \( i_r \) had their traditional Tafel definitions:
where $E_{\text{corr}}$ is the corrosion potential measured in the absence of AC.

Substituting Equations (9) and (8) into Equations (7) led to the final nonlinear differential equation for $E$:

$$\frac{dE}{dt} + \frac{E}{C_i R_s} + \frac{i_{\text{corr}} e^{(E-E_{\text{corr}})/\beta_a}}{C_i} - \frac{i_{\text{corr}} e^{(E-E_{\text{corr}})/\beta_c}}{C_i} = \frac{E_{\text{DC}} + E_0 \sin \omega t}{C_i R_s}$$ (10)

In this model, Lalvani et al. obtained numerical solutions using two different methods, one using a linear model and the other using a perturbation method.\cite{37,38} Based on their models, the corrosion current should be lower at higher frequencies, in agreement with experimental data.\cite{39} Another conclusion from this model is that the ratio of the anodic to cathodic Tafel slopes ($r$) defines a change in corrosion potential caused by the AC perturbation although that point will be rebutted here. In the linear model, they assumed the applied DC potential to be close to the open circuit potential (OCP). For the perturbation analysis they assumed that the ratio of DC corrosion current to the double layer capacitance value is much lower than unity and, therefore, could be neglected.\cite{37,38}

Due to assumptions in their numerical solution, the DC potential does not have any influence on AC corrosion rates, which is in contrast with the results obtained by others. In this work we proposed a model based on Equations (7) by Lalvani.\cite{37} Factors addressed by the new model that previous models have omitted include: the effect of...
solution resistance, mixed cathodic reactions such as transport limited oxygen reduction, and hydrogen evolution which will be explained in section 4.2.
PHASE I: EXPERIMENTAL PROCEDURES AND TECHNIQUES

This section covers the details of experimental procedures and materials used throughout the first phase of the project. It also explains analysis and characterization techniques that were performed for evaluating the data obtained from experiments.

3.1 Materials

The samples used in this work were fabricated from a API grade X65 (UNS K03014) pipe steel. The chemical composition of the material was: C 0.04-wt%, Si 0.2-wt%, Mn 1.5-wt%, P 0.011-wt%, S 0.003-wt%, Mo 0.02-wt% and Fe balance. The steel was in the quenched and tempered condition. The steel coupons were cut into 15x12x5 mm samples with a tapped hole in one end for electrical connection via a threaded rod. Samples were wet-ground with SiC papers, starting from 120 to 600 grit and rinsed with acetone, ethanol and distilled water, sequentially.

3.2 Testing Solution

AC experiments were performed in in 0.1 M NaCl solution to simulate the offshore environment. The solution volume was 300 mL and was made from analytic grade

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(1) American Petroleum Institute (API), 1220 L Street, NW Washington, DC 20005-4070 USA.
reagents and 18.2 MΩ.cm deionized water. All tests were conducted at ambient temperature (22 °C) and open to air. To assess the effect of ferrous/ferric ion content and solution pH on corrosion behavior, three different conditions were examined: i) static solution, ii) intermittent batch replacement of solution (250 mL after each hour) and iii) constant solution replacement at a rate of 8 mL/min. Replacement of solution was performed using a peristaltic pump and to insure the cell was mixed, solution stirring at 60 rpm was used. During the test, an aliquot of solution was taken periodically to measure pH and Fe ion content. In these tests, ultraviolet visible spectrophotometer (UVS) was used to determine ferrous (Fe$^{2+}$) and ferric (Fe$^{3+}$) ion concentration. The Fe$^{3+}$ content was indirectly obtained by calculating the Fe$^{2+}$ concentration, followed by a separate determination of the Fe$_{Total}$ concentration.\textsuperscript{40,41} Before electrochemical measurements, the working electrode (WE) was kept in the test solution for 24 hours at the open circuit potential (OCP) to ensure steady state.

3.3 Electrochemical Set-up

Electrochemical measurements were performed using a PAR 273A, Solartron SI 1287 and PAR 263A potentiostats in a conventional 3-electrode setup. A graphite rod was used as counter electrode (CE) and a saturated calomel electrode (SCE) as reference (RE). A Luggin capillary was used to prevent cross-contamination. The distance between the Luggin capillary and WE was approximately 15 mm while the distance between the CE and WE was approximately 40 mm. In some photographic figures we have decreased this distance between all electrodes to capture them in the same frame but no data were reported for these decreased distances.
Potentiostatic tests on X65 samples were performed at DC potentials of -720, -700, -670, -600, -500, -440 and 0 mV vs. SCE with and without impressed AC potentials. The AC signal was generated using a Solartron 1255 FRA. In this set-up the signal output from the FRA was connected to the external input of the potentiostat. In this manner, the AC signal could be applied between RE and WE through the potentiostat at a constant potential "on top" of the applied DC. AC root mean square (RMS) potentials used were 100, 200, 300, 400, 500 and 600 mV at a frequency of 60 Hz. The schematic of the experimental set up is shown in Figure 9.

![Diagram of Experimental set-up used for AC experiments.](image)

In order to investigate the effect of AC frequency on corrosion rate, tests at the OCP using lower frequencies (0.01, 0.1 and 1000 Hz) were performed. The current-time and potential-time response under various DC and AC potentials were recorded with an acquisition rate of 0.1 points per seconds for low frequencies (i.e. 0.01 and 0.1 Hz) while higher frequencies (i.e. 60 and 1000 Hz) were collected at a rate of 250 points per second. Electrochemical impedance spectroscopy data were taken before and after each
experiment with and without AC at OCP in order to monitor the solution resistance value. The frequency scans were taken from 100 kHz down to 0.01 Hz with 10 mV AC amplitude.

3.4 Weight Loss Testing

Weight loss analysis is one of the most fundamental ways to evaluate and validate the effectiveness of any other electrochemical corrosion measurements.

In this project, after potentiostatic tests, weight loss analyses were carried out to calculate the corrosion rate of samples under influence of AC interference. Weight loss samples according to the ASTM\(^{(2)}\) G1 were weighted before and after immersion in solution during the experiments.\(^{42}\) Immersion time was varied depending on anticipated weight loss and resolution of our balance. For example, for higher RMS AC potentials and or DC potentials the initial immersion time may have been as short as 2 days. For lower AC potentials and or cathodic DC potentials the immersion time was up to 30 days. The samples were weighed using an electronic balance to within 0.1 mg, and each sample was weighed three times. The balance used was a Mettler Toledo (Model ML204/03). After potentiostatic tests, the corrosion product formed on the coupon surface was removed by both mechanical and chemical methods as described in the standard. The mechanical method included scrubbing with a nylon brush and was used to remove loosely adhered corrosion product. To remove tightly bound oxide films, samples were immersed several times for 25 seconds in Clark solution: concentrated HCl (specific gravity 1.19), 2-wt% Sb\(_2\)O\(_3\) and 5-wt% SnCl\(_2\).

\(^{(2)}\) American Society for Testing and Materials (ASTM), 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA, 19428-2959 USA.
CHAPTER IV
PHASE I: RESULTS AND DISCUSSION

4.1 Electrochemical Experiments on X65 in NaCl Solution

This section shows the most significant experimental results and their interpretation of the corrosion behavior of the X65 carbon steel in NaCl solution.

4.1.1 Effect of Solution Composition on Corrosion Rate

Given that the immersion period of the weight loss experiments was relatively long, there was a concern that the change in solution properties over time would make interpretation of the results difficult\textsuperscript{43–49}. For example, sustained cathodic reactions over a period of days in the relatively small volume could have significant effects on solution pH.\textsuperscript{43–47} In addition, if the corrosion rates were high with an impressed AC potential, large amounts of dissolved Fe\textsuperscript{2+} could accumulate in the cell. Each of these factors can influence corrosion rates in pipeline steels.\textsuperscript{48,49} Thus, a series of experiments were designed to optimize solution composition. Figure 10 shows the variation in current density due to changes in the chemical composition of the NaCl electrolyte without solution replenishment and stirring.
Each solid symbol represents data points obtained from the mean steady state current density value from potentiostatic steps at constant DC potential. The solid line represents data taken using the potentiodynamic polarization method (stirred and replenished only).

Figure 10: Effect of solution replenishment and stirring on current density in 0.1 M NaCl.

As seen in Figure 10, current densities obtained from samples in the stagnant solution were consistently lower than those obtained using solution replenishment. UVS analysis of aliquots of solution at anodic potentials and solution pH versus charge passed are presented in Figure 11. We have used charge passed as opposed to time as it is a better reflection of what is occurring on the corroding sample, for example, one would anticipate larger Fe$^{+2}$ concentrations in a stagnant solution with larger charge passed. In contrast to the stagnant solution, solution replenishment / stirring resulted in constant
Fe$^{3+}$ concentration over the course of the immersion period (Figure 11 [a]) and relatively constant pH values of approximately pH = 7.0. Therefore, the lower current density without solution replenishment / stirring was attributed to the combination of pH and Fe$^{3+}$ that decreases corrosion rate.$^{43-49}$ Therefore, for the remaining of the work in NaCl solution, we decided to use solution stirring and replacement to eliminate any external influences other than imposed AC potential on corrosion behavior of carbon steel.

![Graphs showing Fe content and pH changes](image)

Figure 11: Effect of solution replenishment and stirring on: (a) Fe content of the electrolyte at DC=-500 mV vs. SCE; (b) pH of the electrolyte at DC=0 V vs. SCE in 0.1 M NaCl solution.

4.1.2 Influence of Combined AC and DC Potentials on Corrosion Rate

Figure 12 compares corrosion rate with AC (RMS voltage= 600 mV and f=60 Hz) and without AC as a function of DC potential in 0.1 M NaCl solution. Results were obtained by weight loss analysis after the potentiostatic test. The values of mass loss obtained at each of the DC biases were converted to equivalent current densities using Faraday's law:
\[ i = \frac{m \cdot F}{t \cdot \rho} \]  

where \( i \) is current density, \( m \) is the mass loss value, \( F \) is Faraday’s constant equal to 96,485 C.mol\(^{-1}\), \( t \) is total exposure time and \( \rho \) is density of carbon steel (7.8 g.cm\(^{-3}\)).

Figure 12. Effect of AC potential on corrosion rate of carbon steel at different DC biases in 0.1 M NaCl solution.

Weight loss was chosen as it was unclear if the current reported by the potentiostat would reflect the true Faradaic current in the system with an applied AC signal. In other studies where potentiostats have been used to measure corrosion current, polarization curves and (linear polarization resistance (LPR), investigators have employed separate AC and DC loops. In those investigations, an AC voltage is applied between the sample WE and a CE that is separate from the potentiostat CE. A potentiostat is used to apply an DC potential between the WE and RE using a separate CE. However, an inductor (on the order of 10H) is placed between the potentiostat and
the CE preventing the potentiostat from "responding" to the potential fluctuations on the WE created by the AC voltage. The result is that only DC current flows in the potentiostat loop. This type of circuit was first used by Chin and later by Goidanich and others. The use of an inductor in the CE is fundamentally flawed as the AC current generated by the oxidation reaction (above and beyond the oxidation current produced by the DC potential) is not measured by the potentiostat when an inductor is used. For example, consider the current response of the WE to a 60Hz AC perturbation at a given applied DC potential assuming the electrode can be modeled as a simple resistor (e.g. a polarization resistance). In addition to the DC Faradaic current in the system, Faradaic current at 60Hz will flow through the circuit: recall for an AC potential across a resistor \( Z(\omega) = R \). The actual corrosion rate is the sum of these two Faradaic current contributions. However, in setups that use an inductor in the potentiostat loop, the Faradaic component of the AC signal is not part of the current measured by the potentiostat (e.g. polarization curve or LPR). As such, polarization curves measured with an inductor in the CE provide no information with respect to corrosion rate of the sample resulting from the imposed 60Hz AC voltage. Faradaic and non-Faradaic currents are addressed further in later sections of this chapter.

Figure 12 shows the effect of AC potential on corrosion rate of API X65 pipe steel in 0.1 M NaCl solution. Each data point in this Figure represents the average of 3 independent weight loss measurements. As seen in Figure 12, both data sets with and without AC showed the same trend of increasing corrosion rate with increasing DC potential above \( E_{\text{corr}} \). In addition, the corrosion rate in the presence of AC was greater at any given DC bias. For example, the corrosion rate at OCP (-670 mV) with AC was
about 10 times higher than that without AC, consistent with observations made by other authors.\textsuperscript{50,52} These results along with the potentiodynamic polarization data shown in Figure 10 are compared in Figure 13.

![Figure 13](image)

Figure 13. Effect of AC potential on current density of carbon steel at different DC biases in 0.1 M NaCl solution.

As seen in Figure 13, the current densities from mass loss without AC agreed well with the polarization curve. In addition, Figure 4 suggests that at very high DC biases, as the system approaches a combination of mass transport and IR control, the effect of AC was negligible. Finally, while it appears that there is a "shift" in the $E_{\text{corr}}$ during AC, this is a fundamentally incorrect way of viewing the data. The AC signal is an impressed voltage that does not require the oxidation and reduction reactions to be occurring at steady state on the sample. There will be a potential at which the magnitude of the oxidation reaction during the positive portion of the sine wave will be equal to the
reduction reaction, however, this is not the same as $E_{corr}$ as the source of current is not the opposing reaction, rather, the remote power source driving the AC signal. The potential at which this crossover point occurs depends on the relative magnitudes of the anodic and cathodic Tafel slopes, which will be discussed later in this chapter.

To better understand the relationship between AC, applied DC and corrosion rate, mass loss experiments as a function of applied DC and AC potential were conducted (Figure 14).

Figure 14. Effect of different RMS values on the ratio of corrosion rate with AC to the corrosion rate without AC at different DC potentials in 0.1 M NaCl solution.

As seen in Figure 14, corrosion rates decreased with decreasing AC RMS potential at any given DC potential. In addition, there was a decreasing trend in the AC:DC corrosion ratio with increasing DC potentials for all AC RMS levels with the exception of the OCP. Near the OCP the effect of AC was more pronounced as compared to more positive
applied DC potentials. It is believed that this trend owes to a combination of two factors: the magnitude of the non-Faradaic (capacitive) current and the solution resistance.

4.1.3 AC Potentials and Faradaic Currents

One way of analyzing the corrosion rate data obtained herein is to compare it with the total AC current in the system. Nominally, the total AC current varies with time at 60Hz. The total AC current can be separated into three categories: 1) the average positive AC current (AC(+)\), which is the time averaged value of all of the current that is greater than zero, 2) the average negative AC current (AC(-)) which is the time averaged value of all of the current that is less than zero and 3) the average AC current (AC(avrg)) which is the time averaged value of all current (Figure 15 [a]). Figure 15(b) compares the current density calculated from mass loss with AC(+), AC(-), and AC(avrg).

Figure 15. a) Schematic of sinusoidal AC current density from potentiostatic test, b) Comparison of current density with 60 Hz AC (RMS=600mV at different DC biases) from weight loss and AC(+), AC(-) and AC(avrg) in 0.1 M NaCl solution.
As seen in this figure the weight loss data diverges sharply from AC(+) an indication that not all of AC(+) contributes to corrosion reactions, that is not all of the AC(+) is Faradaic. In comparison, the weight loss data agreed almost exactly with the AC(avg).

In fact, the data agrees so well most of the points overlapped. While this phenomenon has been observed before for 60Hz it has not been explained\textsuperscript{53,54} We propose that this finding is specific to mid-range frequencies (1-100 Hz) and occurs because the Faradaic current generated by the cathodic reaction is negligible as compared to the anodic reaction. To evaluate this, consider the equivalent circuit in Figure 16 that includes elements for the solution resistance ($R_s$), the oxidation and reduction charge transfer resistances ($R_o$ and $R_r$), and the interfacial capacitance ($C_i$). Here, it is assumed that $R_o$ and $R_r$ are acting as voltage-controlled nonlinear resistors. Specifically, $R_o$ is related to the anodic Tafel slope ($\beta_a$), and $R_r$ is related to three parameters: the slope of the oxygen reduction reaction ($\beta_c$), the transport limited oxygen reduction current density ($i_L$) and the slope of the hydrogen reduction reaction ($\beta_{H2}$). Both oxidation current (Faradaic) and capacitive current (non-Faradaic) occur during the positive half-cycle of the applied AC signal. Similarly, reduction and capacitive currents coexist during the negative half cycle of the applied AC signal. The magnitude of AC(+), Faradaic plus capacitive current, depends on the values of $R_o$ and $C_i$ (e.g. the RC time constant) and the frequency of the AC signal. Correspondingly, the values of $R_r$, and $C_i$ act independently to control the magnitude of AC(-). With respect to the capacitive current, the magnitude of the positive and negative half-cycles are equal and, as such sum to zero. However, the Faradaic current generated by the oxidation and reduction reactions are independent.
Thus the value of AC(avg) is controlled by the rates of these two reactions. In the case of API X65 pipe steel in seawater, the value of \( R_r \) is high relative to \( R_o \), \( (\beta_a = 0.089, \beta_c = 0.352, \text{ and } \beta_{H2} = 0.205) \). As a result \( i_o + i_r \) resembles \( i_o \). For this reason, AC(avg) approximates the corrosion rate as measured by weight loss as observed in Figure 15. There would be a similar result if there was a cathodic DC bias on the system and the applied AC potential was large enough to make \( i_o \) more significant than the \( i_r \).

![Figure 16. A schematic illustration of the proposed equivalent circuit.](image)

The effect of the RC time constant (\( R_r C_i \) and \( R_o C_i \)) on AC(avg) and \( i_o \) (mass loss) can be seen in the data collected at lower frequencies. In Figure 17, the current values calculated from mass loss for API grade X65 steel in chloride solution exposed to an AC potential (600 mV RMS) at +0.17V SCE vs. OCP are plotted as a function of frequency. As seen in Figure 17, as frequencies decreased from 60 Hz to 0.01 Hz there was less agreement between mass loss and AC(avg) and better agreement between mass loss and AC(+). At low frequencies \( i_C \) went to zero while \( i_o \) and \( i_r \) reached their maximum values.
Because \( i_o > i_r \), AC(+) approximates the mass loss data and AC(avrg) with \( i_r \) now being a measureable “error” in the approximation.

At low frequencies the mechanism of AC induced corrosion is visible on the electrode surfaces as periodic cycling of bubbles. Figure 18(a) through (f) present photographs of both the WE and CE surfaces as a function of time during an experiment at OCP for \( f=0.01 \text{Hz} \) and AC=600 mV RMS. The electrodes in the cell have been reconfigured for photographing resulting in an aberrant RE position and decreased solution resistance.

Figure 17. Comparison of current density with 60 Hz AC (RMS=600mV and DC=-500mV) from weight loss and AC(+), AC(-) and AC(avg) at different frequencies in 0.1 M NaCl solution.
Figure 18. Snapshots of the surfaces of working and counter electrode (a-f), (g) i-t curve and (h) E-t curve during the experiment with AC (at OCP, RMS=600 mV) in one cycle at 0.01Hz along with (i) schematic of the polarization curve without AC.
As can be seen in Figure 18 (a), at the beginning of the sine wave there was a small positive current and corresponding low density of hydrogen bubbles on the CE surface. At the maximum potential of the WE the density of hydrogen bubbles on the CE reached a maximum (Figure 18b). As time continues and the AC potential on the WE decreased so did the hydrogen bubble density on the CE (Figure 18c). At approximately 60 seconds the WE changed from anodic potentials to cathodic; Figure 18(d) shows the corresponding image of the WE during oxygen reduction. As the WE potential becomes more negative the electrode falls below the reversible hydrogen potential and hydrogen bubbles begin to form on the surface.

This periodic cycling of hydrogen bubbles on the WE surface maps the polarization curve of API grade X65 in seawater. To demonstrate this, points corresponding to the photographs of the cell are plotted on the experimental current vs. time and potential vs. time curves (recorded simultaneously) in Figure 18(g) and (h) respectively.

These points are plotted on the experimental polarization curve in Figure 18 (i). It is seen in these figures that the cell current induced by the applied AC potential was proportional to the reaction rate at the WE as indicated by the polarization curve of API grade X65 pipe steel, which is a combination of transport limited oxygen reduction and hydrogen evolution. For comparison to the low frequency data in Figure 18, similar data at 60 Hz were also collected. Unlike the lower frequency data, there was limited hydrogen reduction on the WE in these experiments. This likely occurs because the total AC current at this frequency is predominantly non-Faradaic (capacitive) and the reduction current is small, which is addressed in the modeling section below.
From these results, we concluded that, an applied AC potential across an electrochemical interface polarizes the electrode as a function of time away from its DC potential along its polarization curve. The net effect of this polarization depends on a number of variables including: AC frequency, AC potential, Tafel slopes, interfacial capacitance, solution resistance and applied DC potential. For carbon steel in sodium chloride solution where there is a low anodic Tafel slope, transport limited oxygen reduction, low solution resistance and high interfacial capacitance a 600mV 60Hz AC signal results in increased corrosion rates at all DC potentials investigated here, greater than -0.25V vs OCP.

4.2 AC Corrosion Model Development

We present a new model to predict corrosion rates of carbon steel in the presence of an AC interference. The model is, in part, based on the work by Lalvani’ (Equation [10]).37 One of the assumptions in Equation (10) is that the Faradaic currents \(i_o\) and \(i_r\) can be described by activation control which is not always the case. Typically, at moderate overpotentials, the cathodic reaction is controlled by the diffusion limited oxygen reduction \(i_{r,O2}\) while at lower potentials by hydrogen evolution \(i_{r,H2}\), Equation [12]). As such, we present a modified B-V exponential function that describes the anodic reaction under activation control while the cathodic reaction is assumed to be under mixed control:

\[
i_r = i_{r,O2} + i_{r,H2}\tag{12}
\]

where the mass transport limited oxygen reduction rate is governed by the expression:55
where: $i_L$ is the limiting current density of oxygen reduction and the remaining terms take the usual meaning. The hydrogen evolution reaction rate is governed by the Tafel equation (Equation [14]).

$$i_{r,H_2} = -i_{0H_2}e^{\frac{2.3(-E+E_0)}{\beta_{H_2}}}$$  \hspace{1cm} (14)

where: $i_{0H_2}$ is hydrogen exchange current density and is a function of the nature of the cathode, $E_0$ is the hydrogen standard equilibrium potential that is equal to zero in the SHE scale and $\beta_{H_2}$ is the Tafel slope of the hydrogen evolution reaction.

Substituting Equations (13) and (14) in Equation (12) and following combination of Equations (12), (8) and (7) leads to the nonlinear equation for potential drop across the Faradaic resistance ($E$):

$$\frac{dE}{dt} + \frac{E}{C_iR_s} + \frac{\xi}{C_i} = \frac{E_{DC} + E_0 \sin \omega t}{C_iR_s}$$  \hspace{1cm} (15)

where:

$$\xi = i_{corr} \left( \frac{e^{\frac{2.3(E-E_{corr})}{\beta_a}}}{1 - \frac{i_{corr}}{i_L} + \frac{i_{corr}}{i_L} e^{\frac{2.3(-E+E_{corr})}{\beta_c}}} \right) - i_{0H_2} e^{\frac{2.3(-E-0.244)}{\beta_{H_2}}}$$.  \hspace{1cm} (16)
4.2.1 Model Results of Experiments in NaCl Solution

Even though we have minimized the number of assumptions in Equation (15), finding the analytical solution for this expression would be very difficult. Thus, a numerical solution using MATLAB software and ODE23S solver based on Runge-Kutta Fehlberg method was used. Using the potential drop across the Faradaic resistance from Equation (15), one may easily calculate the time averaged of oxidation current density ($i_o$-model) along with the total current density passing through the system. Specific details are available in Appendix A.

4.2.2 Relationship between Average Current and Mass Loss

It was shown in Figure 15 that AC(avg) agreed well with mass loss data. Figure 19 compares $i_o$ from the model for two different capacitance values with the current densities obtained from experimental data. The other input values used for solving Equation (15) can be found in Table 1 and Table 2. These values were obtained from IR corrected polarization data without AC (i.e. anodic and cathodic Tafel slopes, corrosion current density, corrosion potential and oxygen limiting current density shown in Table 1), and electrochemical impedance spectroscopy (EIS) data.

<table>
<thead>
<tr>
<th>$\beta_a$ (V/dec)</th>
<th>$\beta_c$ (V/dec)</th>
<th>$\beta_{H2}$ (V/dec)</th>
<th>$i_{corr}$ (A.cm$^{-2}$)</th>
<th>$E_{corr}$ (V)</th>
<th>$i_{O2}$ (A.cm$^{-2}$)</th>
<th>$i_{H2}$ (A.cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.089</td>
<td>0.352</td>
<td>0.205</td>
<td>5.10-5</td>
<td>-0.67</td>
<td>7.10-5</td>
<td>1.10-7</td>
</tr>
</tbody>
</table>

Table 1.Fixed input parameters obtained from polarization curve without AC in 0.1 M NaCl solution.
For applied potentials greater than the OCP, the experimental data approached the model values for an interfacial capacitance of 1 mF. However, at applied potentials below OCP, the experimental data were more closely represented by a model using $C_i = 0.1$ mF. Since all of the $C_i$ values are higher than the normal range of double layer capacitances ($20–50 \text{ Fcm}^{-2}$), it is likely that $C_i$ is composed of a series combination of the double layer and oxide capacitances.\textsuperscript{58,59} This capacitance is associated with both double layer and oxide layer. Wren et al. studied the influence of the oxide film on carbon steel on corrosion rate and $C_i$ values for three different potential regions: region I ($\leq -0.6 \text{ V vs SCE}$), region II ($-0.5 \leq E (\text{ vs SCE}) \leq -0.2 \text{ V}$), region III ($0.0 < E (\text{ vs SCE}) < 0.4 \text{ V}$). At different potentials in mildly alkaline solution a unique value of $C_i$ was measured. In addition, the oxide films in each of those regions were identified as Fe$_3$O$_4$, Fe$_3$O$_4$ layer with Fe$_2$O$_3$ and FeOOH respectively. It was concluded that $C_i$ was related to the composition of the oxide films. Further, that the oxide also influenced the nature of the double layer capacitance.\textsuperscript{59} Thus, as it relates to the results in this project, the value of $C_i$ is likely a combination of double layer capacitance and oxide capacitance. From a model perspective, in order to accurately solve Equation (15) for all DC potentials at 60 Hz a series of empirical values of capacitance as a function of potential would be needed.

Fitted values of $C_i$ for each experimental data point in Figure 19 were obtained and the results are shown in Table 2. By using these values along with the other values from Table 1 as input for solving Equation (15), $AC(\text{+})$, $AC(-)$ and $AC(\text{avrg})$ were calculated and plotted in Figure 20.
Figure 19. Comparison of experimental mass loss data at 60Hz and the solution of the Equation (15) for two different capacitance values (0.001 and 0.0001 F).

Table 2. Experimental data and input variables in solving Equation (15) to obtain Figures 19 and 20.

<table>
<thead>
<tr>
<th>E\text{DC} (V)</th>
<th>RMS (V)</th>
<th>f (Hz)</th>
<th>R_s (\Omega.cm^2)</th>
<th>C_i (\mu F.cm^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.74</td>
<td>0.6</td>
<td>60</td>
<td>25</td>
<td>3500</td>
</tr>
<tr>
<td>-0.72</td>
<td>0.6</td>
<td>60</td>
<td>53</td>
<td>420</td>
</tr>
<tr>
<td>-0.7</td>
<td>0.6</td>
<td>60</td>
<td>53</td>
<td>310</td>
</tr>
<tr>
<td>-0.67</td>
<td>0.6</td>
<td>60</td>
<td>69</td>
<td>261</td>
</tr>
<tr>
<td>-0.6</td>
<td>0.6</td>
<td>60</td>
<td>57</td>
<td>257</td>
</tr>
<tr>
<td>-0.5</td>
<td>0.6</td>
<td>60</td>
<td>54</td>
<td>208</td>
</tr>
<tr>
<td>-0.44</td>
<td>0.6</td>
<td>60</td>
<td>50</td>
<td>309</td>
</tr>
</tbody>
</table>
Figure 20. Model Results for 60 Hz AC and 0.6 V RMS for AC(+), AC(-), AC(avg) and io (Equation [15]).

Figure 20 is analogous to Figure 15b but for model data only. In addition to these values, we have also calculated the oxidation current passing through $R_o (i_o)$. This current involves oxidation reactions only and would be analogous to a current calculated from mass loss and Faraday's Law. As in Figure 15b, it is seen that AC(avg) from the model was in a good agreement with the oxidation current as described above.

4.2.3 Influence of Frequency and Capacitance on Corrosion Rate with AC

It is apparent that one of the key parameters in AC corrosion is the value of $C_i$. For a given anodic Tafel slope, the value of $C_i$ determines two factors: 1) the magnitude of the Faradaic current at a given frequency and 2) the high frequency break point at which no Faradaic current is passed. In this section we will explore the response from the
model as a function of AC frequency and $C_i$. We compare model predictions with results for several cases.

The effect of capacitance on each component of the current for frequencies of 0.01 Hz, 60 Hz and 1000 Hz (0.6 V RMS) and an anodic potential of $-0.5$ V is shown in Table 3.

Table 3. Effect of frequency and capacitance on faradaic and non-faradaic current at 0.6 V RMS and DC biases of $-0.5$ V and $-0.7$ for $R_s=48 \, \Omega \cdot \text{cm}^2$ (Table 1 used as Input values (Equation [15])).

<table>
<thead>
<tr>
<th>$E_{\text{DC}}$ (VSCE)</th>
<th>F (Hz)</th>
<th>$C_i$ (F)</th>
<th>$i_o$ (A.cm$^{-2}$)</th>
<th>$i_r$ (A.cm$^{-2}$)</th>
<th>$i_T$ (A.cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-0.5$</td>
<td>0.01</td>
<td>0.001</td>
<td>$5.3 \times 10^{-3}$</td>
<td>$-7.1 \times 10^{-4}$</td>
<td>$4.6 \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.0001</td>
<td>$5.3 \times 10^{-3}$</td>
<td>$-7.1 \times 10^{-4}$</td>
<td>$4.6 \times 10^{-3}$</td>
</tr>
<tr>
<td>$60$</td>
<td>0.001</td>
<td>$1.3 \times 10^{-3}$</td>
<td>$-4.2 \times 10^{-3}$</td>
<td>$1.2 \times 10^{-3}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.0001</td>
<td>$4.0 \times 10^{-3}$</td>
<td>$-1.4 \times 10^{-4}$</td>
<td>$3.8 \times 10^{-3}$</td>
<td></td>
</tr>
<tr>
<td>$1000$</td>
<td>0.001</td>
<td>$1.1 \times 10^{-3}$</td>
<td>$-4.0 \times 10^{-3}$</td>
<td>$1.1 \times 10^{-3}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.0001</td>
<td>$1.1 \times 10^{-3}$</td>
<td>$-4.0 \times 10^{-3}$</td>
<td>$1.1 \times 10^{-3}$</td>
<td></td>
</tr>
<tr>
<td>$-0.7$</td>
<td>0.01</td>
<td>0.001</td>
<td>$3.5 \times 10^{-3}$</td>
<td>$-1.6 \times 10^{-3}$</td>
<td>$2.0 \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>0.0001</td>
<td>$3.5 \times 10^{-3}$</td>
<td>$-1.6 \times 10^{-3}$</td>
<td>$2.0 \times 10^{-3}$</td>
<td></td>
</tr>
<tr>
<td>$60$</td>
<td>0.001</td>
<td>$3.4 \times 10^{-5}$</td>
<td>$-6.9 \times 10^{-3}$</td>
<td>$-4.6 \times 10^{-5}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.0001</td>
<td>$2.0 \times 10^{-3}$</td>
<td>$-4.7 \times 10^{-4}$</td>
<td>$1.5 \times 10^{-3}$</td>
<td></td>
</tr>
<tr>
<td>$1000$</td>
<td>0.001</td>
<td>$2.4 \times 10^{-5}$</td>
<td>$-6.9 \times 10^{-3}$</td>
<td>$-4.5 \times 10^{-5}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.0001</td>
<td>$2.8 \times 10^{-5}$</td>
<td>$-6.9 \times 10^{-3}$</td>
<td>$-4.1 \times 10^{-5}$</td>
<td></td>
</tr>
</tbody>
</table>
Similar trends were observed at a cathodic potential of -0.7V. As seen in this table at both high frequency and low frequency there was little effect of capacitance on the individual components of the current density. For example, the relative magnitudes of each component of current at 0.01Hz was the same for C_i=0.0001F and C_i=0.001F. However, at 60 Hz the difference between the two values of C_i was dramatic. For example, i_O at C_i=0.0001F was a factor of two as compared to C_i=0.001F. This occurs because 60 Hz for this system was close to the high frequency break point. From a practical standpoint, this finding implies that the growth of an oxide or scale on the surface of the material (owing to a corrosion product or mineral deposition from solution/soil) that alters the interfacial capacitance will greatly impact the AC corrosion rate of the material.

Figure 21 shows model results for the individual components of current in the system at two frequencies in the form of current vs. time data. The data at 60 Hz are presented in Figure 21 (a) through (c) where: Figure 21 (a) is the oxidation current, Figure 21 (b) is the reduction current and Figure 21 (c) is the capacitive current. The data at 0.01 Hz are presented in Figure 21 (d) through (f) where: Figure 21 (d) is the oxidation current, Figure 21 (e) is the reduction current and Figure 21 (f) is the capacitive current. The data were calculated for the input values from Table 1 and Table 4 at OCP. These results show that at 60 Hz most of the current is non-Faradaic, that is, most of the current passes through the interfacial capacitance (Figure 21 [c]). Comparison of the oxidation and reduction currents (Figure 21 [a] and [b]) shows that the reduction current, which is controlled primarily by the diffusion limited oxygen current density, is negligible relative to the oxidation current. Because the capacitive current sums to zero and i_r is negligible,
the total current is equal to \( i_0 \). This is consistent with the discussion of Figure 15 and is further confirmation that the average current at 60Hz (AC(avg)) is a good representation of the mass loss of the sample. However, this is limited to DC potentials where the reduction current is controlled primarily by the diffusion limited oxygen current density. In comparison to the 60 Hz data, the waveforms at 0.01 Hz (Figure 21 [d] through [f]) are quite different in magnitude and shape. At this frequency the total current is dominated by the Faradaic current \( i_0 \) and \( i_r \) while the \( i_C \) is negligible. From this finding one would conclude that at this frequency AC(avg) is not a good representation of the mass loss of the sample. This is in agreement with the observation during experiment with AC at lower frequencies (Figure 17).

Figure 21.Comparison of the faradaic and non-faradaic currents at two different frequencies from the model. a) anodic current, b) cathodic current and c) capacitive current at 60 Hz and d) anodic current, e) cathodic current and f) capacitive current at 0.01 Hz.
The total current in the system calculated from the model is compared with the experimental results in Figure 22. In Figure 22 the input values to our model were kept constant (Table 4, the same as Figure 21) for frequencies of 60 Hz and 0.01 Hz. As seen in Figure 22, at these frequencies, there was good agreement in both magnitude and waveform shape between the proposed model and the experimental data. Nevertheless, it should be noted that it is not possible to experimentally collect the individual waveforms for the oxidation and capacitive currents presented in Figure 21.

Table 4 Input variables for solving Equation (15) that used to obtain Figure 21 through Figure 23.

<table>
<thead>
<tr>
<th>$E_{DC}$ (V)</th>
<th>RMS (V)</th>
<th>$f$ (Hz)</th>
<th>$R_s$ (Ω.cm$^2$)</th>
<th>$C_i$ (µF.cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.67</td>
<td>0.6</td>
<td>60</td>
<td>8.7</td>
<td>638</td>
</tr>
<tr>
<td>-0.67</td>
<td>0.6</td>
<td>0.01</td>
<td>6.72</td>
<td>638</td>
</tr>
</tbody>
</table>

Figure 22. Comparison of the total current from the experiment at 60 Hz and 0.01 Hz (a & b respectively) and corresponding calculated current from the model (c & d respectively).
Figure 22 (continued). Comparison of the total current from the experiment at 60, and 0.01 Hz (a& b respectively) and corresponding calculated current from the model (c & d respectively).

The potential drop across the system drives the Faradaic reactions in proportion to the anodic and cathodic Tafel slopes; however, the applied potential ($E_T$) is not the same as the potential drop across the Faradaic resistances ($E$). Comparison between the applied potential at 60, and 0.01 Hz and the corresponding potential across the faradaic resistance is shown in Figure 23 (parameters from Table 4 as in Figure 21 and Figure 22). The data were generated for an applied potential equal to the OCP, approximately -0.67 V$_{SCE}$, and is shown in each figure. As seen in these figures for both cases $E_T$ was higher than $E$. This is a result of a combination of parameters including the magnitude of the Tafel slopes, the capacitive current in the system, and ohmic drop ($R_s$).
Figure 23. Comparison of the applied potential at 60, and 0.01 Hz (a & b respectively) and corresponding calculated potential across the faradaic resistance obtained from solving Equation 15 (c & d respectively)
CHAPTER V
PHASE I: CONCLUSION

Corrosion rates of API grade X65 pipeline steel samples in sodium chloride solution with and without 60 Hz AC at different DC potentials were measured using weight loss analysis. These data are compared with the results from a model for AC corrosion that was developed using a modified Butler-Volmer approach. The model considered the anodic and cathodic Tafel slopes, diffusion limited oxygen transport, interfacial capacitance and solution resistance and good agreement with the results were demonstrated. From this investigation it was concluded that:

- The presence of an applied AC potential increased corrosion rates at all cathodic and anodic DC potentials between \(-0.725 \text{ V}_{\text{SCE}}\) and \(0.0 \text{ V}_{\text{SCE}}\) with the most pronounced increase being at potentials near OCP.

- The corrosion rate measured via weight loss agreed most closely with the average AC current passed across the electrochemical interface and not with the average positive AC current. This was shown to be a result of several factors including a large capacitive current at 60 Hz and a relatively low reduction current limited by oxygen mass transport.

- Conceptually, AC induced corrosion can be thought of as a time-averaged DC polarization: the resulting currents being related to the Tafel slope of the material.

- A frequency of 60 Hz is close to the high frequency breakpoint for
electrochemical systems. As such it is in a critical frequency range as it relates to corrosion rate. Below the high frequency break point corrosion rates can vary widely depending on parameters such as interfacial capacitance and solution resistance. Above the high frequency breakpoint no change in corrosion rate with AC would be observed.
CHAPTER VI

PHASE II: INFLUENCE OF SOIL PROPERTIES ON AC CORROSION RATE

Pipeline corrosion in soil is an electrochemical process that is related to both the pipeline material and its surrounding soil environment. In other words, corrosion development of pipeline in soil depends on the metal/soil interface and local water chemistry. This process is controlled by the dynamics of moisture as well as the transport and migration of oxygen and other species through the soil (micro-environment parameters). Also macro-environment factors such as rain and temperature influence the soil properties and as a result corrosion rate. Romanoff, categorized these parameters to aeration, electrolyte type and electrical factors. Aeration factors include those that have influence on the oxygen moisture diffusion to the metal surface, such as moisture content, and the pore space of soils, i.e. particle size and its distribution. On the other hand, pH and concentration of soluble salts define the electrolyte properties. Romanoff indicated the soil resistivity as an indirect way to measure the soil concentration of dissolved salts. Similar parameters, including moisture content of the soil, dissolved salts, pH, presence of bacteria and oxygen concentration were repeatedly highlighted by other authors.

The electrolyte resistance is an important factor influencing AC corrosion behavior of metal that was shown in the proposed theoretical model for AC corrosion in
phase I (section 4.2). According to this model, higher solution resistance should result in lower corrosion rate. Also, another key parameter in controlling AC corrosion rate was related to the interfacial capacitance.

In this phase of the project, it was tried to investigate the influence of the soil properties such as soil resistivity and its ion content on corrosion behavior of X65 carbon steel in presence of AC. To do that, it was tried to accelerate corrosion rate with decreasing the soil resistance in extracted soil medium by adding salts and increasing its moisture content. Also, by growing artificial mineral scales including CaCO$_3$ and FeCO$_3$, which are directly correlated to the ion content of the soil, the influence of interfacial capacitance on corrosion rate was investigated. Although the investigation was started with extracted soil environment, it ended up using simulated soil solution. The reason for substitution of extracted soil with soil simulating solution was due to the complexity of the extracted soil which will be explained in section 8.1.

6.1 Influence of Soil Resistivity on Corrosion Behavior:

Soil resistivity in the close vicinity of the coating fault is controlled by different parameters such as moisture, soluble salts, the dynamics of moisture and also electrochemical process at the metal surface in CP condition which results in increase in the pH value. Generally, higher soil resistivity results in lower corrosion rate, unless the aeration status and microbiological activities of soils are different. Therefore, the main parameter to characterize soil aggressiveness could be the soil resistivity.\textsuperscript{60–70}
According to the Faraday’s law $i_{AC}$ at a coating defect depends on the alternating voltage and soil resistivity. As noted before on the famous German failure, there is a clear increase in AC corrosion risk with low soil resistivities.$^{34}$

6.1.1 Parameters Influencing the Soil Resistivity

Soil Moisture and Ionic Content

Normally, higher water content of the soil results in higher corrosion rate. The main influence of water is lowering the soil resistivity by solubilizing the salt and increasing the charge carriers.$^{65-70}$

Although increasing of the soil ion contents increases the soil conductivity, different ions have different influences on soil corrosion aggressiveness. By applying cathodic protection (CP) on the pipeline, CP current at coating holidays, results in water and oxygen reduction. As a result, soil pH in the vicinity of the metal increases. CP current transports anions in the soil away from the metal while the cations such as alkaline (calcium and magnesium) and earth alkaline (sodium and potassium) move toward the metal. The intensity of ionic migration and OH$^-\text{ production}$ are directly proportional to corrosion rate. This migration depends on the mobility and concentration of the ions. Table 5 Shows the equivalent conductivity $\Lambda \left(\Omega^{-1}\text{cm}^2\text{mol}^{-1}\right)$ as a measure of ionic mobility of several ions in soil.$^{71,72}$

While AC and CP potentials and soil resistivity are amongst the most important parameters controlling corrosion behavior of the pipeline, there are other variables that influence AC corrosion rate such as scale formation which is promoted by the deposition of minerals such as calcium carbonates and hydroxides.$^{11-28}$ Stalder proposed that the
chemical composition of the environment at the close vicinity of the coating fault is the most important parameter in assessment of AC corrosion rate.\textsuperscript{72}

Table 5. Conductivity of ions in soil.\textsuperscript{71}

<table>
<thead>
<tr>
<th>Cations</th>
<th>$\Lambda$ (\textOmega \text{cm}^2\text{mol}^{-1})</th>
<th>Anions</th>
<th>$\Lambda$ (\textOmega \text{cm}^2\text{mol}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}^+$</td>
<td>349.8</td>
<td>$\text{OH}^-$</td>
<td>197.6</td>
</tr>
<tr>
<td>$\text{Na}^+$</td>
<td>50.1</td>
<td>$\text{Cl}^-$</td>
<td>76.3</td>
</tr>
<tr>
<td>$\text{K}^+$</td>
<td>73.5</td>
<td>$\text{HCO}_3^-$</td>
<td>75</td>
</tr>
<tr>
<td>$\text{Mg}^{2+}$</td>
<td>53.1</td>
<td>$\text{SO}_4^{2-}$</td>
<td>80</td>
</tr>
<tr>
<td>$\text{Ca}^{2+}$</td>
<td>59.5</td>
<td>$\text{NO}_3^-$</td>
<td>71.4</td>
</tr>
</tbody>
</table>

Over time, due to the high pH value in CP condition and presence of cations in the vicinity of the coating fault, alkaline and earth alkaline hydroxides and carbonates might be formed. Earth alkaline cations form a relatively weak dissoluble precipitate on the metal surface while alkaline cations produce highly dissolvable hydroxides. Therefore depending on the ratio between alkaline and earth alkaline cations either high conductivity soil in the vicinity of the metal or low conductivity precipitate on it might be formed which has a direct influence on corrosion rate.\textsuperscript{71,72} Stalder studied the influence of different concentration ratios of earth-alkaline cations (as $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$) to alkaline cations (as $\text{Na}^+$ and $\text{K}^+$) in soil on AC corrosion rate. He stated that, earth-alkaline solid deposits with low solubility lower AC magnitude at the coating holidays or in other words lower AC corrosion rate. He also noted the passivity effect of earth-alkaline cations also decreases the anodic dissolution. On the other hand, hydroxides and carbonates of alkaline cations are soluble and also, they are hygroscopic, i.e. they attract
water. These precipitate accumulate in front of the coating fault and increase the electrical conductivity of the soil which results in higher AC corrosion rate. In the presence of both earth-alkaline and alkaline cations in soil, two reactions (earth-alkaline hydroxide formation and alkaline hydroxide formation) compete with each other and there would be simultaneous insoluble layer build up and conductivity increase in front of the metal. Figure 24 shows the schematic of the proposed model by Stalder that describes the regions in front of a fault location that reactions may take place.\textsuperscript{72}

![Figure 24. Conceptual model of the pH value distribution and possible reaction regions at a fault location.\textsuperscript{72}](image)

In this report the reason of decreasing of corrosion rate due to the scale formation was related to the scale resistance and changes in interfacial capacitance value. As it relates to pipelines, it has been observed on in-service pipelines exposed to AC that the corrosion rate is initially very fast. However, at longer times the rate slows. We proposed that this phenomenon is also the result of scale formation at the metal/soil interface. This will be discussed further in detailed in section 8.5.
6.2 Calcareous Deposits

The first application of the cathodic protection is back in 1824 that was applied by Sir Humphry Davy. His research was the very first study on the CP field that was financed by the British Navy and led to the corrosion protection of the warships with small portion of cast iron in contact with the copper sheeting of the sheep. During his research, he noticed a white layer coating on the copper cathode which was proved to be carbonated lime and carbonate and hydrate of magnesia.

Cathodic protection potentials (-0.85 and lower \( V_{\text{CSE}} \)), depending on the chemistry of the soil in the vicinity of the pipeline, result in occurrence of chemical and electrochemical reactions on the surface of the protected pipeline. In this potential range, there are three different reduction reactions that produce hydroxyl ions (OH\(^-\)). Dissolved oxygen in soil moisture is reduced according to the following reactions:

\[
O_2 + 2H_2O + 2e^- \rightarrow H_2O_2 + 2OH^- \quad (1)
\]

\[
H_2O_2 + 2e^- \rightarrow 2OH^- \quad (2)
\]

and at higher potentials they are followed by the Hydrogen evolution:

\[
2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad (3)
\]

The production of these hydroxyl ions makes the pH difference between the electrode/solution interface and the bulk of the solution. The value of the interfacial pH is determined by the production/removal rate of hydroxyl ions due to the diffusion and/or convection to and from the metal interface which is shown schematically in Figure 25. The amount of the interfacial pH (OH\(^-\) concentration) is a function of the applied CP potential or current. Also, Fu et al. reported that other than applied CP, AC interference
would increase the alkalinity of the soil environment. The level of alkalization depends on the value of AC current density.\textsuperscript{24}

![Schematic of the pH profile in the electrolyte adjacent to a cathodically protected metal surface.](image)

Engell and Forchhammer used a theoretical procedure and calculated a pH of 10.9 on the surface of the metal in seawater in CP condition.\textsuperscript{77} In another work by Wolfson and Hartt the pH values ranging from 10.75 to 11.25 was calculated.\textsuperscript{78} Deslouis et al. also derived an equation to calculate the interfacial pH value. In order to study the influence of the electrochemical /chemical coupled reactions on the interfacial pH, they considered two cases with and without chemical reaction which consumes hydroxyl ions. In a specific condition their equation completely agreed with the work of Engell and Forchhammer. They also directly measured the interfacial pH values on the surface of the mesh gold grid in K\textsubscript{2}SO\textsubscript{4} solution with and without carbonate ions and found a good
agreement between the experimental data and their theoretical calculations.\textsuperscript{79} Also, in another work of Deslouis and collaborators, the interfacial pH at different applied cathodic potentials was obtained experimentally and shown in Figure 26. This experiment was performed on a mesh gold grid immersed in the ASTM D1141 artificial seawater without MgCl\textsubscript{2} salt.\textsuperscript{76}

![Figure 26: Interfacial pH-potential curves for cathodic reactions with different Reynolds number in artificial seawater without Mg salt.\textsuperscript{76}](image)

The two plateaus on this graph were correlated to the electrochemical reaction (1) (with 2 exchanged electrons) and reaction (2) (with 4 exchanged electrons) respectively.

Production of hydroxyl ions on the surface of the pipeline by the electrochemical reactions, increase of the interfacial pH, leads into chemical reactions and produce soluble or insoluble species, which in the presence of earth alkaline cations like calcium and magnesium forms hydroxides (Ca(OH)\textsubscript{2}, Mg(OH)\textsubscript{2}):
Also, when there is a high carbonate content soil in the vicinity of the pipeline, according to reactions (6) and (7), hydroxyl ions reacts with carbonate hydroxides and lead into the formation of calcareous layer on the metallic surface. These reactions are:

\[
\text{OH}^- + \text{HCO}_3^- \rightarrow \text{H}_2\text{O} + \text{CO}_3^{2-}
\]  

That allows CaCO\textsubscript{3} precipitation:

\[
\text{Ca}^{2+} + \text{CO}_3^{2-} \rightarrow \text{CaCO}_3
\]

When iron metal is not completely cathodically protected, other than reduction reactions that increase the pH value, another electrochemical reaction (corrosion of iron, reaction (8)) followed by chemical reaction (formation of iron hydroxide, reaction (9)) would happen:

\[
\text{Fe} \rightarrow \text{Fe}^{3+} + 3e^-
\]

\[
\text{Fe}^{3+} + 3\text{OH}^- \rightarrow \text{Fe(OH)}_3
\]

According to literature and also theoretical calculations, calcium carbonate precipitates at a lower pH compared with magnesium hydroxide precipitation. Also, Fe(OH)\textsubscript{3} precipitates at a significantly lower pH compared to that of CaCO\textsubscript{3}. Engell and Forchhammer calculated the minimum pH of 9.7 and 7.27 for precipitation of Mg(OH) and CaCO\textsubscript{3} respectively. Also, Barchiche et al. reported a minimum pH of 9.3 for Mg(OH)\textsubscript{2} deposition. Yang performed titration experiments to measure the pH values for formation of CaCO\textsubscript{3}, Mg(OH)\textsubscript{2} and Fe(OH)\textsubscript{3}. In her experiments, she used MgCl\textsubscript{2} (0.05 M) and FeCl\textsubscript{3} (0.01 M) solutions and titrated them
both individually and together with 0.01 M, Na(OH) solution. She also did the titration experiment on 0.01M \( \text{FeCl}_3 \) combined with seawater solution with 0.01 M, Na(OH) solution (Figure 27). She showed that the pH of 2.9, 7.58 and 10 are required for precipitation of \( \text{Fe(OH)}_3 \), \( \text{CaCO}_3 \) and \( \text{Mg(OH)}_2 \) respectively in seawater. \(^8\)

![Figure 27: pH titration curves of both (FeCl\(_3\)) and (MgCl\(_2\)) with 0.01M sodium hydroxide (NaOH) solution.\(^8\)](image)

6.2.1 Influence of Calcareous Deposits on Cathodic Protection and DC Corrosion Rate

Both carbonates and hydroxides of earth alkaline cations are insoluble.\(^28\) The formation of calcareous deposits on the surface of the cathodic protected metal is known to enhance the oxygen concentration polarization and reduce the CP current required in long term which improves the CP protection. Calcareous precipitation is more considered in offshore cathodic protection system designing due to the high concentration of earth alkaline cations in marine environment. Figure 28 shows a schematic representation of the time dependency of the polarization curve for carbon steel in seawater. It can be seen
from this figure that the extreme right of the cathodic branch of the curve represents polarisation of the initial clean bare steel surface, which needs high CP current to be protected. By passing time and nucleation and growth of the calcareous deposits, lower CP current density is required for protection.

Figure 28: Schematic of the time dependency of the polarization curve for carbon steel in seawater.\textsuperscript{83}

In another work by Mantel et al. it was shown that the CP current requirement in seawater has a sigmoidal pattern with time (Figure 29). The higher plateau in Figure 29 was related to the initial times of immersion (about 50 hours) that followed by lower current values by passing time.\textsuperscript{84} The influence of the formation of the calcareous layer on required CP current resulted in the consideration of three different CP current densities for offshore structures and pipelines. Those include: high initial current density (for formation of a calcareous layer), mean current density (for long term protection under stable condition) and final current density (for possible depolarization of the
substrate due to the damage of calcareous layer) which will occurred in this order over time.\textsuperscript{83}

![Figure 29. CP current density vs time for A710/no. 600 steel at \(-900\) mV CP potential in seawater at a flow rate of 100 mL/min.\textsuperscript{84}]

There are some general agreements on the way that the calcareous layer deposits provide protection against corrosion. The corrosion prevention mechanism is shown in the schematic diagram in Figure 30. As shown in this figure, CaCO\textsubscript{3} layer act as a physical barrier against oxygen diffusion, which at the constant potential decreases the current (similar to increase of the resistance of the system). Also poor electronic and ionic conductivity of this layer, suppresses oxygen reduction reaction on the outer surface. This scale deposit even might increase the pH of the water film in contact with the metal surface due to accumulation of hydroxyl ions and provide passivation.\textsuperscript{80,82}
6.2.2 Influence of Calcareous Deposits on AC Corrosion Rate

Stadler et al. studied the influence of the formation of the calcareous layer at CP condition in soil on AC corrosion rate. They stated that when chalk layer partially covers the surface of the metal due to the decrease of the surface area of the sample, there is an increase in the local current density on the sample. As a result it seems that even at lower AC current densities than criterion of 30 A.m$^{-2}$, AC corrosion still might occur.\(^{28}\) As discussed before, Stalder et al. proposed a mechanism for AC corrosion that is based on the chemistry of the soil and consequently the scale that forms on the steel-soil interface. He stated that by formation of calcareous layer on the metal surface, lower AC current would reach to the coating defect and AC corrosion rate decreases.\(^{72}\)

In another work by Lilleby, it was shown that at constant applied AC potential on carbon steel under CP protection in sea solution, AC current decreased by passing time.
She correlated this observation to the formation of calcareous layer on carbon steel that was detected by microscope after the experiment. She showed that the decrease of CP current had similar trend of decrease of AC current which indicated the same influence of calcareous layer on both AC and DC current.\textsuperscript{85}

In this work, by producing artificial CaCO\textsubscript{3} layer on X65 pipeline steel, it is tried to shed light on the behavior of the scale formation on the AC corrosion rate.

6.3 Iron Carbonate Deposits

Presence of CO\textsubscript{2} and its dissolution in soil water results in the soil acidification. This environment is very corrosive to carbon and low alloy steel pipes. Human sources and decomposition of organic matters in soil are two frequent sources of CO\textsubscript{2}.\textsuperscript{86} CO\textsubscript{2} corrosion is an electrochemical process with the overall reaction of:

\[ \text{Fe} + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{FeCO}_3 + \text{H}_2 \] (10)

The formation of iron carbonate scale due to its low solubility, depending on CO\textsubscript{2} corrosion condition and different environmental parameters such as pH, pressure, steel composition and temperature can be protective or nonprotective.

There have been extensive works investigating the mechanism of dissolution of iron in aqueous, deaerated CO\textsubscript{2} solutions.\textsuperscript{87–107} However, the main corrosion mechanism includes anodic dissolution of iron and three cathodic reactions.

The aim of the present work is to study the influence of the formation of protective FeCO\textsubscript{3} layer on X65 carbon steel on its corrosion behavior in presence of AC potentials. In the following sections, the mechanism of CO\textsubscript{2} corrosion and different parameters that influence the formation of protective FeCO\textsubscript{3} scale will be discussed.
6.3.1 Mechanism of CO₂ Corrosion

By dissolution of CO₂ in water according to reaction (11) and by hydration of aqueous carbon dioxide, carbonic acid would be formed, which in alkaline pH values dissociates into bicarbonate ions (reaction [12]). In higher pH values, it further dissociates and releases carbonate ions to the environment (reaction [13]).

\[
\begin{align*}
\text{CO}_2 + \text{H}_2\text{O} & \rightarrow \text{H}_2\text{CO}_3 \quad (11) \\
\text{H}_2\text{CO}_3 & \rightarrow \text{H}^+ + \text{HCO}_3^- \quad (12) \\
\text{HCO}_3^- & \rightarrow \text{H}^+ + \text{CO}_3^{2-} \quad (13)
\end{align*}
\]

**Anodic reaction**

The overall anodic dissolution reaction of iron in acidic solution is:

\[
\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^- \quad (14)
\]

In order to interpret the experimental results of CO₂ corrosion of iron, several multi-step mechanisms of reaction (14) were proposed. These multi-step reactions are pH dependent with decreasing reaction order toward 1 and 0 at pH>4.\textsuperscript{103}

The BDD model has been frequently used by other authors. This model presents the dissolution of iron in strong acid as the following multi-steps reactions\textsuperscript{103,108}:

\[
\begin{align*}
\text{Fe} + \text{H}_2\text{O} & \leftrightarrow \text{FeOH}^{+}_{\text{ads}} + \text{H}^+ + \text{e}^- \quad (15) \\
\text{FeOH}^{+}_{\text{ads}} & \rightarrow \text{FeOOH}^{+}_{\text{sol}} + \text{e}^- \quad (16) \\
\text{FeOOH}^{+}_{\text{sol}} + \text{H}^+ & \rightarrow \text{Fe}^{2+}_{\text{sol}} + \text{H}_2\text{O} \quad (17)
\end{align*}
\]

**Cathodic reactions**

According to reactions (12) \& (13), dissolved CO₂ in aqueous solution, increases H⁺ concentration and as a result increases the corrosion rate. Influence of CO₂ on
corrosion rate of iron is more destructive than a strong acid. Corrosion rate in a strong acid that is completely dissociated is limited to the mass transfer of H\(^+\) ions. However the presence of H\(_2\)CO\(_3\) leads to higher hydrogen evolution rate.\(^{103}\)

The cathodic reactions in CO\(_2\) corrosion include carbonic acid reduction (reactions [12] & [13]), proton reduction and water reduction as follows:

\[
\begin{align*}
H^+ + 2e^- &\rightarrow H_2(g) \quad (18) \\
2H_2O(l) + 2e^- &\rightarrow H_2(g) + 2OH^- (aq) \quad (19)
\end{align*}
\]

According to Gray et al. at high pH values due to the increasing of bicarbonate concentration, the dominant cathodic reaction would be carbonic acid reduction.\(^{109}\)

6.3.2 Influence of FeCO\(_3\) Scale Formation on Corrosion Rate

Iron carbonate is the most common type of scale in CO\(_2\) corrosion that could form due to the following reactions:

\[
\begin{align*}
Fe^{2+} + CO_3^{2-} &\rightarrow FeCO_3 \quad (20) \\
Fe + HCO_3^- + e &\rightarrow FeCO_3 + H \quad (21)
\end{align*}
\]

By increase in Fe\(^{2+}\) concentration due to the iron dissolution, the supersaturation (SS) of FeCO\(_3\) according to the Equation (17) increases.\(^{110}\)

\[
SS = \frac{[Fe^{2+}][CO_3^{2-}]}{K_{sp}} \quad (17)
\]

where, Ksp is the solubility product of FeCO\(_3\)

As soon as the SS value becomes higher than one, FeCO\(_3\) precipitation on the electrode surface begins that leads to the protection of the surface.

FeCO\(_3\) acts as a diffusion barrier for corrosion species and also covers a portion of the active area. Therefore it inhibits both cathodic and anodic processes and decreases the
corrosion rate. By continuous dissolution of the steel surface beneath the FeCO₃, it weakens the upper scale and creates voids that would be filled by the ongoing precipitation. If the precipitation rate of FeCO₃ overcomes the corrosion rate, a dense protective scale as thin as 1µm could be formed. However, there could be very thick (100µm) nonprotective scale due to the higher corrosion rate compared to the filling rate of the voids by FeCO₃ particles. It’s believed that the crystal growth rate controls the precipitation rate more than the nucleation rate. However, lower nucleation rate leads to a porous and loose scale. Therefore, lower nucleation period of FeCO₃ (higher nucleation rate) results in more compact FeCO₃ layer.

The precipitation rate of iron carbonate depends on different parameters such as temperature, pH and the water chemistry which is the most important factor. As mentioned before, as soon as supersaturation of FeCO₃ exceeds one precipitation begins. However, at room temperature even with SS>>1, due to the low precipitation rate, unprotective FeCO₃ would be formed. While at higher temperature with low SS, rapid precipitation rate and as a result, a very dense and protective scale was observed.

Influence of pH on FeCO₃ Scale formation

It’s been reported that the pH value has a strong influence on corrosion rate. At pH values lower than 4, according to the reaction (18), pH has a direct influence on the cathodic reaction in CO₂ corrosion. However, the main effect of pH on corrosion rate is indirect and is related to its influence on solubility and supersaturation of FeCO₃. High pH values decrease the solubility of FeCO₃ and result in higher precipitation rate and formation of protective scale. This reflects in rapid decrease in corrosion rate over time. Figure 31 shows the dependency of FeCO₃ solubility on pH and iron ion
contents, calculated by Li et al. This figure shows supersaturated and undersaturated regions separated by two dashed lines. As discussed, in supersaturated region, FeCO$_3$ layer is expected to precipitate while in undersaturated region the dissolution rate of it is faster than its precipitation rate and FeCO$_3$ cannot form or remain.

![Figure 31. Dependency of FeCO$_3$ solubility on C$_{Fe^{2+}}$ and pH in 1 wt% NaCl at 80°C and pCO$_2$ of 0.53 bar.](image)

Gulbrandsen, et al. reported a dramatic decrease in corrosion rate along with a significant increase in OCP in pH values higher than 7. Similarly, Han et al. observed that at high pH values (pH>6.6), the FeCO$_3$ fully covered the metal surface while there was a reduction in corrosion rate that was accompanied by an increase in the corrosion potential that they referred to as self-passivation. Figure 32 shows the experimental results obtained by Han et al.. This figure shows the influence of the pH value on the self-passivation of the steel. It can be seen that the increase in pH from 7.1 to 8 results in a decrease in the self-passivation time and as a result increase in precipitation rate of
protective FeCO₃. Li et al. also proposed a bulk pH threshold for getting a protective FeCO₃ layer that depends on CO₂ partial pressure and temperature. They suggested the pH threshold of 6 in 1 wt% NaCl at 80°C and PCO₂ of 0.53 bar. Figure shows

![Figure 32.Influence of pH on the self-passivation of C1018 steel in 1%wt NaCl at T=80°C and PCO₂=0.53 bar.]

Therefore in this study, in order to obtain a protective FeCO₃ scale, the pH value of 7.2 was considered.

Influence of CO₂ Partial Pressure on FeCO₃ Scale formation

Increase in CO₂ partial pressure (PCO₂) according to reactions (12) and (13) accelerates the cathodic reaction that leads to increase in corrosion rate. However, at higher pH values, higher PCO₂ results in higher superSaturation of FeCO₃ due to the increase in bicarbonate and carbonate ion concentration. Han et al. studied the influence of PCO₂ on the precipitation of FeCO₃. They claimed that the self-passivation
could be only achieved in the presence of CO$_2$ atmosphere. Also, precipitation rate of FeCO$_3$ at high pH value of 8 by increasing of PCO$_2$, increases(Figure 33).^97

![Figure 33. Influence of PCO2 on the self-passivation of C1018 steel in 1%wt NaCl at T=80°C and pH=8.](image)

Therefore in this work, by continuous purging of CO$_2$ during the experiment, it was tried to keep the PCO$_2$ value constant at 0.53 bar at 80°C.

**Influence of Temperature on FeCO$_3$ Scale formation**

Like PCO$_2$, increasing of temperature accelerates the corrosion rate but when other conditions for formation of iron carbonate scales are favorable i.e. high pH value, high temperature results in rapid increase of precipitation kinetic and protective FeCO$_3$ formation. The temperature between 60°C and 80°C has been reported as an optimum temperature for obtaining protective scale depending on water chemistry and flow condition. ^103 Hen at al. also studied the influence of temperature on self-passivation of the steel and FeCO$_3$ precipitation rate (Figure 34). Figure 34 shows that at the same high
pH value of 7.5, the time to reach self-passivation is shorter for higher temperature (80°C) due the higher kinetics.\textsuperscript{97}

Figure 34. Influence of temperature on the self-passivation of C1018 steel in 1%wt NaCl at pH=7.5 and PCO2=0.53 bar.\textsuperscript{97}

In order to facilitate the faster formation of a protective FeCO\textsubscript{3} layer on X65 carbon steel, 80°C was selected as a test temperature.
CHAPTER VII

PHASE II: EXPERIMENTAL PROCEDURES AND TECHNIQUES

This section reviews procedures that were taken to investigate the influence of soil properties such as soil resistivity and its ionic contents on the corrosivity of the soil in presence of AC interference that is divided into four major parts. In the first part, experimental techniques that were performed in extracted soil from a field in Ohio State will be explained. Second part covers AC corrosion propagation tests in soil simulant solution (NS4) which is based on the chemical analysis of the Ohio soil. Finally last two parts contain applied methods to develop pregrown mineral scales, CaCO$_3$ and FeCO$_3$ respectively, on X65 carbon steel coupons.

7.1 AC Corrosion in Extracted Soil Environment

Electrochemical cell used in this part was a 20 L plastic box with 24 cm width, 31 cm length and 27 cm depth. All tests were performed in a three electrode electrochemical set up. Wherein similar sample used in NaCl solution as explained in section 3.1, a rectangular cuboid cut X65 carbon steel (15x12x5 mm), as a WE and a copper-copper sulfate electrode (CSE) as a RE were buried. Also a piece of 316 stainless steel mesh that placed at the bottom of the soil box (31x24 cm) was used as a CE.
7.1.1 Soil Resistivity Measurement

The soil studied in this project was extracted from a field in Ohio with lumpy and rather hard clay structure. The initial water content, pH and composition of the soil are shown in Table 6. These analysis were performed according to relevant standards, namely EPA 9056A for determination of inorganic anions such as SO$_4^{2-}$, NO$_3^-$ and Cl$^-$, EPA6010C for cation contents in aqueous extracted such as Ca$^{2+}$, Mg$^{2+}$, K$^+$ and Na$^+$ and finally for determination of pH the EPA9040C was used.

All tests were conducted at ambient temperature (22 °C). In order to keep the water content of the soil constant, the soil box was completely sealed during the experiments.

More homogeneous soil medium was obtained by subsequent preparation steps included grinding and sieving up to 2mm mesh screen size (Figure 35 [a] & [b] respectively). In order to investigate the importance of the presence of ionic particles and moisture content on the soil resistivity, NaCl solution (30g/L and 70 g/L) with different amount of deionized water with 18.2 MΩ.cm resistivity (10, 15, 20 and 25wt% water) were slowly and gradually sprayed and mixed with the soil (Figure 35 [c]). Finally, due to the importance of pore space of soil, the prepared soil was hammer-packed into the soil box with a moderate amount of compression (Figure 35 [d]). This was done by a manual soil compactor with 2.5kg weight dropped from a height of 305mm. Attempts to measure the soil resistance between WE and RE electrode were made by EIS spectrum and finding the impedance down to 10000Hz. EIS measurements were performed within a frequency range between 10000 Hz and 0.01 Hz with 10mV fluctuation around corrosion potential.
Table 6. Chemical composition and characteristic of the extracted soil.

<table>
<thead>
<tr>
<th>pH</th>
<th>Water content (wt%)</th>
<th>Cl(^-) (mg/kg)</th>
<th>NO(_3)(^-) (mg/kg)</th>
<th>SO(_4)(^{2-}) (mg/kg)</th>
<th>Ca(^{2+}) (mg/L)</th>
<th>Mg(^{2+}) (mg/L)</th>
<th>K(^+) (mg/L)</th>
<th>Na(^+) (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>2.5</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1.4</td>
<td>8.7</td>
<td>2.1</td>
<td>10</td>
<td>25</td>
</tr>
</tbody>
</table>

Figure 35. Soil preparation steps: a) grinding, b) sieving, c) homogenizing and mixing with water and salt and d) compacting in the soil box.

7.1.2 AC corrosion Initiation Tests in Extracted Soil Environment

To study the influence of the presence and formation of earth alkaline hydroxide scales on AC corrosion behavior of X65 carbon steel, a set of experiments in 15wt%
water content soil with added 0.84 g. L$^{-1}$ CaCl$_2$.2H$_2$O and 2.34 g. L$^{-1}$ MgSO$_4$.7H$_2$O, due to the low amount of earth alkaline ions content in the extracted soil (Table 6), were conducted.

For convenience, only about 1 liter of the soil surrounding the sample and reference electrode was mixed with earth alkaline salts. Finally, the combination of salt mixed soil, WE and RE were put in the soil box and filled with the same water content soil. AC experiments were performed at CP potential of $-0.85V_{CSE}$ with different AC amplitude (0.6, 1, 2, 3, 4, 5, 6, 7, 8, 9 V) at 60 Hz between WE and RE.

7.2 AC Corrosion in Simulated Soil Environment

Soil simulant solution (NS4) was substituted for extracted soil medium due to the difficulties encountered with during running experiments in extracted soil environment that will be explained in section 8.1,. The composition of NS4 solution is brought into Table 7.

7.2.1 Materials and Electrochemical Set Up

NS4 solution was made from analytic grade reagents (Table 7) mixed with 18.2 MΩ.cm deionized water. The electrochemical cell contained 300mL solution with X65 carbon steel as WE, a SCE as RE and a graphite rod as CE. Prior to the experiments, by dropwise addition of 0.1M sodium hydroxide solution, pH of the solution was adjusted to 8.2. Experiments conducted at ambient temperature (22 °C) and open to air while solution was stirred at 60 rpm. Due to the lower corrosion rate in NS4 solution compared to NaCl medium (will be shown in section 8.2.2), replacement of solution which was
performed for NaCl environment, was not done for NS4. Prior to the experiments, samples were left at OCP for 24 hours to reach the steady state.

Table 7: Composition of simulated soil solution.\textsuperscript{112}

<table>
<thead>
<tr>
<th>Reagents (g/L)</th>
<th>KCl</th>
<th>NaHCO\textsubscript{3}</th>
<th>CaCl\textsubscript{2}.2H\textsubscript{2}O</th>
<th>MgSO\textsubscript{4}.7H\textsubscript{2}O</th>
</tr>
</thead>
<tbody>
<tr>
<td>NS4</td>
<td>0.122</td>
<td>0.483</td>
<td>0.181</td>
<td>0.131</td>
</tr>
</tbody>
</table>

7.2.2 AC Corrosion Prorogation Tests in Simulated Soil Environment

Potentiostatic Tests

Similar to the experiments performed in NaCl solution (section 3.3), in NS4 electrolyte, potentiostatic tests at DC potentials of -720, -700, -670, -600, -500, -440 and 0 mV vs. SCE with 600 mV AC RMS at 60 Hz were conducted. Moreover, to study the influence of CP potentials on AC corrosion rate, another set of experiments at cathodic potentials (-670, -700, -780 and -1\textsubscript{V SCE}) with higher AC RMS values of 3 and 4.2 V were performed. During the experiment, the current-time and potential-time response under various DC and AC potentials were recorded with an acquisition rate of 250 points per second and were regularly monitored with an oscilloscope. Also, prior to AC experiments, in order to monitor the solution resistance value, EIS spectroscopy at OCP was employed in which the frequency scan was taken from 100 kHz down to 0.01 Hz with 10 mV AC amplitude.
Mass Loss Analysis

To calculate the corrosion rate of samples under influence of AC interference after potentiostatic tests, weight loss analyses with Clark solution were carried out. This was done similar to the procedure used in NaCl solution explained in section 3.4. Depending on anticipated weight loss, immersion time varied from 7 days to 30 days for higher DC potentials and lower cathodic DC potentials respectively.

7.3 CaCO₃ Scale Formation

Calcium carbonate films were deposited and grown on the X65 carbon steel samples using artificial sea solution to simulate mineral scales that might deposit on the surface of the steel in Ca rich content soils during long term exposure to CP. Ultimately, the AC corrosion behavior of prescaled samples were investigated in NS4 solution.

7.3.1 Materials

In this part of the project, to grow a homogenous scale on the surface of X65 carbon steel, the steel coupons were cut into 16x9 cylinder samples with a tapped hole in one end for electrical connection via a threaded rod. Similar to previous experiments in this work, samples were ground with SiC papers, starting from 120 to 600 grit and rinsed with acetone, ethanol and distilled water, sequentially.

7.3.2 Testing Solution

Calcareous precipitation was performed in 500 mL artificial sea solution without magnesium ions due to its inhibition role on the deposition of CaCO₃ layer. Given the fact that the magnesium carbonate layer is much more soluble than the calcium carbonate
layer (having solubility of 1.79 and 0.014 g.L\(^{-1}\) in water respectively)\(^{113}\), in this project it was preferred to produce calcareous layer without magnesium carbonate formation. The concentration of the artificial sea solution was based on the ASTM norm D1141 (American Society of Testing Materials) which is shown in Table 8.\(^{114}\) The solution was made from analytic grade reagents (Table 8) and 18.2 MΩ.cm deionized water. Prior to CaCO\(_3\) deposition the pH of the solution was adjusted to 8.2 with 0.1 M NaOH solution. The pH variation during the experiment was small and as reported by other authors it has a negligible influence on the value of the interfacial pH and as a result on calcareous deposition rate.\(^{80}\) Deposition process was performed at ambient temperature (22 °C) and open to air.

<table>
<thead>
<tr>
<th>Composition</th>
<th>g/L</th>
<th>Composition</th>
<th>g/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>24.53</td>
<td>NaHCO(_3)</td>
<td>0.201</td>
</tr>
<tr>
<td>MgCl(_2)</td>
<td>5.2</td>
<td>KBr</td>
<td>0.101</td>
</tr>
<tr>
<td>Na(_2)SO(_4)</td>
<td>4.09</td>
<td>H(_3)BO(_3)</td>
<td>0.027</td>
</tr>
<tr>
<td>CaCl(_2)</td>
<td>1.16</td>
<td>SrCl(_2)</td>
<td>0.025</td>
</tr>
<tr>
<td>KCl</td>
<td>0.695</td>
<td>NaF</td>
<td>0.003</td>
</tr>
</tbody>
</table>

7.3.3 Electrochemical Set-up

CaCO\(_3\) Precipitation

Electrochemical experiments for formation of CaCO\(_3\) layer were performed in a three electrode setup with X65 as WE, SCE as RE and a platinum mesh as a CE. Calcareous
layers were grown potentiostatically at DC potentials of $-0.8 \text{ V}_{\text{SCE}}$ and $-1 \text{ V}_{\text{SCE}}$, using a Solartron Modulab potentiostat with rotating cylinder electrode. Also, in-situ EIS measurements during precipitation of calcareous layer at different time intervals were carried out. Also, to study the influence of the rotation speed on precipitation of CaCO$_3$, electrodeposition experiments at different revolution per second (rpm) of 120, 200, 400, 600 and 1200 (12.5, 20.9, 41.8, 62.8 and 125.6 radiance per second respectively) were monitored. Figure 36 shows the experimental setup for CaCO$_3$ deposition.

![Experimental setup for CaCO$_3$ deposition](image)

Figure 36: Electrochemical set up for precipitation of calcareous layer.
AC Experiments

The effect of CaCO\textsubscript{3} as an artificial scale on AC corrosion behavior of X65 was investigated by performing potentiostatic tests in presence of 3V RMS AC potential at 60 Hz. The studies were conducted in NS4 solutions at DC potentials of -770, -700, -650 and -600 mV vs. SCE with similar condition as explained in section 7.2.2 and EIS analysis prior to AC experiments.

7.3.4 Surface Analysis

To visualize the morphology, grain size, porosity and composition of the layer formed on the X65 carbon steel, Scanning Electron Microscopy (SEM) and Focused Ion Beam (FIB) using LYRA 3 XMO SEM instrument were applied to the samples after electrochemical deposition in seawater simulant solution. Prior to SEM and FIB analysis, to minimize the charging effect of the calcareous layer due to its non-conductive properties, 10nm platinum layer was sputtered on the samples. Also, to ensure the structure and phase of the deposited layer, XRD analysis using the Rigaku Ultima IV X-ray diffractometer Cu K-\(\alpha\) radiation at 40kV and 35mA in 2\(\theta\) angle range of 5\(^\circ\)-70\(^\circ\) was performed.

7.4 FeCO\textsubscript{3} Scale Formation

In this part, iron carbonate layers on X65 carbon steel in CO\textsubscript{2} atmosphere were precipitated and further studied in presence of AC in NS4 solution. This was done to replicate scale forms on pipeline steels in high carbonate content soils and investigate its influence on corrosion rate.
7.4.1 Materials

Samples investigated in this work were similar to those used in CaCO$_3$ deposition, a cylindrical cut API grade X65 pipe steel specimen as a WE in three electrodes conventional electrochemical cell. Samples were wet-ground to a 600 grit surface finish with SiC sand paper and rinsed with acetone, ethanol and distilled water, sequentially, after which the electrodes were immediately placed into the 300 mL electrochemical cell.

7.4.2 Testing Solution

Iron carbonate films were precipitated on X65 carbon steel specimens in 10%wt NaCl solution with CO$_2$ atmosphere. The solution was made from analytic grade reagent and 18.2 MΩ.cm deionized water.

In order to facilitate a faster formation of a compact and protective FeCO$_3$ layer on the X65 carbon steel, pH value of 7.2 and high solution temperature of 80°C were applied. Also, to have a well-mixed electrolyte, solution was stirred at 120 rpm. The FeCO$_3$ deposition process was conducted at atmospheric pressure. To expel oxygen from the system, at least three hours prior the experiment, the cell solution was purged with high purity CO$_2$ gas with partial pressure (PCO$_2$) of 0.53 bar. CO$_2$ purging of the cell continued throughout the experiment to avoid possible contamination of the electrolyte with oxygen. After about one hour of deaeration and obtaining the required temperature, the bulk pH was adjusted to 7.2 using sodium bicarbonate salt (NaHCO$_3$) or diluted hydrochloric acid (HCl) solution (0.1 M) as required. The pH was monitored during the entire test and had a small variation.
7.4.3 Electrochemical Set-up

FeCO3 Precipitation

For precipitation of FeCO₃ on the surface of X65 carbon steel, specimens were immersed in solution in the absence of any external polarization (OCP) for 20 hours. During the exposure, the potential of the sample using a Solartron Modulab potentiostat was monitored. Also, in-situ EIS measurements during precipitation of FeCO₃ layer at different time intervals were carried out. Figure 37 shows a schematic of the three electrodes experimental set-up with X65 carbon steel as WE, SCE as RE, kept in a Luggin capillary for cross-contamination prevention, and a platinum mesh as a CE.

![Figure 37. Schematic of the electrochemical set up for FeCO₃ formation.](image)

AC Experiments

After 20 hours of FeCO₃ deposition, for preventing the oxidation of the high temperature wet samples in contact with the air, samples were immediately flushed with ethanol to be dehydrated and cooled from 80 °C to room temperature.
Similar to X65/CaCO\textsubscript{3} samples, for AC corrosion analysis, coupons with FeCO\textsubscript{3} layer (X65/FeCO\textsubscript{3}) were investigated in NS4 solution that followed by EIS analysis, all performed prior to AC studies. AC corrosion experiments were performed using potentiostatic tests at DC biases of -770, -700, -650 and -600 mV vs. SCE with 3V RMS AC at 60Hz with the experimental condition that was explained in section 7.2.2.

7.4.4 Surface Analysis

Iron carbonate artificial scale formed on X65 carbon steel after different exposure time in NaCl solution were studied with SEM, FIB and XRD characterization techniques.
CHAPTER VIII

PHASE II: RESULTS AND DISCUSSION

8.1 Electrochemical Experiments on API X65 Carbon Steel in Soil Extracted

This section covers the experimental results and analyses of the corrosion behavior of API X65 carbon steel in soil environment.

8.1.1 Parameters Influencing the Soil Resistivity

Current does not flow just between the two plates placed in soil. It also passes from different paths within the soil medium surrounding the electrodes.” Therefore, if two plates are put in a certain amount of soil, it is expected that the volume of the soil would influence on its resistivity. In order to obtain the optimum soil amount for study in the lab, a series of EIS experiments at the fixed distance between WE and RE at different soil volume were conducted. This was done by gradually increasing of the distance between two partitions in the soil box and filling the gap between them with soil (Figure 38). The soil resistance values were obtained from the real part of the Nyquist plot at high frequency (10^4 Hz).

Figure 39 shows the soil resistance as a function of its volume. This graph shows that the soil resistance depends on the soil box size and increasing the soil volume decreases the soil resistance values.
Ferreira et al. also reported that the soil resistivity in the field was different with that in the laboratory and as a result the electrochemical parameters obtained in the lab were different from the field test results.\textsuperscript{115}

Figure 38. Influence of the soil volume on the soil resistance.

Figure 39. Influence of soil volume on its resistance.
However the maximum soil box that could be used in our laboratory was limited to 20 L soil. Therefore, accelerating corrosion in the laboratory due to the high ohmic drop between WE and RE would be challenging and high soil resistivity is a problem for small volumes of soil used in the laboratory.

Figure 40 shows the influence of soil water content and ions in the soil resistance between WE and RE. This figure shows that the soil resistance decreases with increasing the ionic content of the soil. There is also a decreasing trend in the soil resistance values by increasing the moisture of the soil. As discussed in section 6.1 this is due to the increase in the soil conductivity as a result of increasing the solution salt content in the soil. After adding more than 15wt% of water to the soil, it became muddy. Therefore, for the remaining of the work in soil environment, only 15wt% of water was added to the soil.

![Figure 40. Influence of adding ions and water on the soil resistance in 20 L soil.](image)
8.1.2 AC Experiments in Soil Environment

AC experiments were performed in 20 L, 15wt% water soil with 0.84 g. L$^{-1}$ CaCl$_2$.2H$_2$O and 2.34 g. L$^{-1}$ MgSO$_4$.7H$_2$O. Figure 41 shows the maximum and minimum of the total current recorded during potentiostatic experiments at applied CP potential of -850 mV$_{CSE}$ with different AC potential values at 60 Hz in soil environment. Also, the maximum and minimum current values in NaCl solution from section 4.1.3 with AC amplitude of 0.6mV are shown in this figure. This graph shows that the maximum current at 0.6mV AC in NaCl solution is much higher than that in soil environment at the same AC potential. Even by increasing the AC amplitude in soil to about 7 V (shown by dashed line), the maximum current passing through the system in the soil didn’t reach that in the NaCl solution. This is due to the ohmic drop across the soil between RE and WE. According to the proposed model in section 4.2 by increasing the R$_s$ value (i.e. the resistance between NaCl solution and soil environment) most of the applied potential, (E$_T$ ) drops across the soil and only small portion of AC potential will be applied on WE. As a result, the total current which is summation of capacitive and faradaic current, decreases. Therefore, corrosion rate (Faradaic current) in soil would be much lower than that in NaCl solution at the same applied potential.

Figure 42 shows the total current and total potential during a long term (20 days) potentiostatic experiment at applied CP potential of -0.85V$_{CSE}$ with 3V AC RMS value at 60 Hz. Figure 43 also shows the soil resistance values between WE and CE that were measured with EIS analysis during the experiment. It was observed that with constant applied potential (Figure 42 [b]), the total current (Figure 42 [a]) decreased while there
was an increase in the soil resistance over time from 617 $\Omega$.cm$^{-2}$ to 8475 $\Omega$.cm$^{-2}$ (Figure 43).

Figure 41. a) Schematic of sinusoidal AC current density from potentiostatic test with the marked max and min current densities, b) The maximum and minimum values of the total current during AC experiments in soil and NaCl solution at CP of -0.85V$_{CSE}$.

Figure 42. Experimental results recorded during the experiment in 20 L, 15wt% water soil with 0.84 g. L$^{-1}$ CaCl$_2$.2H$_2$O and 2.34 g. L$^{-1}$ MgSO$_4$.7H$_2$O with -0.85 V$_{CSE}$ CP and 3 V RMS at 60Hz and a) i-t curve.
Figure 42 (continued) Experimental results recorded during the experiment in 20 L, 15wt% water soil with 0.84 g. L\(^{-1}\) CaCl\(_2\).2H\(_2\)O and 2.34 g. L\(^{-1}\) MgSO\(_4\).7H\(_2\)O with -0.85 V\(_{\text{CSE}}\) CP and 3 V RMS at 60Hz b) E-t curve.

Figure 43. Variation of the soil resistance during the experiment over time.

As explained before, higher soil resistance results in larger ohmic drop across the soil which leads to the lower AC current passing through the system. Decreasing of the total current (\(i_C+i_O+ir\)) results in decreasing of each of its components. Since oxidation current density is correlated to the corrosion rate, increase of soil resistance leads to
decrease of corrosion rate. Scully et al. also observed a decrease in corrosion rate over time during DC electrochemical measurements in soil. They reported that there is an inverse dependence of soil corrosion on soil resistivity. Electrochemical reactions on the metal surface lead to the changes in its surrounding soil and as mentioned before, ionic migration from or toward the metal or properties of the corrosion scales might influence the soil resistivity. Figure 44 shows the soil in the vicinity of the coupon after 20 days of the experiment which was completely dry, hard and rocky compared to rest of the soil in the cell. The depletion of moisture in soil could be due to the electrochemical reactions on the surface of the WE (water reduction). As a result, consumption of water and slow movement and dynamic of water in clay soil led into the increase of soil resistance as observed in Figure 43.

Figure 44. Dry soil near the coupon after the experiment with AC.
Since due to the high resistance of the soil, most of the applied potential (AC or DC) was dropped across the soil and not the electrochemical interface as desired, acceleration of corrosion experiments were not possible. This was strictly a result of the small soil volume that could be used in the laboratory and not an issue for field studies on buried pipes. Also organic chemicals and even bacteria might be existing in the real soil that highly correlate to the excavation site and is not necessarily applied to anywhere else. Therefore, reproducibility in the laboratory experiments in soil environment could also be difficult. Therefore due to the complexity of the extracted soil, investigation of AC corrosion behavior in soil was discontinued and instead, studies were performed in soil simulated solution. The use of these solutions is a well-accepted practice in the corrosion research community. Soil simulated solution has close chemical composition to the soil but with lower resistivity and more homogeneity compared to soil environment.

8.2 Electrochemical Experiments on API X65 carbon steel in NS4 Solution

This section explains electrochemical techniques that were performed on API X65 carbon steel in NS4 solution to study its corrosion behavior.

8.2.1 AC and DC influence on Corrosion Rate of X65 in NS4 Solution

To study the influence of soil species on AC corrosion rate, electrochemical experiments on X65 samples were performed in NS4 soil simulated solution. These experiments were similar to those that carried out in NaCl solution. A set of potentiostatic experiments with AC (RMS voltage of $0.6V_{SCE}$ at 60Hz) as a function of DC potentials were performed. At each DC bias, using mass loss measurements and Faraday’s law
(Equation [(27)]), current densities were calculated. These results along with the polarization curve of X65 samples without AC in NS4 solution are shown in Figure 45.

Similar to NaCl solution, by increasing DC potentials there is an increase in corrosion rate and current density in NS4 electrolyte. Assuming that the polarization curve in NS4 solution is a close representation of the current density at each DC bias without AC, (as observed for NaCl solution in Figure 10)

Figure 45 shows that by applying AC there is an increase in corrosion rate. By comparing the amount of difference in current densities with and without AC, there was a decreasing trend by increasing DC biases which is probably due the IR drop and that the system being controlled by mass transport.

Figure 45. Effect of AC potential on current density of carbon steel at different DC biases in NS4 solution.
8.2.2 Influence of IR Drop on AC Corrosion Rate of X65 Carbon Steel

Figure 46 compares current densities of X65 carbon steel obtained from mass loss analysis after AC experiments in two different solutions. The data in this figure were collected at the applied AC potentials of 0.6V RMS at 60 Hz. This figure shows that the current density and consequently, corrosion rate with AC in NaCl solution at the same values of applied anodic DC biases and AC potentials is higher than that in NS4 solution. Also, EIS results showed that the solution resistance in NS4 is higher than that in NaCl solution (for about one order of magnitude, Figure 47).

![Figure 46. Comparison of current density with AC on X65 in different solutions.](image)
It was concluded that higher IR drop across the NS4 solution resistance resulted in decrease in current density that was observed in Figure 46. Figure 48(a) shows the total applied potential in the system at -0.7VSCE DC bias in presence of 0.6V RMS AC at 60 Hz. Also, the potential drop across the working electrode with two different solution resistance values of 50 and 200 Ω.cm² using the proposed model in phase I were calculated and are shown in Figure 48(b). The input variables for solving Equation (15) are brought in Table 1 and Table 9. The OCP value of -0.67V_{SCE} is shown by dotted line in Figure 48.

![Graph showing solution resistance comparison](image)

*Figure 47. Comparison of solution resistance in different solutions by EIS analysis before experiment at OCP.*
As discussed before, due to the ohmic drop across the solution resistance, only a small portion of applied potential depending on the $R_s$ value, reaches to the working electrode interface.

Figure 48. (a) The total applied potential at 60 obtained from solving Equation 15.
Figure 48 (continued). (b) Corresponding calculated potential across the faradaic resistance obtained from solving Equation 15.

Figure 48 (b) shows lower potential drop values across the working electrode for higher solution resistance. It should be noted that the corrosion rate of the working electrode at potential values lower than OCP is negligible and one could assume the potentials higher than OCP (\(E_{\text{Oxidation}}\) in Figure 48 [b]) as a measure of corrosion. According to Figure 48 (b), although the mean value of E (AVG(E)) for lower solution resistance has a lower value but it has higher \(E_{\text{Oxidation}}\) compared to that at higher \(R_s\) which results in higher corrosion rate. Therefore AVG(E) is not the only contributing factor in the corrosion rate and the RMS(E) value should also be considered.

According to the proposed model in phase I and the Kirchhoff’s laws, solution resistance can influence both DC and AC potential drop across the interface and as a result, affect Faradic current. Rearranging Equation (3) in section 2.1, the potential drop across the electrochemical interface (E) equals to:
The DC bias value could be obtained from the mean value of a periodic function in the time domain. Therefore the DC potential drop across the interface (AVG(E)) is:

\[ \text{AVG}(E) = \text{AVG}(E_T - i_T R_s) \]  

(19)

Distributing Equation (19):

\[ \text{AVG}(E) = \text{AVG}(E_T) - \text{AC}(\text{avrg}) \times R_s \]  

(20)

where \( \text{AVG}(E_T) \) is the applied DC bias.

Also, Figure 49 compares current densities obtained from weight loss analysis in NS4 solution at different DC biases at 60Hz with the AC(\text{avrg}), AC(+) and AC(−) values.

Figure 49 Comparison of current density with 60 Hz AC (RMS=600mV at different DC biases) from weight loss and AC(+), AC(−) and AC(\text{avrg}) in NS4 solution.
Similar to the observations in phase I, Figure 49 shows that at the frequency of 60Hz, the mean value of $i_T$ is a good indicator of $i_O$ (could be obtained from mass loss measurements). As explained before, this is due to the high capacitive current and a relatively low reduction current. Therefore, knowing the AC(avg) value, $\text{AVG}(E)$ equals to:

\[
\text{AVG}(E) = \text{AVG}(E_T) - i_O R_s \tag{21}
\]

Figure 50 shows the current density values obtained by mass loss measurements in NaCl and NS4 solutions at IR corrected DC biases calculated from Equation (21). This figure shows that the influence of AC in increasing the current density in NaCl is still more than that in NS4 solution. The reason is due to the AC potential drop across the solution resistance. RMS value of potential drop across the interface could be calculated using Equation (22).

\[
\text{RMS}(E) = \text{RMS}(E_T - i_T R_s) \tag{22}
\]

In order to calculate RMS (E), a high speed data acquisition system for recording $i_T$ values is necessary. In this project for 60 Hz frequency, data were collected at a rate of 250 points per second. Therefore, AC potential drop across the solution resistance couldn’t be calculated. According to Equation (22), higher Rs in NS4 solution results in higher RMS drop across it which leads to lower faradaic current density in NS4 solution compared to NaCl solution.
The values of the AVG(E) and RMS(E) could be obtained directly from the calculated E values from the model or from Equations (21) and (22). Results from both methods have equal values as shown in Table 10.

<table>
<thead>
<tr>
<th>Rs (Ω.cm²)</th>
<th>AVG(Eₜ-iₒRₛ) (V)</th>
<th>AVG(E) (V)</th>
<th>RMS(Eₜ-iₜRₛ) (V)</th>
<th>RMS(E) (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>-0.76</td>
<td>-0.76</td>
<td>0.79</td>
<td>0.79</td>
</tr>
<tr>
<td>200</td>
<td>-0.68</td>
<td>-0.68</td>
<td>0.69</td>
<td>0.69</td>
</tr>
</tbody>
</table>

To have a better comparison between these two solutions, the value of current density calculated by weight loss in presence of AC was divided by the value of current density corrected by weight loss.
density at the same $E_{DC}$ from polarization curve without AC. Results are plotted in Figure 51 which also shows the OCP values of X65 in two different solutions, -0.7 $V_{SCE}$ and -0.67 $V_{SCE}$ for NS4 and NaCl solutions respectively.

![Figure 51](image)

Figure 51. Comparison of the influence of NS4 and NaCl solution on the ratio of the AC corrosion current density to DC corrosion current density at different DC biases at 600mVRMS.

In AC experiments in NaCl solution, it has been observed that the influence of AC at OCP is more pronounced and by increasing the polarization the influence of AC decreases (Figure 14). Figure 51 also confirms that the value of $i_{AC}/i_{DC}$ decreases by increasing DC biases from OCP. The influence of AC on increasing corrosion rate of X65 in NS4 solution is almost analogous to the same in NaCl solution at the same polarization value. Additionally the increase of $R_s$ affects both AC and DC current densities in similar fashion.
8.2.3 Influence of CP and RMS Current on AC Corrosion Rate of X65 Carbon Steel

In this project unlike most of researches in the field of AC, instead of applying AC current, AC potential was applied to the system. It is proposed that the AC mitigation criteria based on the value of the AC current density is not reliable. This is due to the complex nature of AC current in circuits with a capacitance as explained in detail in section 4.2. It was shown that at 60Hz or higher frequencies, the capacitive current is predominant and the faradaic current (causing corrosion) is only a small portion of the total current.

Figure 52 shows corrosion rate obtained from mass loss measurements at different cathodic DC biases with 3V AC at 60 Hz (solid circular data points). Also RMS current densities recorded during experiments with an oscilloscope are shown in this graph (solid rectangular data points). The 30A.m⁻² AC current threshold for AC mitigation criteria is marked with a dashed line.

This figure shows that by decreasing CP potentials to -780 mV_{SCE}, there is a decrease in corrosion rate with AC. On the other hand, the highest RMS current value in this graph (210A.m⁻²) was related to the data point with the lowest corrosion rate at -780mV_{SCE}. Corrosion rate with AC at -780mV_{SCE} was negligible (0.9 mpy) even though AC current was 7 times higher than the AC current threshold. Furthermore, decrease of AC current followed by increase of the AC corrosion rate. These observations, contradict with the common belief about AC corrosion, that increasing AC current, increases the corrosion rate. Also, Figure 52 disaffirms the 30 A.m⁻² threshold as a criterion for AC mitigation. This criterion states that by increasing AC RMS current density more than 30A.m⁻², there is an increase of AC corrosion rate.

102
According to the proposed model in phase I, AC current includes both capacitive and faradaic current and only faradaic current leads to corrosion. At higher frequencies such as 60 Hz, most of the current passes through the interfacial capacitance and only small portion of the AC current results in corrosion. At lower DC biases, due to the increase of the polarization resistance ($R_p$) in the system, most of the current is capacitive current while by increasing DC biases, $R_p$ decreases and has more contribution in the value of the total current. Increasing of the faradaic current by decreasing $R_p$, results in decreasing of the capacitive current and consequently, decreasing of the total RMS current. This behavior will be explained in more detail in section 8.5.2 and shown in Figure 88. Therefore, as already observed, AC current is not a reliable parameter to be considered as an AC corrosion threshold.

Figure 52. Postmortem corrosion rate measured by mass loss along with AC RMS current densities recorded by oscilloscope during AC experiment of X65 carbon steel in NS4 solution at different DC biases with 3V AC RMS at 60 Hz.
Figure 53 obtained after 20 days immersion of X65 carbon steel in NS4 solution at different DC biases (-780 and -1 V\textsubscript{SCE}) in presence of 4.2 V RMS at 60 Hz. Also for comparison, the current density of the sample exposed to 3V RMS at -780mV\textsubscript{SCE} is brought in this figure (solid circular data point). As expected from both experimental results and proposed model in phase I, it was observed that by increasing RMS value from 3V to 4.2V, current density at -780mV\textsubscript{SCE} DC potential increased.

![Figure 53: Influence of CP on current densities measured by mass loss after AC experiment of X65 carbon steel in NS4 solution at different DC biases with 4.2V AC RMS at 60 Hz](image)

Also, Figure 53 shows that by decreasing CP potential to -1V with 4.2V AC, current density decreased and even became much lower than that at -780 mV\textsubscript{SCE} with 3V AC. According to the proposed model in phase I if it’s assumed that $C_i$ value remains
constant, decreasing of CP biases results in passing more current through $i_r$ which means there would be less $i_O$ or faradic current in the system. Although, some authors stated that decreasing DC biases leads to overprotection and higher corrosion rate in presence of AC, based on the proposed mechanism for AC corrosion in phase I and also observations from Figure 53, it is concluded that by decreasing CP biases, AC corrosion rate could be completely mitigated.\textsuperscript{26,27}

8.3 Calcareous Deposition on X65 Coupons

In this section, experimental findings and corresponding analyses of calcium carbonate deposition on API X65 carbon steel will be discussed.

8.3.1 Determination of Calcareous Deposition Potential Using Cathodic Polarization Experiment

To produce an evenly distributed layer of calcium carbonate on the surface of the X65 carbon steel with electrochemical techniques, it was necessary to maintain a high interfacial pH all over the steel surface. This could be done by holding the potential of carbon steel coupons at lower values than that of the oxygen reduction reaction. To do that, the first step was finding the appropriate potential region that was done by performing linear sweep in cathodic region in artificial seawater without Mg ions. Figure 54, shows the current-voltage curves at different rotation speed of the rotating cylinder electrode ($\omega$), 120, 600 and 1200 rpm (12.5, 63 and 126 radian/s respectively). As it can be seen the corrosion potential for all the three rotation speeds is about $-0.42 \text{ V}_{SCE}$.
This plot only shows one plateau region, which means that the first step of oxygen reduction reaction (reaction (1)) is merged into the second reaction (reaction (2)) due to its higher reaction rate. This behavior was also observed by Barchiche et al.. This figure also shows that by increasing the rotation speed, the limiting current density increases. From this figure two different potentials of -0.8 and -1 V$_{SCE}$ were selected to perform potentiostatic experiments for deposition of calcareous layer that assumed to be optimal for the accelerated scaling test. The optimized cylinder rotation speed will be determined in the following section.
8.3.2 Influence of Rotation Speed and Applied Potential on Calcareous Deposits

In order to investigate the scaling processes of calcite layer formation on X65 carbon steel potentiostatic experiments at -0.8V_{SEC} and -1 V_{SCE} were conducted. These potential will produces different interfacial pH values. While the electrode was polarized at each of the two mentioned potentials the oxygen reduction current was recorded as a function of time. Figure 55 shows the potentiostatic experiments at -0.8 and -1 V_{SCE} performed at different cylinder rotation speeds. The rotation speeds (ω) chosen were 120, 200, 400, 600 and 1200 rpm (12.5, 21, 42, 63 and 126 radian/s respectively). For comparison, current results for each potential and rotation speed were normalized by the initial current value (I_0). Figure 55 shows a decreasing trend in the current (oxygen reduction rate with time). This owes to calcium deposition on the surface of the metal. Calcium precipitation and growth of the deposit on the surface of the metal covers the active surface of the carbon steel and decreases the oxygen reduction rate vis-à-vis current. Therefore, the current reduction could be taken as a measure of the growth of the deposited layer. The Avrami equation for phase change at constant temperature is:

\[
\phi = \exp(-Kt^n)
\]

(23)

where \(\phi\) is the fraction of untransformed material at time \(t\), \(K\) is an overall rate constant, \(n\) is Avrami exponent (=1-4) that depends on nucleation and growth mechanisms. It’s been reported that the value of \(K\) is also a function of “\(n\)”, although this is not explicitly revealed by Equation [23]. Therefore the Avrami equation was modified to Johnson–Mehl–Avrami (JMA) equation which is:
\[ \phi = \exp\left(-\left(Kt\right)^n\right) \]  

Equation (24) could also be written as:\textsuperscript{119,120}

\[ \ln(-\ln\phi) = n\ln K + n\ln t \]  

The normalized current data \((I / I_0)\) in Figure 55 could be taken as \(\phi\) or the fraction of untransformed material at the surface. These graphs have inverse “s” shapes, typical of Avrami relationships for nucleation and growth mechanisms. Drawing \(\ln(-\ln(I / I_0))\) vs. \(\ln(t)\) from the data in Figure 55, results in linear relationships which means that they follow the Avrami equation (Equation [23]). This can be seen in Figure 56 for the two potentials at 600 rpm rotating speed. The overall rate constant value \((K)\) for the two graphs in Figure 56 is calculated from Equation (25) as 0.00029 and 0.00019 for \(-1V\) and \(-0.8V\) potentials respectively. The Avrami exponent \((n)\) for these two potentials had similar values of about 3.6 which is indicative of three dimensional growth.\textsuperscript{121–123} Higher rate constant at \(-1V_{SCE}\) than \(-0.8V_{SCE}\) could be explained by the existence of higher driving force with increasing absolute DC potential. Correspondingly, the particle size obtained at \(-1V_{SCE}\) is smaller than that obtained at \(-0.8V_{SCE}\) as shown by SEM results in Figure 57. These images were collected after 70 hours of experiment. The particle size is determined by the competing rates of nucleation and growth. As confirmed by the finer structure seen in SEM results, the scale formation at \(-1V_{SCE}\) has been performed with higher nucleation rate. The nucleation and growth mechanism will be discussed in more detail in the following section.

The cubic morphology of the deposited layer seen in Figure 57 indicates calcite formation with conventional rhombohedral crystallization with sharp edges.\textsuperscript{80} At DC
potential of -1V_{SCE}, hydrogen evolution was observed which led to the existence of uncovered spots in the coating. Therefore the DC potential of -0.8 V_{SCE} was used for following deposition procedures of the CaCO₃ layer.

Coming back to Figure 55, it is also observed that in rotation speeds from 120 to 600 rpm, the rate of reduction in I/I₀ values increases with increasing the rotation speed. This means that the calcareous layer formation is being controlled by mass transport in this range. In both applied potentials (-0.8 and -1 V_{CSE}), for rotation speeds of 600rpm there is a precipitous drop in current (I/I₀) and similar drop is observed even by doubling the rotation speed to 1200rpm. This means that there is no longer a dependence on ω and the calcareous layer formation is not being controlled by mass transport anymore. Instead, in rotational speeds higher than 600 rpm, the growth rate is being mostly controlled by the crystallization kinetics of CaCO₃. Such influence of the rotation speed on the formation rate of CaCO₃ has been observed by other authors. In order to eliminate the influence of mass transfer in the experimental condition, 600 rpm was selected for the following experiments.

![Figure 55. Results from potentiostatic tests showing the influence of rotation rate on the CaCO₃ deposition a) DC=-1V_{SCE}, b)-0.8V_{SCE}.](image)
Figure 56. Relationship between Ln(-Ln(I/ I_0)) and Ln(t) obtained from Figure 55 at 600 rpm at two different DC potentials of -1 and -0.8 V_{SCE}.

Figure 57 SEM photographs of the deposits formed at 600 rpm on a steel substrate at: (a) -0.8 (b) -1 V_{SCE}. 
8.3.3 Progressive Nucleation and Growth of the Calcareous Layer

As mentioned in the previous section, the reduction in the normalized current shown in Figure 55 follows the Avrami equation, corresponding to the formation of the calcite layer. A similar curve is shown in Figure 58 obtained from calcite deposition performed at -0.8 V_{SCE} with 600 rpm electrode rotation. The overall behavior of calcite formation is determined by the combination of nucleation and growth. As can be seen there are two plateaus on the current reduction, which correlate with two plateaus in the Avrami curve of the calcite formation over time. During the first plateau the rate of calcite formation is limited by the rate of nucleation. With the progress of deposition, nucleation rate will increase and at the same time, growth of the nucleated sites starts with an increasing rate. This is when the overall rate of calcite formation starts to reach its maximum. Over time the overall growth rate will start to decline, the nucleation rate drops to zero and the rest of the process (including the second plateau) will be controlled by the reducing rate of growth. Current measurements showed that even after four hours of immersion, I/I_0 value didn’t reach zero and therefore the metal surface was accessible to the diffusion of dissolved oxygen.

Analogous to the explained sequence of nucleation and growth, Figure 59 shows the progressive formation of CaCO_3 and coverage of the surface with decreasing I/I_0 values which are marked in the Figure 58. The particle coverage ratio and the particle sizes were also estimated using the Photoshop software. The measured coverage ratios at each of the images are provided in Table 11 and also drawn vs. deposition time in Figure 60. This figure represents the calcite formation curve explained in the previous paragraph.
Figure 58: Potentiostatic result at DC=−0.8 V<sub>SCE</sub> and 600 rpm.

Table 11: Measured particle size and blocked area from SEM observation at different I/I<sub>0</sub> values.

<table>
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<tr>
<td>Particle size (µm)</td>
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<td>8.6</td>
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<td>12.1</td>
<td>12.1</td>
</tr>
</tbody>
</table>
Figure 59. SEM photographs of the nucleation and growth process of CaCO$_3$ formed at 600 rpm on X65 carbon steel polarized at -0.8V$_{SCE}$ at different time of percoipitation, a)1700s b) 3300 c)5700s d)8900s and e) 9500s
Figure 60. Covered area versus deposition time.

Figure 61 shows the XRD pattern of the CaCO$_3$ deposits obtained at -0.8V$_{SCE}$. This figure also confirmed that cubic morphology of the deposited layers are related to calcite formation.

Figure 61. XRD analysis (λ-Co-K$_{a1}$ radiation) of the deposits.
The cross sectional morphology of calcite layers obtained by Focus Ion Beams (FIB). FIB images in Figure 62 show approximate thickness and cross section of the CaCO₃ scale after 20 hours and 70 hours of deposition. Although the maximum thickness of the CaCO₃ layer after 20 hours (6.78 µm) was lower than that after 70 hours (8.06 µm), but it seems that after 20 hours, all over the surface was covered by CaCO₃ particles and there is a compact layer of calcite on the surface of the metal. Based on these results, 20 hours can be considered as being a good deposition time for the purpose of scale producing for AC experiments.

Figure 62. FIB cross section of calcite layer after the experiment a) 20 hours.
8.3.4 EIS Analysis on Calcite Films

In addition to SEM analysis of the crystallization behavior of the CaCO\textsubscript{3} layer which is post mortem, in-situ EIS analysis during deposition process was performed. In order to study the nucleation and competing growth of CaCO\textsubscript{3}, a four hour deposition experiment was carried out and every 15 minutes, EIS analysis was conducted.

Figure 63 shows the Nyquist and Bode phase plots of the EIS results. For less than three-hour period of experiment, a flattened capacitive loop on the Nyquist plot was observed (Figure 63 [a]). This could be due to the non-homogeneity of the surface or non-uniform current distribution during calcite formation at the metal surface that results in deviation from the real double layer capacitance.\textsuperscript{125,126} In addition, at lower frequency,
the capacitive loop is followed by a line which is characteristic of the diffusion phenomenon related to the limited diffusion process.

The Bode plot for less than three-hours (Figure 63 [b]), also shows a peak that by increasing the deposition time, shifts to the right as shown by arrow. After three hours of experiment, as can be seen from Figure 63 (c) a supplementary high frequency loop appears (another peak on the Bode plot (Figure 63 [d]). This feature could be related to the development of dielectric properties of the calcite film. Again at this time, the shape of low frequency loop involves specific line to the diffusion phenomenon in the low frequency domain.

Further growth behavior of the CaCO$_3$ layer has been studied using EIS in 10 hours intervals up to 70 hours. This analysis following the study explained in the previous section was performed to find an appropriate deposition time for the purpose of making coupons for AC experiment. Figure 64 shows the Bode graphs (magnitude and phase) of experimental curves of X65 carbon steel at -0.8 V$_{SCE}$ and 600 rpm for total immersion of 70 hours.

At the short deposition time (less than 3 hours), there is only one slope on Bode magnitude plot and one peak on the Bode phase plot which by increasing immersion time and more covering of the interface by CaCO$_3$ layer, shifts to the right.

This shift is due to the decrease in the double layer capacitance as a result of decrease in the active surface of the metal. After three hours of deposition time, at higher frequency, another peak on Bode phase plot (two slopes on Bode magnitude plot) which is related to the calcite film appears and over time the height of it increases. This pattern shows the growth of film and increase of the film resistance.
Figure 63. AC impedance diagram during calcite deposition at -0.8 V SCE ad 600 rpm. a& b) Nyquist and Bode plot respectively for I/I₀>0.3, c& d) Nyquist and Bode plot respectively when I/I₀<0.15.
Figure 64. AC impedance diagram during calcite deposition at -0.8 V_{SCE} and 600 rpm for 70 hours of experiment. a) Bode magnitude plot and b) Bode phase plot.
8.3.5 The Analysis of EIS Results Using Equivalent Circuit Modeling

The equivalent circuit for interpretation of EIS results for calcareous deposit was considered based on SEM and EIS observations and also models that proposed by other authors.

Deslouis et al. studied the electrochemical behavior of carbon steel in sodium chloride solution using rotating disk electrode. They proposed an equivalent circuit with both anodic and cathodic branches being in parallel with the double layer capacitor $C$ in which $R_1$ represented the anodic charge transfer resistance, $R_2$ is the cathodic branch associated with the cathodic charge transfer resistance, $R_s$ is the solution resistance and $Z_D$ is the diffusion limited Warburg impedance (Figure 65). It was confirmed by SEM results (Figure 59) that in short deposition times (between first plateau and second plateau), the metal is covered with CaCO$_3$ islands. Therefore, for such a geometry an equivalent circuit based on Deslouis model was proposed (Figure 66 [a]). Since in this project, calcareous deposition was performed at cathodic potential (-0.8 V$_{SCE}$), in this system anodic reaction (iron oxidation) doesn’t happen and $R_1$ was omitted from Deslouis’s model. In addition, EIS results showed a flattened capacitive loop that was correlated to non-homogeneous double layer capacitance. Figure 66 (a) shows an equivalent circuit for short time of deposition. In this circuit, Charge transfer process of oxygen reduction was associated with the cathodic charge transfer resistance $R_c$ and its respective constant phase element (CPE$_c$). Also oxygen diffusion through the calcite particles was associated with the Warburg diffusion impedance, $W_s$ and finally $R_s$ represented solution resistance in the system.
SEM results (Figure 59) showed that when about 90 percent of the surface was covered by CaCO$_3$ particles (second plateau), two time constants on EIS spectrums would appear and after that a continuous calcite film covers the metal. It should be noted that Devos et al. also studied the reduction process of oxygen during the progressive coverage of the metal substrate with calcareous layer and they have reported that after 80 percent coverage of the metal surface, these two time constants that are related to the oxygen reduction reaction would appear on the EIS results. Therefore the equivalent circuit that applies for organic coatings, was considered for longer deposition time (Figure 66 [b]). This model was already used by several authors. 

(a) 
(b)
In this circuit, calcite layer growth was associated with $R_f$ and $\text{CPE}_f$. The EIS experimental results were studied by the Zview software (EIS data fitting computer program).

The fitting Nyquist and Bode plots of experimental data obtained using the proposed ECs in Figure 66 for 1 and 3 hours of calcite layer deposition are shown in Figure 67 and Figure 68 respectively. It can be seen that the fitting results match the experimental data very well.

Figure 67. EIS measurements and model fits of Nyquist plots (a) and corresponding Bode plots (b) and (c) of X65 electrodes after 1 hour calcite deposition at -0.8 V$_{SCE}$ at 600 rpm ($I/I_0 > 0.3$). Inset in (a): the equivalent circuit.
Figure 68. EIS measurements and model fits of Nyquist plots (a) and corresponding Bode plots (b) and (c) of X65 electrodes after 3 hours calcite deposition at -0.8 V\text{SCE} at 600 rpm (I/I_0<0.15). Inset in (a): the equivalent circuit.

The EIS experiment results of longer deposition times of 70 hours (Figure 64) were fitted using proposed equivalent circuits and shown in Table 12. Figure 69 summarizes the fitted values shown in Table 12. Figure 69 (a) and (b) show that by passing time and growth of the calcite layer, there is an increase in both $R_c$ and $R_f$ values. Increasing $R_c$ indicates the increase of covered surface area with calcite layer (Figure 69 [c]). CPEf-P value is proportional to the water uptake (absorbing moisture from the environment) of the calcareous layer. The increase in CPEf-P values (Figure 69 [d])
means the porosity of the layer and its water uptake has decreased which is due to the calcite particle growth over time.

Table 12. Fitting results for equivalent circuit elements at -0.8VSCE and 600rpm.

<table>
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<tr>
<th>t (hr)</th>
<th>R&lt;sub&gt;c&lt;/sub&gt; (Ω)</th>
<th>R&lt;sub&gt;f&lt;/sub&gt; (Ω)</th>
<th>CPE&lt;sub&gt;dft&lt;/sub&gt; (F)</th>
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<th>Ws&lt;sub&gt;R&lt;/sub&gt; (Ω.s&lt;sup&gt;-0.5&lt;/sup&gt;)</th>
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Figure 69. Summary of the fitted values from EIS analysis (Table 12), variation of a) R<sub>c</sub>, b) R<sub>f</sub>.
The value of charge transfer resistance \( R_c \) follows the surface of the bare metal. Therefore the area of uncovered surface of the metallic substrate could be calculated by using the variation of the \( R_c \) from EIS fitting results with \( I/I_0 \) and applying Equation (26):

\[
\text{covered area (\%)} = \left(1 - \frac{R_i}{R}\right) \times 100
\]

where \( R_i \) is the initial charge transfer resistance \( (I/I_0=1) \) and \( R \) is \( R_c \) value at different \( I/I_0 \).

Figure 70 shows the percentage of the covered area of the surface of the X65 coupon during calcareous layer formation. The \( R \) values that were used in Equation (26) for getting this figure, obtained from fitting the short interval EIS spectrums for 20 hours deposition period. Also the estimated covered area values from SEM results (Table 11) are brought in this graph.

This figure shows that by decreasing \( I/I_0 \) there is a progressive coverage of the surface by \( \text{CaCO}_3 \) layer as was also observed in Figure 59.
8.4 Iron Carbonate Deposition on X65 Coupons

In this section, experimental findings and corresponding analyses of iron carbonate deposition on API X65 carbon steel will be discussed.

8.4.1 Self-Passivation of X65 Carbon Steel in CO₂ Atmosphere

Figure 71 shows the open circuit potential (OCP) evolution of the bare X65 carbon steel sample immersed in NaCl solution in CO₂ atmosphere for 70 hours. This figure shows increasing of the OCP value from -0.8 V_{SCE} to -0.3 V_{SCE} of the bare sample (beginning of immersion) by formation of the protective ferrous carbonate over time. This behavior was reported by other authors and correlated to the semi passivation of the carbon steel by covering of the ferrous carbonate layer.⁹⁶–⁹⁸

Han et al. related the change pattern of the OCP to the nucleation and growth of the passive phase.⁹⁸ Also, according to the classic thermodynamics, by formation of the
iron carbonate film, the OCP value should be either constant or decreased. This is due to the surface coverage or diffusion barrier for cathodic species by formation of FeCO$_3$ respectively. The former is responsible for retarding both anodic and cathodic reactions while the latter leads to decreasing of cathodic reaction rate.

![Graph of OCP evolution](image)

**Figure 71.** The open circuit potential (OCP) evolution of X65 carbon steel immersed in 10wt% NaCl solution in CO$_2$ atmosphere for 70 hours.

Therefore, increasing of OCP suggests higher decreasing of the anodic reaction rate compared to the cathodic reaction rate, which could be related to the passivation characteristics of steel.$^1$ Figure 72 is the schematic of the corrosion kinetic of the active-passive transition. Point “A” (lower OCP value) on this figure is related to the actively corroding surface of the steel immediately after immersion in the solution that over time
and by formation of the FeCO₃ covering layer, jumps to the point “B” (higher OCP value).  

It’s been reported that by precipitation and full coverage of the surface by compact FeCO₃, replenishment of protons which are consumed by corrosion at the carbon steel surface, will be retarded and lead to increase of the interfacial pH. The formation of the high local pH between FeCO₃ layer and steel surface, might lead to the steel passivation (self-passivation) and formation of passive films such as Fe(OH)₂ and Fe₃O₄. Figure 73 shows the schematic of the Pourbaix diagram that can justify the formation of the passive Fe₃O₄ layer on the steel surface by increasing the interfacial pH value.

The self-passivation phenomenon results in decrease of the corrosion rate and at the same time, increase of potential to a more positive value. Han et al. claimed that the self-passivation time depends on both pH of the bulk solution and the temperature. They observed that higher pH and temperature values result in shorter self-passivation time.
They also reported that CO₂ is the main component of the self-passivation and only existence of high pH and temperature couldn’t result in the passivation process of steel.⁹⁸ As already explained in section 6.3.2, higher pH value increases the precipitation rate of FeCO₃ by decreasing the solubility of it. On the other hand, although higher temperature accelerates the corrosion process, at higher pH values with higher scale precipitation rate, the kinetics of the FeCO₃ formation accelerate even more which results in remarkable decrease in the corrosion rate.¹⁰³ Li et al. also suggested that the corrosion protectiveness obtained after FeCO₃ layer formation (appeared as an increase in OCP value), other than the composition of the layer, could be associated to the adherence of the thin inner FeCO₃ film formation due to the increase of interfacial pH. They assumed that the thin adherent corrosion product blocks large portion of the steel surface which leads into the retarding of the anodic dissolution of iron. Also due to the presence of the electronic path from the steel surface through the corrosion products (will be explained in the next section), the cathodic reaction is not affected as much.¹⁰⁰
As shown in Figure 71, after about 20 hours of immersion, several peaks in OCP potential appeared which was followed by decrease in the charge transfer resistance values that will be shown in section 8.4.5. The difference in potential between the bare surface area of the steel and its passivated covered area results in the initiation of galvanic corrosion. This fluctuation of the potential could be due to the galvanic corrosion as a result of electrolyte penetration through FeCO$_3$ layer pores over time followed by repassivation of the surface which will be explained in more detail in section 8.4.5.

8.4.2 Progressive Coverage of the Surface by FeCO$_3$

As discussed in previous section, by full coverage of the steel surface over time, there is about 500mV$_{SCE}$ increase at OCP potential value (Figure 71). During immersion of the sample at OCP in 10%wt NaCl solution with CO$_2$ atmosphere, carbon steel samples at different stages of the precipitation of FeCO$_3$ were taken for surface analysis (marked in Figure 74). Figure 75 shows the progressive formation of FeCO$_3$ and coverage of the surface over time. This figure shows that by increasing of immersion time, there was an increase in the number of FeCO$_3$ particles and even after about five hours of immersion (point C), before the sudden increase of the OCP value, there were still some uncovered spots on the surface of the carbon steel. Finally, after increasing of the potential, as explained in previous section, the carbon steel surface was fully covered with prism shaped FeCO$_3$ particles (point D). The particle coverage ratio and the particle sizes were also estimated using the Photoshop software. The measured coverage ratios at each of the images are provided in Table 13.
For SEM analysis, samples prepared without applying any conductive coatings such as gold. Provided that FeCO₃ has a low-conductivity, there should be specimen charging and low quality SEM images. Quite the reverse, as shown in Figure 75, SEM photographs didn’t show any charging on the samples which was also observed by other authors.¹⁰⁰ This means that the sample is electrically conductive. This conductivity could come from metallic compositions of X65 carbon steel or iron oxide phases in corrosion product.¹⁰⁰

![Figure 74. Open circuit potential trend of X65 carbon steel in 10%wt NaCl solution in CO₂ atmosphere.](image-url)
Figure 75. SEM photographs of the formation process of FaCO3 on X65 carbon steel immersed in 10wt% NaCl solution in CO2 atmosphere at different precipitation time, a) 1.5 h b) 3h c) 5h and d) 8h.

Table 13. Measured particle size and blocked area from SEM observation at different deposition time.

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<th>3</th>
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<td>Apparent covered area (%)</td>
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<td>60</td>
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<td>100</td>
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<td>Particle size (µm)</td>
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8.4.3 EDS Analysis of the FeCO$_3$ Layer:

Figure 76 shows the EDS results of the chemical composition of the surface of the X65 carbon steel immersed in 10wt% NaCl solution in CO$_2$ atmosphere after 1.5 hours. Figure 76 (b) is the EDS analysis of the uncovered spot ((A) in Figure 76 [a]) while Figure 76 (c) shows the EDS result of the prism shaped particle on the surface (B) in Figure 76 [a]). Since the elemental quantification of carbon and oxygen is problematic (light elements), approximate quantitative EDS results of point (A) and point (B) on Figure 76 (a) are presented in Table 14 and Table 15 respectively.

Figure 76 (b) along with the results from Table 14, show the presence of the considerable amount of oxygen (7.1%wt) other than the Fe phase. This suggests that the surface of the X65 carbon steel after immersion in 10wt% NaCl solution in CO$_2$ atmosphere was corroded. Since hydrogen couldn’t be detected by this technique, it’s not possible to identify the presence of any hydroxides. Also Figure 76 (c) shows the appearance of the carbon peak and increase of the intensity of the oxygen signal, 48.84%wt (Table 15), compared to the uncovered spot, 7.1%wt (Table 14). These results confirm formation of FeCO$_3$ particle.

In order to identify the phase of FeCO$_3$ component, XRD analysis was performed. Figure 77 shows the XRD pattern of the FeCO$_3$ deposits after 20 hours of immersion. This figure confirmed that prism shaped morphology of the deposited layer is related to siderite formation.

Although, EDS and XRD analysis couldn’t confirm the presence of other metallic compositions or oxide phases in the corrosion product, their existence were indirectly evidenced by SEM observation as discussed in the previous section. Also, Han et al.
found Fe$_3$O$_4$ with a nanometer scale as an inner corrosion protection layer by using XRD in combination with grazing incidence diffraction (GIXRD).$^{98}$

Figure 76. EDS analysis on the surface of the sample immersed in 10wt% NaCl solution in CO$_2$ atmosphere after 1.5 hours of immersion a) SEM image of the surface b) EDS analysis of point (A).
Figure 76 (continued). EDS analysis on the surface of the sample immersed in 10wt% NaCl solution in CO$_2$ atmosphere after 1.5 hours of immersion c) EDS analysis of point (B).

Table 14. Quantitative EDS analysis of point (A) in Figure 76 (a).

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<th>Error %</th>
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<td>Fe L</td>
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<td>78.9</td>
<td>3.95</td>
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</table>

Table 15. Quantitative EDS analysis of point (B) in Figure 76 (a).

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<tr>
<td>Fe L</td>
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<td>12.48</td>
<td>8.85</td>
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<tr>
<td>C K</td>
<td>16.15</td>
<td>26.76</td>
<td>9.39</td>
</tr>
</tbody>
</table>

Figure 77. XRD phase analysis of the FeCO$_3$ layer.
8.4.4 FIB Cross-Sectional Morphology of the FeCO$_3$ Layer

Thickness and porosity of siderite particles, is an important factor that determines its protectiveness against corrosion. Although, Li et al. observed good corrosion protection for FeCO$_3$ layer that wasn’t even dense. They related this corrosion protection to the formation of the thin (1$\mu$m) adherent inner layer of FeCO$_3$. On the other hand, Han et al. found Fe$_3$O$_4$ with a nanometer scale as an inner corrosion protection layer.

Therefore, FIB cross sectional analysis on the surface layer of samples at different immersion times was performed. FIB images in Figure 78 show approximate thickness and cross section of the FeCO$_3$ scale after 20 hours and 70 hours of immersion (Figure 78 (a) & (b) respectively). This figure shows that the maximum thickness of the FeCO$_3$ layer after 20 hours (3.5$\mu$m) was almost the same as that after 70 hours. At high temperature, due to the accelerated precipitation of FeCO$_3$, interfacial solution returns to its thermodynamic equilibrium state. Therefore, over time, high supersaturation of FeCO$_3$ couldn’t sustain and precipitation rate of FeCO$_3$ decreases.

Figure 78 also shows that after 20 hours of immersion, all over the surface was covered by compact layer of FeCO$_3$ particles. Based on these results, 20 hours can be considered as being an optimum deposition time for the purpose of scale producing for AC experiments.
Figure 78. FIB cross section of siderite layer after the experiment a) 20 hours and b) 70 hours.
Unlike FIB images of the cross section of X65 carbon steel with CaCO₃ layer (Figure 62), Figure 78 shows the rough interface between the substrate and FeCO₃ particles. This could be due to the selective corrosion of ferrite, due to the lower over potential of FeC₃, and exposing of the cementite phase as iron substrate corroded away. After a brief corrosion of the substrate, due to difficulty in diffusion of the species between the solution and narrow gap of cementite, Fe²⁺ concentration in the Fe₃C gaps increases and according to Equation (17), leads to increases of supersaturation of FeCO₃. This results in formation of FeCO₃ between cementite gaps which is shown in Figure 79. Over time, Fe²⁺ concentration increases all over the surface and FeCO₃ forms all over the interface.

![Figure 79. FIB cross section of siderite layer showing formation FeCO₃ between narrow gap of Fe₃C.](image)

Micro galvanic corrosion between ferrite and cementite results in increase of the active surface area of the metallic substrate. FIB image after 70 hours of immersion (Figure 78 [b]) showed an increase of the interface up to about 1.4 times of its initial value which was approximated with the Photoshop software.
8.4.5 EIS Analysis on Siderite Films:

The active adsorption state:

Figure 80 shows the EIS results of the X65 carbon steel for the first 1.5 hours of exposure. Figure 80(a) shows the Nyquist diagram with two time constants, a flattened capacitive loop in the high-medium frequency range (HF/MF), and an inductive loop in the low frequency (LF) range.

Figure 80. Impedance results obtained for a X65 carbon steel at different exposure times (first 1.15 hr) in 10 wt.% NaCl solution saturated with CO2: Nyquist (a) and Bode plots (b and c) representations.
Figure 80(b) & (c) show the phase angle and Bode representation of the EIS spectra, respectively. Also, the HF/MF peak and the LF valley in the Bode phase plot (Figure 80 [b]) represent the capacitive loop and inductive loop, respectively.

The capacitive semicircle is related to the active state of the interface of the X65 carbon steel exposed to the CO$_2$ saturated solution. The Nyquist plot (Figure 80 [a]) shows a decreasing trend of the amplitude of the capacitive loop over time. This suggests that the cathodic reaction (hydrogen reduction) is more favorable as a charge transfer process. It’s been reported that the presence of cementite (Fe$_3$C) as a part of the X65 carbon steel results in such a behavior.$^{94}$ Fe$_3$C is an electronic conductor that has a lower overpotential compared to the ferrite phase ($\alpha$-Fe) in X65 carbon steel. This potential difference, results in selective dissolution of $\alpha$-Fe and hydrogen reduction on the Fe$_3$C (microgalvanic corrosion).$^{87,89,90}$ This results in accumulation of loose and non-protective Fe$_3$C on the X65 carbon steel surface during initial corrosion process that act as the cathodic site and accelerates the corrosion rate of carbon steel.$^{93}$ Gulbrandsen et al. also reported an increase in corrosion rate of X65 carbon steel exposed to CO$_2$ environment and they related this behavior to the presence of Fe$_3$C.$^{94}$

The inductive loop in Figure 80(a) was correlated to the adsorption of intermediate corrosion products according to the following reactions that shows the active dissolution of the metal:$^{89,105,106}$

$$\text{(FeX)}$$

(22)

$$\text{(FeX)} \rightarrow \text{(FeX)}$$

(23)

$$\text{(FeX)}$$

(24)

where could be OH$^-$ and Cl$^-$.  

140
Figure 81 shows the EIS spectrum after 1.5 hours of immersion in 10 wt.% NaCl solution saturated with CO$_2$. The Nyquist plot in Figure 81(a) shows an increasing trend of the amplitude of the capacitive loop over time.

![Nyquist plot](image)

Due to the high temperature and pH, after a short period of dissolution of the surface of the bare steel, surface supersaturation of FeCO$_3$ exceeded and solid FeCO$_3$ was formed at the steel surface. Surface coverage of X65 carbon steel by FeCO$_3$ particles...
limited the supply of the corrosion reactants and decreased the active surface area for corrosion reaction.\textsuperscript{98} Therefore after about 1.5 hours of immersion, decrease of the corrosion rate, due to the coverage of the surface of the steel with FeCO\textsubscript{3}, overcame the micro galvanic corrosion rate between ferrite and cementite. This phenomenon led into an increase of the capacitive loop and decrease in the corrosion rate and as a consequence, the LF inductive loop shrank. The Bode phase plot (Figure 81 [b]) also shows a gradual increase of the maximum peak over time.\textsuperscript{134}

The active-FeCO\textsubscript{3} layer state

After about 8 hours of immersion, the interfacial CO\textsubscript{2} corrosion mechanism evolved and emerged as a sudden increase in the OCP value (Figure 71). SEM micrograph at this point showed a complete coverage of the surface area with FeCO\textsubscript{3} layer (Figure 75[d]). This development of the siderite layer also modified the impedance properties.

Figure 82 represents the EIS spectrum after 10 hours of exposure. By precipitation of FeCO\textsubscript{3} all over the interface, large area of Fe(OH)\textsubscript{ads} no longer can form which results in disappearance of the inductive loop in the Nyquist plot in Figure 82(a).\textsuperscript{134} Also, this figure shows appearance of a supplementary HF loop. Bode phase plot (Figure 82[b]) and the Bode magnitude plot (Figure 82[c]) also, verified the presence of another HF response; two maximum peaks and two slopes characteristic of different time constants presented in the system, respectively. This new HF peak in the Bode phase plot in Figure 82(b) is related to the siderite layer. By precipitation of compact FeCO\textsubscript{3} layer the interfacial pH between metal/scale layer increases. This is due to inhibition of protons replenishment which are consumed by corrosion at the steel surface. This leads to the
formation of the passive phase on the metal surface which is reflected in the Nyquist diagram in Figure 82(a) that has a typical form of the passive film (arc-shape with small curvature).\textsuperscript{134} Large radius of LF semicircle signifies high corrosion protection provided by the passive film. The same feature also reflected in the Bode phase plot (Figure 82[b]) that with decreasing the frequency to 100 Hz, the phase angle of impedance increased to about -80° and remained almost constant for the lower frequencies.

Figure 82. Impedance results obtained for a X65 carbon steel at different exposure times in 10 wt.% NaCl solution saturated with CO2: Nyquist (a) and Bode plots (b and c) representations.
Figure 83 shows the EIS results after 20 hours of immersion of X65 carbon steel in CO₂ atmosphere. Over time, the phase angle within the low frequency range as shown in Figure 83(b) was found to become smaller while there was a decreasing trend in the capacitive loop in Nyquist plot (Figure 83 [a]). These observations suggest increasing of corrosion rate over time that could be due to the porosity of the iron carbonate layer and will be explained in the following section after EIS fitting analysis.

![Figure 83](image_url)

**Figure 83.** Impedance results obtained for a X65 carbon steel after 20 hours of exposure in 10 wt.% NaCl solution saturated with CO₂: Nyquist (a) and Bode plots (b and c) representations.
8.4.6 Analysis of EIS Results Using Equivalent Circuit Modeling

Based on SEM observations and EIS results, the equivalent circuits (EC) represented in Figure 84 were considered to characterize the evolution of the interface of X65 carbon steel in CO\textsubscript{2} electrolyte.

SEM results (Figure 75) confirmed the precipitation and growth of FeCO\textsubscript{3} islands on the surface of X65 carbon steel in short deposition times (before an abrupt increase in OCP). Similar to EC proposed for CaCO\textsubscript{3} deposition in section 8.3.5, for such a geometry an equivalent circuit based on Deslouis model was suggested, but this time with additional inductive components (Figure 84[a]). This model has been widely used by several authors for interpretation of the steel–CO\textsubscript{2} interface with an adsorbed intermediate product.\textsuperscript{89,99,106,107} In this circuit, $R_s$ represents the solution resistance, $R_c$ is the charge transfer resistance with its respective constant phase element (CPE\textsubscript{dl}), $RL$ is the inductive resistance and $L$ is the inductance.

SEM images (Figure 75) showed that after a sudden increase in OCP value, the surface of X65 carbon steel was almost covered by FeCO\textsubscript{3} particles. At this time, when a continuous siderite film covered the metal, two time constants on EIS spectrums appeared (Figure 82). Therefore the equivalent circuit (Figure 84 [b]) that applies for organic coatings and was already used by several authors was considered for longer deposition times.\textsuperscript{89,93} In this circuit, iron carbonate layer growth was associated with $R_f$ and $CPE_f$.

The fitting Nyquist and Bode plots of experimental data obtained using the proposed ECs in Figure 84 for short and long term of immersions (2 and 20 hours) are
shown in Figure 67 and Figure 68 respectively. It can be seen that the fitting results match the experimental data very well.

The impedance parameters obtained by fitting of the EIS experimental results using the proposed ECs in Figure 84 are listed in Table 16.

Table 16 shows that for the first 60 minutes of immersion, the value of $R_C$ decreases from 79 to 47 ohms while $\text{CPE}_{\text{dl}}$ increases from 1370 to 2930 microfarads. This is due to the continuous dissolution of the ferrite phase due to the increase of the Fe$_3$C area or in other words, the physical-electrical properties of the corrosion products. As discussed in section 8.3.5, $R_C$ values are inversely proportional to the available area for the charge transfer reaction while there is a direct relationship for $\text{CPE}_{\text{dl}}$. By continuous corrosion of ferrite, cementite phase leaves behind and increases the active surface area which results in increase of capacitance and corrosion rate. Using $R_C$ values, the area ratio (as shown in Equation [(27)]) was calculated. The active surface area after 60 minutes of immersion (maximum area) was about 1.68 times of its initial value. Also as mentioned in section 8.4.4 using FIB images, an estimated surface area after 70 hours of immersion was
approximated to be about 1.4 times of its initial value. This difference could be due to the dissolution of lamellar cementite phase over time.

\[
\text{Area ratio} = \left( \frac{R_C}{R_{C,i}} \right)
\]  

(27)

Figure 85. EIS measurements and model fits of Nyquist plots (a) and corresponding Bode plots (b) and (c) of X65 electrodes after 2 hours immersion in 10wt% NaCl solutions in CO2 atmosphere. Inset in (a): the equivalent circuit.
Figure 86. EIS measurements and model fits of Nyquist plots (a) and corresponding Bode plots (b) and (c) of X65 electrodes after 20 hours immersion in 10wt% NaCl solutions in CO2 atmosphere. Inset in (a): the equivalent circuit.

Table 16 also shows a decrease of $R_L$ values for the first 60 minutes of immersion which is proportional to the coverage of adsorbed components at the surface of X65 carbon steel.\(^8^9\)

Although selective dissolution of the ferrite phase increases the active surface area, it also leads to the increase of Fe\(^{2+}\) ion contents at both electrochemical interface and in the narrow gaps of the remained lamellar Fe\(_3\)C. According to Equation (17), increase of the Fe\(^{2+}\) concentration, increases $S_{FeCO_3}$ and when $S_{FeCO_3}>1$, precipitation of
FeCO₃ starts. However, it takes time for Fe²⁺ content to reach the threshold value of FeCO₃ precipitation all over the interface. Based on EIS results, it was concluded that during the short period of exposure (first 1 hour), there was an overall increase in the active surface area that overtook the blocking effect of FeCO₃ precipitation and led into decrease of Rₜ. However, after 1 hour of immersion, increase of covered surface area by FeCO₃ particles overcame the growth rate of cementite areas and led into the increase of Rₜ and correspondingly decrease of CPEₗₜ values.

By formation of a compact siderite layer after about 8 hours of immersion, due to retarding of proton replenishment at the metal/electrolyte interface, there is an increase in interfacial pH value that leads to spontaneous passivation of the substrate. EIS fitting results after coverage of the surface with FeCO₃ layer showed a sudden increase in Rₜ values as the FeCO₃ grows at the pores. On the other hand, the value of Rₜ remained with small modification over time which suggest the formation of homogenous siderite layer.

As mentioned before, CPEf-P value is proportional to the water uptake and porosity of the film layer. Table 16 shows decreasing trend in CPEf-P values which means the porosity of the layer increased over time and led to the decrease of Rₜ values after 20 hours of immersion. As mentioned before, decrease in superstauration of FeCO₃ at high temperature at the beginning of immersion leads to the decrease in precipitation rate of FeCO₃ which is due to the accelerated formation of FeCO₃ layer. This phenomenon was in agreement with the FIB cross section observations that the thickness of the iron carbonat layer after 20 and 70 hours of immersion were almost the same. Knowing that the thickness of the film after 20 hours of immersion remained almost constant, over time, solution would penetrate through the film’s pores and increase its
water uptake. When the solution reaches the metal surface at the pore bottoms, corrosion rate increases which reflects as a decrease in $R_c$. Dissolution of the substrate at the pore bottoms decreases the OCP value that once again by subsequent increase in the Fe$^{2+}$ content, FeCO$_3$ precipitates and leads to the formation of the OCP peak (Figure 71).

Table 16. Equivalent circuit elements in Figure 84 obtained to fit the impedance spectra of Figure 80 through Figure 83.

<table>
<thead>
<tr>
<th>$t$ (hr)</th>
<th>$R_c$ (Ω)</th>
<th>$R_L$ (Ω)</th>
<th>CPE $dlt$ (Ω)</th>
<th>CPE $dlP$ (F)</th>
<th>CPE $fT$ (F)</th>
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8.5 Electrochemical Experiments on X65 with Interfacial Scales in NS4 Solution

In this part, electrochemical behavior and corrosion rate of API X65 carbon steel with and without artificial scales in NS4 solution is investigated and compared.

8.5.1 EIS Analysis Prior to the AC Experiments

EIS analysis on both bare and scaled X65 carbon steel samples after 24 hours immersion at OCP, prior to AC experiments, was performed. The equivalent circuits proposed in Figure 66 (a) and (b) were considered for fitting EIS results of bare X65 carbon steel sample and coupons with scales respectively. Fitting results are shown in Table 17. In addition, the values of the CPEs were converted to the effective capacitance \( \text{C}_{\text{eff}} \), in order to compare the interfacial capacitance values. These values obtained using the proposed model by Hsu and Mansfeld that is shown in Equation (28):

\[
\text{C}_{\text{eff}} = \text{CPET}(\omega_{\text{max}})^{\text{CPEP}-1}
\]  

(28)

where \( \omega_{\text{max}} \) is the frequency at which the imaginary part of the impedance \( (Z'') \) has a maximum, \( \text{C}_{\text{eff}} \) is the effective capacitance and CPET is the constant phase element with the power of CPEP.

EIS fitting results indicate decrease of interfacial capacitance values \( \text{C}_{\text{eff}} \) after scales formation on X65 carbon steel. On the other hand, Table 17 shows that for X65 carbon steel with scales, the values of \( \text{C}_{\text{eff,f}} \) were much smaller than the values of the \( \text{C}_{\text{eff,dl}} \). Therefore, the equivalent circuit shown in Figure 66 (b) was simplified to the EC in Figure 87.
Table 17. Fitted values from EIS spectrum before AC experiments at OCP.

<table>
<thead>
<tr>
<th>material</th>
<th>Sample</th>
<th>R_c</th>
<th>R_f</th>
<th>CPE_{dl}T</th>
<th>CPE_{dl}P</th>
<th>C_{eff,dl}</th>
<th>CPE_{f}T</th>
<th>CPE_{f}P</th>
<th>C_{eff,f}</th>
</tr>
</thead>
<tbody>
<tr>
<td>X65</td>
<td>R1</td>
<td>85</td>
<td>3.7E-3</td>
<td>0.69</td>
<td>3.9E-3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>R2</td>
<td>80</td>
<td>3.3E-3</td>
<td>0.7</td>
<td>3.4E-3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>R3</td>
<td>79</td>
<td>4.3E-3</td>
<td>0.68</td>
<td>4.8E-3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>X65/CaCO3</td>
<td>A1</td>
<td>1200</td>
<td>236</td>
<td>2.0E-4</td>
<td>0.47</td>
<td>1.6E-4</td>
<td>2.3E-7</td>
<td>0.85</td>
<td>5.8E-8</td>
</tr>
<tr>
<td></td>
<td>A2</td>
<td>796</td>
<td>56</td>
<td>6.0E-4</td>
<td>0.43</td>
<td>6.4E-4</td>
<td>1.1E-7</td>
<td>0.93</td>
<td>5.9E-8</td>
</tr>
<tr>
<td></td>
<td>A3</td>
<td>1801</td>
<td>53</td>
<td>1.1E-4</td>
<td>0.56</td>
<td>7.7E-5</td>
<td>1.0E-7</td>
<td>0.94</td>
<td>5.5E-8</td>
</tr>
<tr>
<td>X65/FeCO3</td>
<td>B1</td>
<td>357</td>
<td>19</td>
<td>5.8E-4</td>
<td>0.71</td>
<td>2.4E-4</td>
<td>1.7E-5</td>
<td>0.81</td>
<td>9.7E-6</td>
</tr>
<tr>
<td></td>
<td>B2</td>
<td>270</td>
<td>14</td>
<td>2.3E-4</td>
<td>0.72</td>
<td>2.0E-4</td>
<td>9.4E-5</td>
<td>0.7</td>
<td>9.4E-6</td>
</tr>
<tr>
<td></td>
<td>B3</td>
<td>231</td>
<td>18</td>
<td>4.5E-4</td>
<td>0.66</td>
<td>2.8E-4</td>
<td>5.2E-5</td>
<td>0.72</td>
<td>5.8E-6</td>
</tr>
</tbody>
</table>

Figure 87. Simplified equivalent circuit of X65/CaCO_3 considering only when the C_{eff,f}<<C_{eff,dl}.

Scale formation on X65 carbon steel results in decrease of the active surface area of the metal that reflects in decrease in the C_{eff,dl} and increase in the values of R_c. On the other hand, by neglecting C_{eff,f}, the pore resistance of the scale becomes in series with the solution resistance (Figure 87). This results in decrease of the ohmic drop across the WE interface.
As long as the film scale layer remains stable and the area of the uncovered metal doesn’t change during the AC experiment, variations in the EC’s elements due to the scale formation as shown in Table 17, result in the total current drop in the system. This will be further discussed in the following section.

8.5.2 Application of the Proposed Model on AC Corrosion of Scaled Metal

Here, it is attempted to explain the AC corrosion behavior of CaCO$_3$ and FeCO$_3$ coated samples using the proposed model discussed in section 4.2. Although, for this discussion there is no need to distinguish between oxidation and reduction resistances as in Figure 16, and the combined effects of the two could be analyzed using the $R_p$. Therefore for simplicity, the equivalent circuit for the system could be reduced to a simple Randle’s circuit.

Assuming a constant potential in the system, first we analytically solved the interfacial potential drop across $R_p$ shown in Equation (29) as:

$$E = \frac{E_{DC}}{\sqrt{\left(1 + \frac{R_s}{R_p}\right)^2 + (\omega R_s C)^2}} e^{-j\varnothing} + \frac{E_0}{\sqrt{\left(1 + \frac{R_s}{R_p}\right)^2 + (\omega R_s C)^2}} e^{-\frac{\pi}{2} - j\varnothing}$$

where $E$ is the potential drop across the capacitor, $E_{DC}$ is the applied DC potential, $E_0$ is the applied RMS AC potential, $R_s$ is the solution resistance, $C$ is the capacitance and $R_p$ is the polarization resistance. Also the value of $\varnothing$ could be calculated by:

$$\varnothing = \tan^{-1} \frac{\omega R_s C}{1 + \frac{R_s}{R_p}}$$

$$\text{(30)}$$
Using the numerical solutions of the Equation (29) for the constant parameters in Table 18, Figure 88, Figure 89 and Figure 90 were obtained. In these figures the effects of the variation of the values of $R_p$, C and $R_s$ on $i_F$, $i_C$, $i_T$ and E are shown. The values of $i_F$, $i_C$, $i_T$ and E are equivalent to faradaic current density, capacitive current density, total current density ($=i_C+i_F$) and potential drop across $R_p$ respectively. It should be noted that in each figure one of the values of $R_p$, C and $R_s$ have been varied while the other two have remained constant.

In Figure 88 $R_p$ is the changing parameter. It can be seen that the increase in $R_p$ will result in increase of the interfacial potential drop (Figure 88[d]). Since C has remained constant, the increase in E results in increase of $i_C$ (Figure 88[c]). Despite of the increase in E, the change in $i_F$ has been influenced rather by the increase of $R_p$ and has therefore decreased (Figure 88[a]). The value of $i_T$, depending on the amount of the change in each of its components ($i_F$ and $i_C$) could decrease or increase. For the specific set of input parameters used, it can be seen that at first, the increase in $R_p$ results in a sharp drop in the value of $i_T$. After that further increase in $R_p$, results in a slight increase of $i_T$ (see the magnified portion in Figure 88[b]).

<table>
<thead>
<tr>
<th>$R_p$</th>
<th>$R_S$</th>
<th>C</th>
<th>$E_{DC}$</th>
<th>$E_{AC}$</th>
<th>$f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>100:10:10000</td>
<td>100</td>
<td>1E-5</td>
<td>0.3</td>
<td>0.6</td>
<td>60</td>
</tr>
<tr>
<td>4500</td>
<td>100</td>
<td>1E-8:1E-6:1E-4</td>
<td>0.3</td>
<td>0.6</td>
<td>60</td>
</tr>
<tr>
<td>4500</td>
<td>10:10:1000</td>
<td>1E-5</td>
<td>0.3</td>
<td>0.6</td>
<td>60</td>
</tr>
</tbody>
</table>

Table 18.Input parameters used to obtain Figure 88, Figure 89 and Figure 90 respectively.
Figure 88. Influence of the variation of the $R_p$ on a) polarization current, b) total current, c) capacitive current and d) interfacial potential across the capacitor in the Randles circuit.

Figure 89 shows the effects of the change of $C$ while $R_P$ and $R_S$ have remained constant. The decrease in the value of $C$ (right to left in figure) has resulted in the increase in $E$ (Figure 89 [d]) which itself leads to the increase in $i_F$ (Figure 89 [a]). Again, despite the increase in $E$, the value of $i_C$ have decreased due to the dominant effect of the decrease in $C$ (Figure 89 [c]). This also results in the decrease in $i_T$ due to the higher values of $i_C$ over $i_F$ (Figure 89 [b]).

For Figure 90, which shows the effect of variation $R_S$, the values $E$, $i_F$, $i_C$ and therefore $i_T$, all monotonically decreased with the increase in $R_S$. This is because here, $C$ and $R_P$ have been constant and therefore, $i_F$ and $i_C$ have only been influenced by $E$.

The effects shown in Figure 88 to Figure 90 will be used as a tool for explaining some of the otherwise confusing results that will be presented in the following sections.

These results show that the decrease in the total current ($i_T$) doesn’t necessarily lead the decrease in the C.R.(proportional to $i_F$). This is against the commonly accepted idea of the effect of the total current on C.R.. The notion that higher total current leads to higher corrosion rate has even been the basis for determination of AC mitigation criteria.
The important parameter that affects C.R is the faradaic current density, which depends on polarization resistance, solution resistance and the interfacial capacitance.

![Figure 89](image1)

**Figure 89.** Influence of the variation of the C on a) polarization current, b) total current, c) capacitive current and d) interfacial potential across the capacitor in the Randle’s circuit.

![Figure 90](image2)

**Figure 90.** Influence of the variation of the R_s on a) polarization current, b) total current, c) capacitive current and d) interfacial potential across the capacitor in the Randle’s circuit.

The purpose for the above analysis was mainly to obtain a general idea of different effects of contributing parameters in AC corrosion rate. Because the Randle’s
circuit does not differentiate the $i_O$ and $i_R$, to make sure that the overall behavior shown in
Figure 88 to Figure 90 are consistent with what would be obtained from the model
proposed in section 4.2, a comparison of model results have been made which is shown
in Table 19. The input values were taken from Table 1 with DC potential of -0.67 and AC
RMS of 0.6 V at 60 Hz.

Solution was obtained by altering the values of C, $R_s$ and $\beta_a$ (proportional to $R_p$).
These values are shown in Table 19. The top row is the reference set of values and other
rows have one of the parameters changed (highlighted).

<table>
<thead>
<tr>
<th>C</th>
<th>$R_s$</th>
<th>$\beta_a$</th>
<th>$i_O$</th>
<th>$i_R$</th>
<th>$i_{C(RMS)}$</th>
<th>$i_{RMS}$</th>
<th>$E_{peak}$</th>
<th>$E_{mean}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1E-3</td>
<td>70</td>
<td>0.089</td>
<td>6.1e-5</td>
<td>-6.21e-5</td>
<td>0.00876</td>
<td>0.00876</td>
<td>-0.607</td>
<td>-0.669</td>
</tr>
<tr>
<td>1E-4</td>
<td>70</td>
<td>0.089</td>
<td>1.17e-3</td>
<td>-1.86e-4</td>
<td>0.0072</td>
<td>0.0077</td>
<td>-0.469</td>
<td>-0.737</td>
</tr>
<tr>
<td>1E-5</td>
<td>70</td>
<td>0.089</td>
<td>2.66e-3</td>
<td>-1.1e-3</td>
<td>0.0013</td>
<td>0.00496</td>
<td>-0.467</td>
<td>-0.781</td>
</tr>
<tr>
<td>1E-3</td>
<td>200</td>
<td>0.089</td>
<td>5.3e-5</td>
<td>-6.2e-5</td>
<td>0.00316</td>
<td>0.00316</td>
<td>-0.645</td>
<td>-0.667</td>
</tr>
<tr>
<td>1E-3</td>
<td>70</td>
<td>0.02</td>
<td>2-4</td>
<td>-6.4e-5</td>
<td>0.00873</td>
<td>0.00875</td>
<td>-0.645</td>
<td>-0.667</td>
</tr>
<tr>
<td>1E-3</td>
<td>70</td>
<td>0.005</td>
<td>4.6e-4</td>
<td>-6.7e-5</td>
<td>0.00866</td>
<td>0.00879</td>
<td>-0.659</td>
<td>-0.692</td>
</tr>
</tbody>
</table>

This table shows that by decreasing the capacitance value, there is an increase in
both oxidation and reduction currents. This is a result of increase and decrease of the
peak value and mean value of the interfacial potentials respectively, while there is a
decrease in both capacitive and total current. Also by increasing $R_s$, all current values
decreased. This is due to the decrease of the peak value and increase of the mean value
of the interfacial potentials. Finally, by the decrease in $\beta_a$ which is equivalent to the decrease of the polarization resistance in the Randle’s circuit, both $i_o$ and $i_R$ increased. However, since there was a constant decrease in $i_C$, $i_T (=i_o+i_R+i_C)$ experienced a decrease followed by an increase. All the above trends are consistent with those discussed before on the results obtained from the Randle’s circuit.

8.5.3 Scale Formation Influence on AC Corrosion Behavior of X65 Carbon Steel in NS4 Solution

Electrochemical experiments in presence of AC potential of 3 V under cathodic protection condition, on X65 pipeline steel with artificially made calcium carbonate and iron carbonate scales in soil simulant solution were conducted. Figure 91 shows current densities obtained by mass loss analysis in presence of AC at different DC biases on scaled samples and compares them with that of the bare X65 carbon steel. It is noted here that in this figure, the current density values have been calculated based on the same area as used for X65 coupons, which is the total area of the bare sample before coating. This area is not the actual area involved in the corrosion reaction for the samples that are initially mostly covered with calcium carbonate or iron carbonate scales. The actual area from which the current is passed through is the uncovered active spots. This is important because the life of a given pipe would depend on the actual corrosion penetration rate within the area of the pinholes.

To obtain corrosion rates based on the actual pinhole bottom areas, the estimated effective areas of the uncoated metal as explained in previous sections cannot be used since those are only the initial conditions of the samples. The amount of uncovered area is subject to change during the progress of the corrosion process due to the delamination
and pulverization of the scales by the corrosion products. It was indeed observed both visually and with SEM imaging that the active area of corrosion for the specimens changed dynamically during the corrosion test. This makes it virtually impossible to come up with a precise measurement of the corrosion rates in the active surfaces. More importantly, not a general correction factor could be applied to the data because of the fact that the way the active areas changed during the AC experiments varied significantly from one scale to another or even from one DC bias to another.

![Figure 91](image.png)

Figure 91. Comparison of current densities obtained by mass loss analysis and considering of apparent area on X65, X65/CaCO$_3$ and X65/FeCO$_3$ in NS4 solution with 3V applied AC.

The evolution of the scaled surfaces during the corrosion test for each of the experiments will be explained in detail as follows. Accordingly, each of the data points shown in
Figure 91 will be adjusted to a closer approximation based on the way that each scale evolved during the experiment.

The active surface area prior to AC experiment could be calculated by the ratio of the charge transfer resistance of the bare metal ($R_C$) to that of the coated samples before AC experiments using the EIS technique. The percentage of the initial active area for each of the samples that were used in the corrosion tests are brought in Table 20. It is noteworthy that the pinhole area calculated this way for CaCO$_3$ scaled samples are in acceptable agreement with that calculated for the same samples in section 8.3.5 using the $I/I_0$ values (shown in Table 21).

Table 20. The uncovered active area percentage before AC experiment.

<table>
<thead>
<tr>
<th>Material</th>
<th>Sample name</th>
<th>$R_C$-initial Before AC experiment ($\Omega$)</th>
<th>Uncovered area before AC test (%)</th>
<th>$\frac{R_C\text{-initial}(X65)}{R_C\text{-initial}} \times 100$</th>
</tr>
</thead>
<tbody>
<tr>
<td>X65</td>
<td>R</td>
<td>80</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td></td>
<td>A0</td>
<td>2057</td>
<td>3.89</td>
<td></td>
</tr>
<tr>
<td></td>
<td>A1</td>
<td>1200</td>
<td>6.67</td>
<td></td>
</tr>
<tr>
<td>X65/CaCO$_3$</td>
<td>A2</td>
<td>795.5</td>
<td>10.06</td>
<td></td>
</tr>
<tr>
<td></td>
<td>A3</td>
<td>1801</td>
<td>4.44</td>
<td></td>
</tr>
<tr>
<td></td>
<td>B0</td>
<td>2138</td>
<td>3.74</td>
<td></td>
</tr>
<tr>
<td>X65/FeCO$_3$</td>
<td>B1</td>
<td>356.5</td>
<td>29.65</td>
<td></td>
</tr>
<tr>
<td></td>
<td>B2</td>
<td>269.8</td>
<td>38.72</td>
<td></td>
</tr>
<tr>
<td></td>
<td>B3</td>
<td>206.6</td>
<td>22.44</td>
<td></td>
</tr>
</tbody>
</table>
Table 21. Uncovered surface area of X65/CaCO$_3$ samples after CaCO$_3$ deposition obtained from Figure 70.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>I/10</th>
<th>Uncovered percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>A0</td>
<td>7E-3</td>
<td>3</td>
</tr>
<tr>
<td>A1</td>
<td>8E-3</td>
<td>4</td>
</tr>
<tr>
<td>A2</td>
<td>2E-2</td>
<td>4</td>
</tr>
<tr>
<td>A3</td>
<td>4E-3</td>
<td>3</td>
</tr>
</tbody>
</table>

The final active area was then calculated based on the reduction in the Rc values after the AC corrosion test as shown in Table 22. The active area fractions for CaCO$_3$ and FeCO$_3$ scaled samples are summarized in Table 23 and Table 24 respectively. Figure 92 shows the adjusted values or closest obtainable approximation of the actual corrosion rates for each of the data points in Figure 91. For the case of X65/CaCO$_3$, for the first two data points at lower DC biases (-0.77 and -0.7 V$_{SCE}$) the corrosion progression did not significantly compromise the structural integrity of the scale. The surface areas of the pinholes were therefore estimated by averaging the initial and final areas of the pinholes.

Table 22. The uncovered active area percentage after AC experiment with 3V RMS at 60 Hz.

<table>
<thead>
<tr>
<th>Material</th>
<th>Sample name</th>
<th>DC biases (V$_{SCE}$)</th>
<th>Rc-final (Ω)</th>
<th>Uncovered area after AC test $\frac{R_{c-\text{initial(X65)}}}{R_{c-\text{final}}} \times 100$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X65/CaCO$_3$</td>
<td>A1</td>
<td>-0.77</td>
<td>876</td>
<td>9.13</td>
</tr>
<tr>
<td></td>
<td>A2</td>
<td>-0.7</td>
<td>629.6</td>
<td>12.71</td>
</tr>
<tr>
<td></td>
<td>A3</td>
<td>-0.65</td>
<td>91.7</td>
<td>87.24</td>
</tr>
</tbody>
</table>
Table 22 (continued). The uncovered active area percentage after AC experiment with 3V RMS at 60 Hz.

<table>
<thead>
<tr>
<th>Material</th>
<th>Sample name</th>
<th>DC biases (V&lt;sub&gt;SCE&lt;/sub&gt;)</th>
<th>Rc-final (Ω)</th>
<th>Uncovered area after AC test (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X65/CaCO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>A4</td>
<td>-0.6</td>
<td>84.8</td>
<td>94.34</td>
</tr>
<tr>
<td></td>
<td>B1</td>
<td>-0.77</td>
<td>1800</td>
<td>4.44</td>
</tr>
<tr>
<td></td>
<td>B2</td>
<td>-0.7</td>
<td>149.2</td>
<td>76.05</td>
</tr>
<tr>
<td></td>
<td>B3</td>
<td>-0.65</td>
<td>105.2</td>
<td>77.37</td>
</tr>
<tr>
<td></td>
<td>B4</td>
<td>-0.6</td>
<td>103.4</td>
<td>53.62</td>
</tr>
</tbody>
</table>

Table 23. The uncovered active area percentage of X65/CaCO<sub>3</sub> before and after AC experiment with 3V RMS at 60 Hz.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>DC biases</th>
<th>Uncovered area prior to AC test (%)</th>
<th>Uncovered area after AC test (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>-0.77</td>
<td>3.89</td>
<td>9.13</td>
</tr>
<tr>
<td>A2</td>
<td>-0.7</td>
<td>6.67</td>
<td>12.71</td>
</tr>
<tr>
<td>A3</td>
<td>-0.65</td>
<td>10.06</td>
<td>87.24</td>
</tr>
<tr>
<td>A4</td>
<td>-0.6</td>
<td>4.44</td>
<td>94.34</td>
</tr>
</tbody>
</table>
Table 24. The uncovered active area percentage of X65/FeCO$_3$ before and after AC experiment with 3V RMS at 60 Hz.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>DC biases</th>
<th>Uncovered area prior to AC test (%)</th>
<th>Uncovered area after AC test (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>-0.77</td>
<td>3.74</td>
<td>4.44</td>
</tr>
<tr>
<td>B2</td>
<td>-0.7</td>
<td>29.65</td>
<td>76.05</td>
</tr>
<tr>
<td>B3</td>
<td>-0.65</td>
<td>38.72</td>
<td>77.37</td>
</tr>
<tr>
<td>B4</td>
<td>-0.6</td>
<td>22.44</td>
<td>53.62</td>
</tr>
</tbody>
</table>

Figure 92. Current densities obtained by mass loss analysis and considering the uncovered area of scaled samples in NS4 solution with 3V applied AC at 60 Hz.

The corrosion rate of X65/CaCO$_3$ samples at higher DC potentials ($E_{DC}=-0.65$ and $-0.6V_{SCE}$) was much higher. At these potentials, the calcareous layer did not remain stable.
(judging by the physical appearance of the samples shown in Figure 93[b]) and pulverized at early stages of the experiment. This means that much of the corrosion has occurred with an active area close to the final covered area which is not very different than the apparent area (Table 23). Therefore, the approximated value of the current density for $E_{DC}$ of -0.65 and -0.6 $V_{SCE}$ are provided based on the final active area instead of the average as highlighted in Table 23.

(a)  
(b)  

Figure 93. The surface area of the X65/CaCO$_3$ sample a) Samples after 30 days of exposure to 3V AC at CP=−0.77$V_{SCE}$ in NS4 solution b) during the experiment with AC at DC=−0.65$V_{SCE}$.

For the case of X65/FeCO$_3$ the situation is more complex. The active area of corrosion for these tests changed in a range that was neither close to the initial uncovered area nor to the apparent area. While the physical appearance of the samples during the corrosion test did not show significant pulverization, however, as judged by the sizeable reduction in the EIS resistance values (shown in Table 24), it can be said that a considerable portion of the initially covered area have been corroded. Therefore, the current density values calculated for X65/FeCO$_3$ samples in Figure 92 were also estimated based on the average of the initial and final active area as highlighted in Table 24.
Comparing the adjusted values of current density shown in Figure 92, it can be said that the corrosion rate in X65/FeCO$_3$ samples is lower than that of the X65/CaCO$_3$ and the bare metal. This could be due to the existence of semi-passive FeCO$_3$ layer (as discussed in section 8.4.1) that could, to some extent, protect the substrate. The CaCO$_3$ does not provide such protection and based on the observations explained above is also not as stable as the FeCO$_3$ scale.

These findings are in agreement with SEM images taken after AC corrosion test under $-0.6V_{SCE}$ DC bias and 3V RMS at 60 Hz, taken after mechano-chemical removal of scale and corrosion product using Clark solution shown in Figure 94 (a)-(f). As can be seen after the removal of scale and corrosion products, the surface features for the X65 and X65/CaCO$_3$ are quite similar. For X65/FeCO$_3$ however, most of the surface has remained un-attacked and the existing pits seem to be shallower.

(a)  
(b)

Figure 94. SEM micrographs after AC experiments at DC=-0.6$V_{SCE}$ with 3V RMS at 60 Hz. (a)&(b) bare sample (API X65 carbon steel).
Figure 94 (continued). SEM micrographs after AC experiments at DC=−0.6V_{SCE} with 3V RMS at 60 Hz, (c)&(d) X65/CaCO₃, (e)&(f) X65/FeCO₃.
Artificial CaCO$_3$ and FeCO$_3$ scale layers were grown on the X65 carbon steel to investigate the influence of scale formation on AC corrosion rate. The corrosion behavior of samples with scale in presence of AC potentials, were compared to that of the bare X65 steel. The CaCO$_3$ coating was obtained and optimized using potentiostatic experiments at different DC potentials. Also, the FeCO$_3$ layer was precipitated on X65 carbon steel in CO$_2$ atmosphere and was characterized by SEM and in-situ EIS analysis. From these investigations the following conclusions were achieved:

- During CaCO$_3$ deposition, a monotonic decrease of the current, confirmed the deposition of CaCO$_3$ due to the increases of the interfacial pH value, which corresponds to decrease of the oxygen reduction rate.

- At the beginning of CaCO$_3$ deposition (less than three hours), for rotation speeds higher than 600rpm, a sudden decrease in the current values was observed that is due to the convection controlling kinetics of the oxygen reduction reaction.

- SEM and XRD characterizations confirmed the formation of calcite layer at DC potentials of -0.8 and -1 V$_{SCE}$ but due to the hydrogen evolution at -1V$_{SCE}$, the potential of -0.8V$_{SCE}$ was selected as a deposition potential for the rest of the experiments.
• SEM micrographs along with EIS results showed that when \( I/I_0 \) becomes less than 0.1, about more than 90 percent of the surface of the metal is covered with calcareous layer.

• X65 carbon steel corrosion in CO\(_2\) atmosphere at high pH and temperature, led to formation of compact siderite layer.

• Fully covered metal substrate with FeCO\(_3\) was accompanied by an abrupt increase in the corrosion potential value due to the self-passivation of the X65 carbon steel surface.

• FeCO\(_3\) deposition time of 20 hours was confirmed to have fully covered the substrate based on both in-situ EIS fitting results and FIB cross section images.

• Against what might be the present understanding of the effect of current density \( (i) \) on the AC corrosion, it was shown that \( i \) is not a good candidate as a basis of AC mitigation criteria.

• Also, it was observed that by decreasing the DC potential (increase in CP protection), there was a decrease in corrosion rate with AC.

• The corrosion rate of the CaCO\(_3\) and FeCO\(_3\) coated specimens could not be calculated with high accuracy due to the difficulty in estimating the actual active area of the metal through the pores of the scale layer. However, closest possible approximation was made based on the behavior of the evolution of the surface for each sample.

• Although in presence of AC experiments, the total current on both scaled samples reduced, but after adjusting the current density \( (i) \) with the approximated surface area it was shown that this is only true for the X65/FeCO\(_3\) samples.
CHAPTER X
FUTURE STUDIES

The main issues concerning this research were to find out the influence of different parameters on the AC corrosion rate; and more importantly, understand the mechanism by which AC causes corrosion. However due to continuous changes of the active area of the sample during corrosion process, determination of real corrosion rate of scaled samples was not possible which requires further investigations. Additionally to study the influence of the soil environment on AC corrosion rate, AC experiments in field could be performed. This could be evaluated by burring and electrically bonding the X65 carbon steel samples to an active pipeline parallel to a transmission power line. Results from these corrosion experiments as well the necessary soil and transmission line parameters for the location will be used as parameters in the proposed AC mechanism. Similar to laboratory experiments, other than bare X65 carbon steel, coupons with artificial scales will be also exposed to the soil environment in the field, however, for longer periods of time. The AC current and potential on the pipeline will also be monitored with time such that it can later be correlated with results from corrosion experiments.


71. AC Corrosion on Cathodically Protected Pipelines: Guidelines for Risk Assessment and Mitigation Measures. (Booklet, Ceocor, 2001).


177


APPENDIX

Matlab Solution for Equation (15)

%All electrochemical potentials are vs. SCE.

% inputs units
R %Ω.cm^2 (solution resistance).
C %F.cm^-2 (interfacial capacitance).
i_corr %A.cm^-2 (corrosion current density without AC).
E_corr %V (corrosion potential without AC).
B_a %V/dec (anodic Tafel slope).
B_c %V/dec (cathodic Tafel slope).
E_DC %V (DC bias potential).
i_lim %A.cm^-2 (oxygen limiting current density).
E_AC %V (AC potential amplitude).
f %Hz (frequency).
t0 %S (initial time).
tf %S (final time).
dt %S
B_H %V (Hydrogen Tafel slope).
i_H %A.cm^-2 (Hydrogen exchange current density).
w=2*pi()*f; %angular frequency.

tspan = [t0:dt:tf];

%%

%Initial conditions:

%initial current density.

%i0= -(i_corr*(exp(2.3*(E_DC-E_corr)/B_a)-exp(2.3*(-E_DC+E_corr)/B_c))... 
   ./((1-i_corr/i_lim+i_corr/i_lim*exp(2.3*(-E_DC+E_corr)/B_c))) - ........
   i_H*exp(-2.3*(E_DC+0.244)/B_H)). Ref55

%initial potential.

%E0=E_DC-i0*R

E0=E_DC-(i_corr*(exp(2.3*(E_DC-E_corr)/B_a)-exp(2.3*(-
E_DC+E_corr)/B_c))... 
   ./((1-i_corr/i_lim+i_corr/i_lim*exp(2.3*(-E_DC+E_corr)/B_c))) - .........
   i_H*exp(-2.3*(E_DC+0.244)/B_H))*R;

%%

%equation (19).

rhs = @(t,E) -E/(C*R)-(i_corr*(exp(2.3*(E-E_corr)/B_a) ... 
   -exp(2.3*(-E+E_corr)/B_c)/(1-i_corr/i_lim+i_corr/i_lim ... 
   *exp(2.3*(-E+E_corr)/B_c)))-i_H*exp(-2.3*(E+0.244)/B_H))/C ... 
   +(E_DC+E_AC*sin(w*t))/(C*R);

options = odeset('AbsTol',1e-9,'RelTol',1e-9);

[t,E]=ode23s(rhs,tspan,E0);
%%

%current densities:

\[ i_a = i_{corr} \exp(2.3 \times (E - E_{corr})/B_a) ; \]  
\hspace{1cm} \text{%anodic current density.}

\[ i_c = (-i_{corr} \exp(2.3 \times (E + E_{corr})/B_c)) / ... \]

\[ (1 - i_{corr}/i_{lim} + i_{corr}/i_{lim} \exp(2.3 \times (E + E_{corr})/B_c)) ... \]

\[ -i_H \exp(-2.3 \times (E + 0.244)/B_H) ; \]  
\hspace{1cm} \text{%cathodic current density.}

\[ \text{dE} = \text{diff}(E) ; \]
\[ \text{dt} = \text{diff}(t) ; \]
\[ \text{dEdt} = \text{dE} / \text{dt} ; \]
\[ i_{CC} = C \times \text{dEdt} ; \]  
\hspace{1cm} \text{%double layer current density.}

\[ i = i_a + i_c ; \]
\[ i_{total} = i(2:end) + i_{CC} ; \]  
\hspace{1cm} \text{%total current density.}

\[ i_{avg} = \text{trapz}(t,i_a)/tf ; \]  
\hspace{1cm} \text{%anodic time averaged current density.}

\[ i_{total\_avg} = \text{trapz}(t(2:end),i_{total})/tf ; \]  
\hspace{1cm} \text{%total time averaged current density.}
## Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$i_{corr}$</td>
<td>Corrosion current density ($A.cm^{-2}$)</td>
</tr>
<tr>
<td>$i_0$</td>
<td>Oxidation current density ($A/cm^2$)</td>
</tr>
<tr>
<td>$E_{corr}$</td>
<td>Corrosion potential (V)</td>
</tr>
<tr>
<td>$i_r$</td>
<td>Reduction current density ($A/cm^2$)</td>
</tr>
<tr>
<td>$\beta_a$</td>
<td>Anodic Tafel slope (V/dec)</td>
</tr>
<tr>
<td>$i_C$</td>
<td>Capacitive current density ($A/cm^2$)</td>
</tr>
<tr>
<td>$\beta_c$</td>
<td>Cathodic Tafel slope for oxygen reduction reaction (V/dec)</td>
</tr>
<tr>
<td>$i_T$</td>
<td>Total current density passing through the system, capacitive + Faradaic ($A/cm^2$)</td>
</tr>
<tr>
<td>$E$</td>
<td>Potential across the Faradaic resistance (V)</td>
</tr>
<tr>
<td>$E_T$</td>
<td>Total applied potential (V)</td>
</tr>
<tr>
<td>$i_1$</td>
<td>Oxygen limiting current density ($A/cm^2$)</td>
</tr>
<tr>
<td>$E_{DC}$</td>
<td>DC potential (V)</td>
</tr>
<tr>
<td>$i_{H2}^0$</td>
<td>Hydrogen exchange current density ($A/cm^2$)</td>
</tr>
<tr>
<td>$E_0$</td>
<td>Peak potential (V)</td>
</tr>
<tr>
<td>$\beta_{H2}$</td>
<td>Cathodic Tafel slope for hydrogen evolution reaction (V/dec)</td>
</tr>
<tr>
<td>$r$</td>
<td>The ratio of anodic to cathodic Tafel slopes</td>
</tr>
<tr>
<td>$R_s$</td>
<td>Solution resistance ($\Omega.cm^2$)</td>
</tr>
<tr>
<td>RMS</td>
<td>Root mean square value</td>
</tr>
<tr>
<td>$R_o$</td>
<td>Oxidation resistance ($\Omega$)</td>
</tr>
<tr>
<td>AC(+)</td>
<td>The time-averaged positive AC current density ($A/cm^2$)</td>
</tr>
<tr>
<td>$R_r$</td>
<td>Reduction resistance ($\Omega$)</td>
</tr>
<tr>
<td>AC(-)</td>
<td>The time-averaged negative AC current density ($A/cm^2$)</td>
</tr>
<tr>
<td>$C_i$</td>
<td>Interfacial capacity ($F/cm^2$)</td>
</tr>
<tr>
<td>AC(avg)</td>
<td>The time-averaged AC current density ($A/cm^2$)</td>
</tr>
<tr>
<td>$i_w$</td>
<td>Current density obtained from mass loss ($A.cm^2$)</td>
</tr>
<tr>
<td>$f$</td>
<td>Frequency (Hz)</td>
</tr>
</tbody>
</table>