Corrosion research on rock bolts and steel sets for sub-surface reinforcement of the Yucca Mountain repository

Dhanesh Chandra  
*University of Nevada, Reno*, dchandra@scs.unr.edu

Jaak J.K. Daemen  
*University of Nevada, Reno*, daemen@mines.unr.edu

Amy J. Smieicinski  
*University of Nevada, Las Vegas*, smieicins@unlv.nevada.edu

Follow this and additional works at: https://digitalscholarship.unlv.edu/yucca_mtn_pubs

Part of the Metallurgy Commons, and the Structural Materials Commons

Repository Citation

Available at: https://digitalscholarship.unlv.edu/yucca_mtn_pubs/73

This Technical Report is brought to you for free and open access by the Yucca Mountain at Digital Scholarship@UNLV. It has been accepted for inclusion in Publications (YM) by an authorized administrator of Digital Scholarship@UNLV. For more information, please contact digitalscholarship@unlv.edu.
Corrosion Research on Rock Bolts and Steel Sets for Sub-surface Reinforcement of the Yucca Mountain Repository
Subtask of Long-Term Drift Stability
Task 18 YM Project
Document ID: TR-03-017
Prepared for U.S. DOE/UCCSN Cooperative Agreement Number DE-FC28-98NV12081
April 23, 2004
2000-2003
submitted to United States Department of Energy
Office of Civilian Defense Radioactive Waste Management
Yucca Mountain Project
1551 Hillshire Drive, Suite A
Las Vegas NV 89134-6321
submitted by University of Nevada, Reno
Dhanesh Chandra, Co-PI (Corrosion Team Leader)
Venugopal Arjunan, Post Doctoral Fellow
Ahmet Yilmaz*, Ph.D. YM Project, UNR 2003
Vinay Deodeshmukh*, MS, YM Project, UNR 2002
Joshua Lamb*, Ph.D Candidate, YM Project, UNR 2004
Jaak Daemen, PI (Project Director)

Prepared by Corrosion Team Leader
Dhanesh Chandra
Co-Principal Investigator
Metallurgical and Materials Engineering, Mail Stop 388
College of Engineering
University of Nevada, Reno 89557

Project Director
Jaak Daemen
Principal Investigator
Mining Engineering, Mail Stop 173
Mackay School of Mines
University of Nevada, Reno 89557

Originator: Dhanesh Chandra

Approvals:

Technical Reviewer, Jaak Daemen
Apr. 23, 2004
Approval Date

Principal Investigator, Jaak Daemen
Apr. 23, 2004
Approval Date

QA Manager, Amy Smiecinski
4-23-04
Approval Date
EXECUTIVE SUMMARY

Corrosion resistance of Yucca Mountain (YM) carbon steel rock bolt (0.44%C) and I-beam steel sets (0.08%C) towards electrochemical/general corrosion, stress corrosion cracking (SCC), and hydrogen embrittlement (HE) susceptibility has been determined using simulated YM waters in this Task 18 for YM site underground repository tunnel support. These findings show the corrosion behavior of these structural support members with and without applied stresses in simulated YM environments. The simulated YM waters were increased in nominal concentrations from 1x to 100x (three different levels) for electrochemical and other corrosion studies. The effect of temperature, of significance to YM repository, on the corrosion behavior are presented using electrochemical as well as electro-mechanical studies. Conventional ASTM general corrosion tests, such as (ASTM G-85 YM water spray Fog tests), ASTM G-31 (Immersion Tests), ASTM G-85 (modified YM water Spray), ASTM G-60 (Cyclic Humidity) tests were performed. Electrochemical corrosion tests include potentiodynamic tests and impedance spectroscopy, stress corrosion cracking, hydrogen cracking. In addition, effect isolation of ions such as HCO$_3^-$, SiO$_2^-$, that play critical role in affecting the corrosion rates of steels, have been determined. Microstructural and phase characterization of rock bolt and I-beam materials were performed by using scanning electron microscopy (SEM), x-ray photoelectron microscopy (XPS), and x-ray diffraction (XRD) analyses.

In the present study, and we have measured higher corrosion rates for the (0.08%C) low carbon steel I-beam as compared to higher carbon (0.44%C) rock bolts; normally high carbon steels will undergo more corrosion than low carbon steels. It postulated that it may be due to: (a) Environmental effects due to the electrochemical reactions in this YM (electrolyte) in which dissolution as well as deposition of extrinsic ions are dynamic processes that make the corrosion process more complex, (b) Uniform distribution of carbides in rock bolts due increased Pearlite areas, as compared to the I-beams that have much smaller amounts of Pearlite.

The variation of corrosion rates (CR) of rock bolts and I-beam as a function of temperature (between 25° and 85°C) is very interesting; these have been performed using de-aerated and aerated conditions showing lower and upper CR limits. A striking result is that the corrosion rate of rock bolts and I-beam increased with temperature from 25° to 45°C, thereafter there is a decrease in corrosion rate at higher temperatures for the 100x YM waters (65° and 85°C). This CR maxima appears around 45°C for both these steels, in most cases, particularly, 100x (nominal) YM waters. This can be explained taking into account the following competing factors: (1) temperature and ionic concentration generally increase the CR due to increased reaction rates, and on the other hand (2) dissolved oxygen effects decrease as the temperature is increased; it appears that the convergence occurs around 45°C after which the corrosion rates start to decrease. The decrease in CR at higher temperatures can be mainly attributed to the decrease in oxygen solubility and the adsorption of ionic species such as Mg and Si providing resistance to further corrosion, as determined by XPS analyses. The corrosion rates obtained for the rock bolts from polarization tests using deaerated and aerated electrolytes are plotted in Figure 1(a). These plots show that in deaerated condition the corrosion rates are significantly low as compared to the oxygenated electrolytes; thus these deaerated conditions show lower corrosion limits. However, in the case of rock bolts, at 1x and 10x the corrosion rate increased with temperature up to 85°C (Figure 1(a)). In the case of I-beams, this trend in the decrease in corrosion rates was observed at all concentration levels [1, 10, and 100x in Figure 1(b)]. Data points, for example, CH-887 indicates cyclic humidity corrosion rates of 887 μm/year, and other general or immersion corrosion tests have been incorporated in Figures 1 (a and b) and show a reasonable agreement with the electrochemical results.

Corrosion Rates (CR) for rock bolts and I-beam Steel Sets (supplied from YM site) measured using YM waters as per ASTM-G5 (short term) potentiodynamic polarization tests as function of temperature and concentration of YM waters are summarized below (μm/year):  
- **Rock Bolts-Nitrogenated (Deaerated) Conditions for 1x, 10x, and 100x YM waters**: CR Range @25°C: 35-50 μpy, CR Range @45°C: 55-65 μpy, CR Range @65°C: 107-110 μpy, CR Range @85°C: CR Range: 159-162 μpy.  
- **Rock Bolts-Oxygenated (Aerated) Conditions for 1x, 10x, and 100x YM waters**: CR Range @25°C: 100-210 μpy, CR Range @45°C: 250-480 μpy, CR Range @65°C(1x and 10x): 550-710 μpy and CR Range @65°C(100x): 220 μpy, CR Range @85°C(1x and 10x): 1050-1100 μpy and CR Range @65°C(100x): 150 μpy.  
- **Steel Sets-Nitrogenated (Deaerated) Conditions for 1x, 10x, and 100x YM waters**: CR Range @25°C(1x-10x): 43-66 μpy, CR Range @25°C(100x): 15 μpy CR Range @45°C(1x-10x): 46-68 μpy, CR Range @45°C(100x): 33 μpy, CR Range @65°C(1x-10x): 53-71 μpy, CR Range @65°C(100x): 64 μpy, CR Range @85°C (1x-10x): 64-110 μpy, CR Range @85°C (100x): 55 μpy.
• Steel Sets-Oxygenated (Aerated) Conditions for 1x, 10x, and 100x YM waters: CR Range @25°C(1x-10x): 216-370 μpy, CR Range @25°C(100x): 794 μpy CR Range@45°C(1x-10x): 769-1103 μpy , CR Range@45°C(100x): 1384 μpy ,CR Range @65°C(1x-10x): 382-934 μpy , CR Range @65°C(100x): 82 μpy, CR Range @85°C (1x-10x): 163-351 μpy , CR Range @ 85°C (100x): 71 μpy. 10x): 163-351 μpy, CR Range @ 85°C (100x): 71 μpy.

Figure 1(a) Effect of temperature and electrolyte concentration (1, 10, and 100x), and oxygen (aerated/deaerated) concentration on the corrosion rate (μm/year) of Rock bolts. Note: the data points in bold symbols with corrosion rates in μm/year are of the conventional (long-term) ASTM Immersion experiments, YM water spray and humidity tests on rock bolt samples. (Nitrogenated Curve: Corrosion rates from Table 4.3; Oxygenated Curve: Corrosion rates from table 4.4; Immersion tests-Air corrosion rates as determined from Fig. 7.10; YMW. Spray corrosion rates as determined from Fig. 7.11; Cyclic humidity corrosion rate from: 018VA.001 File: cyclic humidity.doc)

Figure 1(b) Effect of temperature and electrolyte concentration (1, 10, and 100x), and oxygen (aerated/deaerated) concentration on the corrosion rate of I-beams. Note the data points of long-term YM water spray and humidity tests. (Oxygenated and Nitrogenated curves from corrosion rates found in Table 5.1; YM Water spray corrosion rate as determined from Fig. 7.11; Cyclic humidity corrosion rate from: 018VA.001 File: cyclic humidity.doc)

Electrochemical hydrogen permeation through steel plates revealed that the medium carbon steel are more resistant towards hydrogen induced cracking (HIC) than the low carbon steel as the critical hydrogen concentration (C_H) was found to be higher (36.15ppm) than low carbon steel (8.13ppm); in this case there were no external stresses applied to the steels. The density of trapping sites in medium carbon steel and improved the HIC resistance due to the presence of high C, Mn and S contents. The measured diffusivity of medium carbon steel was lower than that of low carbon steel due to increased absorption of hydrogen at irreversible sites in rock bolt steel. Hydrogen concentration values obtained for carbon steels in YM ground water electrolytes indicate that increased ionic species concentration decreases the uptake of hydrogen. In addition, it is determined that silicate (SiO_3^{2-}) ions in combination with bicarbonate (HCO_3^-) ions impart good protection against hydrogen permeation in chloride solution as compared to that for any of these ions alone in the case of rock bolts. This is due to the reduced passive current density due to the preferential adsorption of silicate at the defects or pits on the passive film. The formation of CaCO_3 deposit reduced the hydrogen permeation and corrosion rate of carbon steel when the electrolyte concentration was increased. These results were obtained from polarization, SEM and XPS analyses. Details of these can be found in the manuscripts and papers published that are listed in the following pages.
Dynamic electro-mechanical testing performed on the YM site I-beam exhibited “Portevin-LeChatelier” (PLC) type dynamic strain aging (DSA) effect in the plastic zone at 85°C and at different potentials as shown in Figures 2 (a and b). In addition, we have conducted similar experiments at cathodic potentials 500 mV below Ecorr (not shown here) that revealed hydrogen embrittlement effect due to reduction in elongation values, as well as current measurements. As expected, PLC or DSA effects were not observed in the I-beam specimens at room temperature under electrochemical potentials. However, increasing the temperature to ~55°C initiated the PLC effect and remained for all the temperatures between 55° and 85°C; it is expected to continue at higher temperatures but we do not have data for this at this time. Fractography performed on these I-beam samples also supported SCC/HE for this steel.

In the Task 18 YM program, we have established key procedures for evaluation of the corrosion rates of steels. At UNR Corrosion Laboratory, we have the expertise in our group, with MS and Ph.D. graduate students, corrosion scientists experienced in carbon and stainless steel and other materials corrosion research, and Post-Doctoral fellows to conduct detailed YMP research. In addition, we have performed hydrogen permeation experiments that lead us to understand mechanism involved in hydrogen embrittlement of these steels. We have already established QA procedures for establishing corrosion mechanisms using X-ray photon electron spectroscopy (XPS), SEM and TEM, and X-ray Diffraction. At UNR, we have a slow strain-rate testing (SSRT) machine for stress corrosion cracking and hydrogen embrittlement experiments. We have designed and fabricated electrochemical cells to perform stress corrosion testing. Also, we have “Gamry” Potentiostats to carry out DC and AC experiments. Thermogravimetric analyzer (TGA) facilities are now available at UNR to conduct the dry oxidation tests for monitoring the weight changes accurately, at any temperature. We have presented our work at YM issues discussed at Nuclear Materials sessions at TMS and other meetings. Presentations and publications based on this work are listed in pages iv-vi.

Figure 2(a) Load vs elongation plot of I-beam taken at Ecorr (85°C) showing the Luder band region and extended “Portevin-LeChatelier” Type dynamic straining (DSA) Effect. These data were taken at a constant strain rate of 1.6x10^-6/sec using SSRT Universal Testing machine. (018AY.006 File: serrations at 85C and ecc.doc).

Figure 2(b) Stress-Strain plots of I-beam that UTS is higher at 85°C but the steel is less ductile at 85°C at potential of +50 mV above Ecorr. (85°C: 018AY.003 File: SSRT 85oC.xls 25°C: 018AY.003 File: SSRT RT.xls).
YM Project Presentations at the Nuclear Waste Disposition Sessions at the TMS and other Corrosion Research Related Meetings of YM Project Task 18
Prof. Dhanesh Chandra's, Group at the Metallurgical and Materials Engineering, University of Nevada, Reno, 2000-2003

Graduate Students With Thesis Directly Related YM Project Task 18


Graduate and Undergraduate Students who worked on the YM Task No. 17


Publications:


3. X-ray Photoelectron Spectroscopic Analyses of Corrosion Products Formed on Rock Bolt Carbon Steel in Chloride Media With Bicarbonate and Silicate Ions, V. Deodeshmukh 1, A. Venugopal 1, A. Yilmaz 1, J. Daemen 1, and D. A. Jones 1, S. Lea 2 and M. Engelhard 2; 1Metallurgical and Materials Engineering, University of Nevada, Reno, NV 89557, USA, 2 Pacific Northwest National Laboratory, Richland, WA-99352, USA In review in Corrosion Science-Cambridge University, For correspondence refer to manuscript number GTB/2003/1483.

4. "Electrochemical Corrosion Behavior of Low Carbon I-Beam Steels In Simulated Yucca Mountain Repository Environment" by Venugopal Arjunan, Joshua Lamb, Dhanesh Chandra, Jaak Daemen, Denny
Jones, Mark Engelhard* and Scott Lea*, Metallurgical & Materials Engineering Division, Mail Stop 388, College of Engineering, University of Nevada, Reno, NV 89557 *Pacific Northwest National Laboratory, Richland, WA 99352. Has been received for publication in “Corrosion Journal”. For correspondence, please refer to the manuscript number 30802.

5. “Hydrogen Diffusion and Trapping Effects In Low and Medium Carbon Steels For The Proposed Yucca Mountain Repository,” Venugopal Arjunan, Vinay Deodeshmukh, Joshua Lamb, Dhanesh Chandra*, Jaak Daemen and Denny Jones, Metallurgical & Materials Engineering Division, Mail Stop 388, College of Engineering, University of Nevada, Reno, NV has been received for publication in “Corrosion Journal”. For correspondence, please refer to the manuscript number 30707.


Presentations at National and International Meetings:


In place of “Hydrogen Trapping Effects in Proposed Containment Alloy 22 for Yucca Mountain (YM)” Repository, Venugopal Arjunan1, Dhanesh Chandra1, Joshua Lamb1, Raul Rebak2, Jaak Damen1 and Denny Jones1, 1University of Nevada, Reno, Mackay School of Mines, MS 388, Reno, NV-89557 USA, 2Lawrence Livermore National Laboratory, Livermore CA 94551 To be Presented at the TMS Meeting in Chicago Illinois, Nov. 9-12, 2003.

12. “Effect of Reversible and Irreversible Trapping on Hydrogen Induced Cracking Resistance of Steel Sets (SS) and Rock Bolts (RB) Proposed for Yucca Mountain (YM) Repository,” Venugopal Arjunan1, Vinay Deodeshmukh2, Joshua Lamb1, Dhanesh Chandra1, Jaak Damen1 and Denny Jones1 1University of Nevada, Reno, Mackay School of Mines, MS 388, Reno, NV-89557 USA, 2Dept of Materials Science and Engineering, Iowa State University, Ames IA TMS Nov. 2003. To be presented at the TMS Meeting in Chicago Illinois, Nov. 9-12, 2003.

Students who worked on the YM Project Task 18
1. Dr. Ahmet Yilmaz, PhD (2003, UNR-Advisor: D. Chandra
2. Mr. Vinay Deodeshmukh, MS 2003, UNR-Advisor: D. Chandra
3. Dr. Wen Ming Chien, Ph.D 2003 UNR-Advisor: D. Chandra
4. Dr. Joshua Lamb, Ph.D expected 2005 UNR-Advisor: D. Chandra
ACKNOWLEDGEMENTS

We extend our sincerest gratitude and appreciation US Department of Energy (USDOE) for the support of this research program. We gratefully acknowledge the hard work of our graduate students; Dr. Ahmet Yilmaz who completed his Ph.D. dissertation research very diligently on our YM DOE project, Mr. Vinay Deodeshmukh who worked hard and did his MS thesis, and Mr. Joshua Lamb who is currently working on his Ph.D research and has made significant contribution to our project. This report has been compiled mainly from graduate student research and manuscripts prepared for publications of this YM project research. We gratefully acknowledge contributions of Dr. Venugopal Arjunan (Post-Doctoral Fellow), who helped Mr. Deodeshmukh (MS) and Mr. Lamb (Ph.D candidate 2003), for the bicarbonate, silicate work, hydrogen permeation work, and numerous discussions on corrosion related matters. We thank Dr. Russell Jones, Dr. Don Baer, Dr. Scott Lea and Dr. Mark Engelhard, of Pacific Northwest National Laboratory, Richland, Washington for the great cooperation and allowing our students and staff to conduct XPS work. We also gratefully thank Dr. Denny Jones for his helpful discussions. We thank Glen McMillion for the use of the Potentiostats. We also extend special thanks to the Harry Reid Center staff, Ms. Sherry Marks, and Quality Assurance personnel for their help, including Ms. Amy Smieckinski, Mr. Raymond Keeler, Mr. Morrie Roosa, Mr. Robert Fulwider, Ms. Barbara Roosa and Mr. Terry Mueller. We would also like to acknowledge MATCO in Pittsburgh, PA who performed the cyclic humidity tests and National Exposure Testing in Sylvania, OH where the salt spray tests were performed.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>I. INTRODUCTION</th>
<th>Page No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>II. BACKGROUND AND THEORITICAL</td>
<td>5</td>
</tr>
<tr>
<td>2.1. Electrochemical Corrosion Mechanism</td>
<td>5</td>
</tr>
<tr>
<td>2.2. Corrosion of Steel in Water</td>
<td>6</td>
</tr>
<tr>
<td>2.3. Faraday’s Law</td>
<td>6</td>
</tr>
<tr>
<td>2.4. Nernst Equation</td>
<td>7</td>
</tr>
<tr>
<td>2.5. Pourbaix Diagrams</td>
<td>7</td>
</tr>
<tr>
<td>2.6. Polarization</td>
<td>8</td>
</tr>
<tr>
<td>2.7. Polarization Resistance</td>
<td>9</td>
</tr>
<tr>
<td>2.8. Electrochemical Impedance Spectroscopy</td>
<td>9</td>
</tr>
<tr>
<td>2.9. Passivation in Metals and Alloys</td>
<td>11</td>
</tr>
<tr>
<td>2.10. Pitting</td>
<td>12</td>
</tr>
<tr>
<td>2.11. Hydrogen Permeation Studies</td>
<td>13</td>
</tr>
<tr>
<td>2.12. Environmentally Induced Cracking</td>
<td>14</td>
</tr>
<tr>
<td>2.13. References for Background and Theoretical section</td>
<td>17</td>
</tr>
<tr>
<td>III. EXPERIMENTAL</td>
<td>20</td>
</tr>
<tr>
<td>3.1. Materials and Specimen Preparation</td>
<td>20</td>
</tr>
<tr>
<td>3.2. Cell Design and Experimental Set-Up for Electrochemical Tests</td>
<td>20</td>
</tr>
<tr>
<td>3.3. Electrochemical Impedance Spectroscopy</td>
<td>23</td>
</tr>
<tr>
<td>3.4. Environmentally Assisted Corrosion Tests</td>
<td>24</td>
</tr>
<tr>
<td>3.5. Scanning Electron Microscopic (SEM-EDS) Studies</td>
<td>25</td>
</tr>
<tr>
<td>3.6. Optical Microscopy</td>
<td>25</td>
</tr>
<tr>
<td>3.7. X-ray Photoelectron Spectroscopy (XPS)</td>
<td>25</td>
</tr>
<tr>
<td>3.8. Hydrogen Permeation Experiments</td>
<td>27</td>
</tr>
<tr>
<td>3.9. Weight Loss Measurements</td>
<td>28</td>
</tr>
<tr>
<td>3.10. Salt Spray Testing</td>
<td>29</td>
</tr>
<tr>
<td>3.11. Cyclic Humidity Tests</td>
<td>29</td>
</tr>
<tr>
<td>3.12. References for the Experimental Section</td>
<td>29</td>
</tr>
<tr>
<td>IV. RESULTS AND DISCUSSIONS- ELECTROCHEMICAL CORROSION RESULTS OF ROCK BOLTS</td>
<td>32</td>
</tr>
<tr>
<td>4.1. Summary of Electrochemical Corrosion Results of Rock Bolts</td>
<td>32</td>
</tr>
<tr>
<td>4.2. Polarization Studies on Rock Bolts from YM Project Site</td>
<td>32</td>
</tr>
<tr>
<td>4.3. Impedance Spectroscopy Results on Rock bolts</td>
<td>39</td>
</tr>
<tr>
<td>4.4. Surface Characterization by Optical, Scanning Electron Microscopy, and X-ray Photoelectron Spectroscopy Studies</td>
<td>40</td>
</tr>
<tr>
<td>4.5. Effect of Temperature and YM Water Concentration on Rock bolts</td>
<td>51</td>
</tr>
<tr>
<td>4.6. References for Section IV Results on Corrosion of Rock bolts</td>
<td>53</td>
</tr>
<tr>
<td>V. ELECTROCHEMICAL CORROSION RESULTS ON STEEL SETS</td>
<td>60</td>
</tr>
<tr>
<td>5.1. Summary of Polarization studies on I-Beams From YM Project Site</td>
<td>60</td>
</tr>
<tr>
<td>5.2. Characterization of the surface products by Optical Microscopy</td>
<td>62</td>
</tr>
<tr>
<td>5.3. X-ray Photoelectron Spectroscopy of the I-beam Specimens after corrosion</td>
<td>63</td>
</tr>
<tr>
<td>5.4. References for the Polarization Results of I-Beams</td>
<td>66</td>
</tr>
<tr>
<td>VI. HYDROGEN PERMEATION RESULTS IN ROCK BOLTS AND STEEL SETS</td>
<td>68</td>
</tr>
<tr>
<td>6.1. Summary of Hydrogen Permeation</td>
<td>68</td>
</tr>
<tr>
<td>6.2. Diffusion and Trapping</td>
<td>68</td>
</tr>
<tr>
<td>6.3. Hydrogen permeation in Simulated YM water</td>
<td>68</td>
</tr>
<tr>
<td>6.4. Effect of Anions on Hydrogen Permeation in 3.5% NaCl</td>
<td>73</td>
</tr>
<tr>
<td>6.5. Critical Hydrogen Concentration</td>
<td>76</td>
</tr>
<tr>
<td>6.6. References for Hydrogen Permeation in Rock Bolts and Steel Sets section</td>
<td>77</td>
</tr>
<tr>
<td>Section</td>
<td>Page</td>
</tr>
<tr>
<td>------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>VII. GENERAL CORROSION RESULTS OF YM I-BEAMS AND ROCK BOLTS</td>
<td>78</td>
</tr>
<tr>
<td>7.1 Summary of Humidity, Fog Tests, and Immersion Tests</td>
<td>78</td>
</tr>
<tr>
<td>7.2. Cyclic Humidity Test on Rock Bolt (RB) and Steel Set (SS)</td>
<td>78</td>
</tr>
<tr>
<td>As per MATCO Associates in Pittsburgh, PA</td>
<td></td>
</tr>
<tr>
<td>7.3. General Corrosion Behavior of Rock Bolts and I-beam</td>
<td>80</td>
</tr>
<tr>
<td>7.4. Metallographic Evaluations</td>
<td>81</td>
</tr>
<tr>
<td>7.5. Corrosion Rates by Basic Lab Immersion Tests</td>
<td>82</td>
</tr>
<tr>
<td>7.6 Corrosion Rates by YM Water Spray and Humid Environment Tests</td>
<td>84</td>
</tr>
<tr>
<td>7.7 References for the section VIII-General Corrosion</td>
<td>85</td>
</tr>
<tr>
<td>VIII. ENVIRONMENTALLY INDUCED CRACKING OF STEEL SETS</td>
<td>86</td>
</tr>
<tr>
<td>8.1 Summary of Stress Corrosion Cracking and Hydrogen Embrittlement</td>
<td>86</td>
</tr>
<tr>
<td>8.2 Stress Corrosion Cracking and Hydrogen Embrittlement Studies on YM I-beam Steel Sets</td>
<td>86</td>
</tr>
<tr>
<td>8.3 SSRT Results</td>
<td>89</td>
</tr>
<tr>
<td>8.4 Stress-Strain behavior at Low Temperature (25°C)</td>
<td>90</td>
</tr>
<tr>
<td>8.5 Current Transients at Low Temperature (25°C)</td>
<td>93</td>
</tr>
<tr>
<td>8.6 Portevin-LeChatelier Effect, PLC, Effect at High Temperature (85°C)</td>
<td>94</td>
</tr>
<tr>
<td>8.7 Stress-Strain Behavior at 85°C</td>
<td>98</td>
</tr>
<tr>
<td>8.8 Current Transients at 85°C</td>
<td>99</td>
</tr>
<tr>
<td>8.9 Comparisons of the SSRT I-beam Results At Different Temperatures</td>
<td>100</td>
</tr>
<tr>
<td>8.10 References for Environmentally Induced Cracking</td>
<td>112</td>
</tr>
<tr>
<td>IX. SUMMARY AND CONCLUSIONS</td>
<td>113</td>
</tr>
<tr>
<td>APPENDIX A1</td>
<td>117</td>
</tr>
<tr>
<td>APPENDIX A2</td>
<td>129</td>
</tr>
<tr>
<td>APPENDIX A3</td>
<td>134</td>
</tr>
</tbody>
</table>
## LIST OF FIGURES

### CHAPTER I

| Figure 1.1 | Schematic and photograph of the YM tunnel with Steel sets and rock bolts in place. The photos of the YM site (above) and the tunnel (below) were taken from the YM website | 2 |
| Figure 1.2 | Estimated temperatures after emplacement, on and around the waste package Canister [4] | 3 |

### CHAPTER II

| Figure 2.1 | Hypothetical Cathodic and Anodic Polarization Diagram [9b] | 6 |
| Figure 2.1a | Electrochemical corrosion mechanism of steel in neutral waters | 7 |
| Figure 2.2 | Pourbaix Diagram for Pure Iron [11] at the activity of $10^{-6}$ g-equiv/L | 8 |
| Figure 2.3 | A: Corrosion potential and rate ($I_{corr}$) under activation control. B: Linear polarization and under concentration polarization control. C: Linear portion of the polarization curve at low over-voltage near $E_{corr}$. | 10 |
| Figure 2.4 | Equivalent circuit of Randles type (left). Nyquist Plot (right), the complex plane response of Randles type equivalent circuit. The gray curve shows the response in the case of a Warburg Impedance | 11 |
| Figure 2.5 | Data Interpretation from electrochemical impedance spectra for a corroding electrode simulated by parallel-connected resistance $R_p$ and capacitance $C_{eq}(left)$ Bode Plots, Randles Cell (right), and Equivalent circuit model. | 12 |
| Figure 2.6 | Typical passivation in the anodic region (solid curve). $I_{pass}$ is passivation current and $E_{corr}$ is corrosion potential. Dotted lines represent no passivity. | 12 |
| Figure 2.7 | Actual Hydrogen permeation transients obtained from Devanathan and Stachurski Cell to calculate material property of RBCS | 14 |
| Figure 2.8 | General susceptible potential regions to stress corrosion cracking around $E_{prot}$ and $E_{pit}$ on the potentiodynamic polarization diagram | 16 |
| Figure 2.9 | The sequence of events occurring at a propagating crack tip during SSRT. A: Passive surface prior to pitting, or brittle film fracture due to straining. B: Pitting or cracking, exposing the fresh metal to the electrolyte C: Dissolution and re-filming of exposed surface, but yet another crack. D: Continuation of the processes | 16 |
| Figure 2.10 | Schematic of stress-strain curve of carbon steel, showing PLC effect in the plastic region with serrations after the Luder bands | 17 |

### CHAPTER III

| Figure 3.1 | A. Rock bolts (shown with arrows) from YM site (B) Steel set (I-beam 8") from YM site (C) A cross section at xx in Figure B. | 21 |
| Figure 3.2 | Photographs of the specimens prepared from the rock bolts and I-beam shown in Figure 3.1. Specimens prepared for (A) Potentiodynamic and EIS tests are shown in the top left photograph, (B) Electromigration are shown in top-middle photograph, (C) Immersion experiments are shown in top right photograph, (D) Stress corrosion cracking | 21 |
embrittlement studies in bottom left photograph (I-beam), and
(E) For YM water or salt spray tests in the bottom right photograph

Figure 3.3 Schematic of the apparatus used for Potentiodynamic and EIS tests for rock bolts and I-beam

Figure 3.4 Experimental set-up for potentiodynamic linear polarization and impedance spectroscopy

Figure 3.5 Polarization behavior of carbon steel in 3.5% NaCl + silicate + bicarbonate+ sulfate, pH = 8

Figure 3.6 Nyquist plots showing the impedance changes on Carbon Steel in 3.5% NaCl + silicate + bicarbonate + sulfate at different potentials shown in above Figure 3.5 at points A, B, C, D, and E at pH = 8

Figure 3.7 Experimental set-ups for environmental cracking, such as SCC and HIC, and strain aging determination [2]

Figure 3.8 (A) Photographs of the SSRT Universal Testing Machine showing the specimen in position held between pull rod made for YM project specimens and glass electrochemical cell (B) Detailed photo of the electrochemical cell with electrical connections (C) Close up of the specimen and heater rod

Figure 3.9 (Left) Schematic of the electrochemical cell with the electrodes and sample. (Right) A typical Potentiodynamic scan plot showing anodic and cathodic regions for the YM 100x water. The SCC/HE tests were conducted at Ecorr and other potentials. Two examples, at which SCC curves were obtained (at -620 and -680 mV; potentials above the Ecorr) are shown in this diagram

Figure 3.10 Schematic of Devanathan-Staruchi cell showing the two compartments for permeation of hydrogen. This experiment requires two potentiostats

Figure 3.11 A photograph of Hydrogen Permeation cell at UNR used for this work

Figure 3.12 Laboratory setup at UNR used to perform dipping immersion tests to measure corrosion rates by measuring weight loss of the coupons after corrosion experiments

Figure 3.13 Salt spray testing at NET, Ohio Columbus (a) Photograph of the equipment (b) Sample conditions before experiment and (c) after experiment

CHAPTER IV

Figure 4.1 Effect of Deaeration on passivation of RBCS in 1X YM water solution (018AY.002)

Figure 4.2 Molar Effect of Silicate ions on the RBCS (018VD.003)

Figure 4.3 Molar effect of bicarbonate ions on Icorr and Ip of RBCS (018VD.003)

Figure 4.4 Potentiodynamic Polarization Curves of RBCS in Water (A) No additional ions (B) 0.01M SiO\text{3}^{2-} (C) 0.5M HCO\text{3}^- (D) 0.5M HCO\text{3}^- + 0.01M SiO\text{3}^{2-}(018VD.003)

Figure 4.5 Nyquist Curves of RBCS in Water (A) 0.01M SiO\text{3}^{2-} (B) 0.5M HCO\text{3}^- (C) 0.5M HCO\text{3}^- + 0.01M SiO\text{3}^{2-}(018VD.001)

Figure 4.6 Molar Effect of Bicarbonate ions in presence of 3.5% NaCl (018VD.003)
Figure 4.7 Effect of chloride ions in presence of 0.5M bicarbonate ions (018VD.003) 36
Figure 4.8 Effect of silicate ions on passivity in 3.5 % NaCl(018VD.003) 37
Figure 4.9 Potentiodynamic polarization curves of RBCS in 3.5% NaCl solution with (A) No new ions (B) 0.01M SiO$_3^{2-}$ (C) 0.5M HCO$_3^-$ (D) 0.5M HCO$_3^- + 0.01M$ SiO$_3^{2-}$ (018VD.003) 37
Figure 4.10 Nyquist Curves of RBCS in 3.5% NaCl (A) 0.01M SiO$_3^{2-}$ (B) 0.5M HCO$_3^-$ (C) 0.5M HCO$_3^- + 0.01M$ SiO$_3^{2-}$ (018VD.001) 38
Figure 4.11 Polarization behavior of RBCS in plain water (018VD.003) 39
Figure 4.12 Potentiodynamic polarization plots of RBCS in 3.5% NaCl solution containing 0.5M HCO$_3^-$ (a) No precharging and (B) Hydrogen precharged for 30 minutes at -1.2 V, showing virtually no difference in the scans (top) (018VD.003) 41
Figure 4.13 Potentials Chosen from polarization curves of RBCS using 0.5M HCO$_3^-$ and 0.5M HCO$_3^- + 0.01M$ SiO$_3^{2-}$ to perform impedance spectroscopy shown in Figures 4.14 and 4.15 (bottom) (018VD.003) 41
Figure 4.14 Impedance spectra measured for RBCS in presence of 0.5M HCO$_3^-$ added to 3.5% NaCl solution at potentials (A) $E_{corr}$ (B) -580mV (C) -375mV and (D) -290mV marked as P1, P2, P3 and P4 in Figure 4.12 (018VD.001) 42
Figure 4.15 Impedance spectra measured for RBCS in presence of 0.5M HCO$_3^- + 0.01M$ SiO$_3^{2-}$ added to 3.5% NaCl solution at potentials (A) $E_{corr}$ (B) -580mV and (C) -375mV and (D) -290mV marked as P1, P2, P3 and P4 in Figure 4.12 (018VD.001) 43
Figure 4.16 Bode plots measured for RBCS in presence of 0.01M SiO$_3^{2-}$ added to 3.5% NaCl solution at potentials (a) $E_{corr}$ (b) -550mV on the polarization curve (018VD.001) 44
Figure 4.17 Potentials Chosen from polarization curves in case of 0.5M HCO$_3^-$ and 0.5M HCO$_3^- + 0.01M$ SiO$_3^{2-}$ to perform SEM (Figures 4.19 to 4.21), Optical Images (Figures 4.18) and XPS spectra (also included in Appendix of this chapter) (018VD.003) 44
Figure 4.18 Optical images of 1 mm of RBCS in HCO$_3^-$ solution (A) Active- Passive Transition (B) Passive Potential (C) After Potentiodynamic Scans (NQA) 45
Figure 4.19 SEM morphology of the samples observed after impedance experiments in presence of 0.5M HCO$_3^-$ added to 3.5% NaCl solution (A) Pre-passive (P2) (B) Passive (P4) and (C) after potentiodynamic polarization and the corresponding EDS spectra also shown (018VD.004) 45
Figure 4.20 SEM morphology of the samples observed after impedance experiments in presence of 0.5M HCO$_3^- + 0.01M$ SiO$_3^{2-}$ added to 3.5% NaCl solution (A) Pre-passive (P2) B) Passive (P4) and (C) after potentiodynamic polarization and the corresponding EDS spectra also shown (018VD.004) 46
Figure 4.21 Optical images of 1 mm of RBCS in HCO$_3^- +$ SiO$_3^2- $ solution (A) Active- Passive Transition (B) Passive Potential (C) After Potentiodynamic scans (NQA) 47
Figure 4.22 SEM morphology of RBCS observed after impedance at passive potential (A) and after potentiodynamic polarization (B) in presence of 0.01M SiO$_3^{2-}$ added to 3.5% NaCl solution(018VD.004) 47
Figure 4.23 Photoelectron spectra obtained from RBCS of O 1s (A) and C 1s (B) and Fe(2p) (C) 49
polarized at the pre-passive potential marked in Figure. 4.16 in 3.5% NaCl solution containing 0.5M HCO₃⁻ (018VD.005)

Figure 4.24 Depth Profile of (A) Pre-passivated (B) Passivated Films obtained from XPS analyses of RBCS of O 1s (A) and C 1s (B) and Fe(2p) (C) polarized at the pre-passive potential marked in Figure. 4.16 in 3.5% NaCl solution containing 0.5M HCO₃⁻ (018VD.005)

Figure 4.25 Potentiodynamic polarization curves for rock bolt in deaerated simulated 1X YM water at various temperatures, such as 25°C, 45°C, 65°C, and 85°C (018AY.002)

Figure 4.26 Potentiodynamic polarization curves for rock bolt at 25°C in various deaerated simulated YM waters, such as 1X, 10X, and 100X (018AY.002)

Figure 4.27 Temperature effect on corrosion rates of rock bolt in simulated deaerated concentrated YM waters (018AY.002)

Figure 4.28 Temperature effect on corrosion rates of rock bolt in simulated aerated concentrated YM waters (018AY.002)

Figure 4.29 Specimen surface appearances after polarization scanning. Left: De-aerated 100X waters, Right: Aerated 100X waters which is sooty and easily scratched by hand

Figure 4.30 Transparent scale formation and pitting over rock bolt in deaerated 100X YM waters (NQA)

Figure 4.31 Precipitate formation and pitting over rock bolt in aerated 100X YM waters. Oval inclusions appear as the initiation site for the pitting (NQA)

Figure 4.32 Nyquist Plot for MCS rock bolt in de-aerated 1X YM water at various temperatures (018JL.003)

Figure 4.33 Nyquist Plot for MCS rock bolt in deaerated water at RT for various concentrations (018JL.003)

CHAPTER V

Figure 5.1 A (Left) Polarization plots of I-beam measured in deaerated (nitrogenated) YM solutions (a) 1x, (b) 10x, (c) 100x (A, B, C, D indicates temperatures 25°C, 45°C, 65°C and (b) 85°C respectively) (018JL.002)

Figure 5.1 B (Right) Polarization plots of I-beam measured in aerated (oxygenated) YM solutions (a) 1x, (b) 10x, (c) 100x (A, B, C, D indicates temperatures 25°C, 45°C, 65°C and 85°C respectively). (018JL.002)

Figure 5.2 Impedance plots recorded on carbon steel in deaerated 100x YM water at (a) 25°C and (b) 85°C (018JL.002)

Figure 5.3 Impedance plots recorded on carbon steel in aerated 100x YM water at (a) 25°C, (b) 45°C and (c) 85°C (018JL.002)

Figure 5.4 Depth Profile analyses of carbon steel as a result of polarization in 100x YM water at different temperatures. Spectra a, b and c are oxygenated (018VD.005)

Figure 5.5 Depth Profile analyses of carbon steel as a result of polarization in 100x YM water at different temperatures under nitrogenated conditions; spectra d and e. (018VD.005)
Figure 5.6 Corrosion rates of I-beam as a function of temperature and electrolyte concentration in deaerated condition. Results of Lian et al. [1] are included (018JL.002)

Figure 5.7 Corrosion Rates of Rock bolts as function of temperature and concentration in aerated conditions. Results of Lian et al. [1] are included. (018JL.002)

CHAPTER VI

Figure 6.1 Hydrogen permeation transients for carbon steels in 0.1M NaOH solution (018VD.002)

Figure 6.2 Normalized Hydrogen permeation transients for carbon steels in 0.1M NaOH solution (018VD.002)

Figure 6.3 Load-Elongation curve for SSCS I-beam sample. (018AY.003)

Figure 6.4 Effect of Cold Work on hydrogen permeation of I-beam steel SSCS I-beam in 0.1 M NaOH. (018VD.002)

Figure 6.5 Effect of electrolyte concentration on the hydrogen permeation of I-beam steel (SSCS) A) 1x, B) 10x, and C) 100x. (018VD.002)

Figure 6.6 Effect of electrolyte concentration on the potential variation as a result of cathodic hydrogen charging on SSCS at 1mA/cm², A) 1x, B) 10x and C) 100x. (018VD.002)

Figure 6.7 X-ray diffraction pattern showing the deposition of CaCO₃ scale on SSCS after cathodic hydrogen charging experiments, A) 100x and B) 10x YM electrolyte. (018VD.004)

Figure 6.8 Nyquist plots during hydrogen permeation experiment for SSCS in 100x YM water before and after Hydrogen Charging (018VD.001)

Figure 6.9 Polarization behavior of I-beam SSCS in simulated YM water with increasing electrolyte concentrations A) 1x, B) 10x and C) 100x (018VD.003)

Figure 6.10 Polarization behavior of rock bolt RBCS in simulated YM water with increasing electrolyte concentrations A) 1x, B) 10x and C) 100x (018VD.003)

Figure 6.11 Effect of A) no added ions B) HCO₃⁻, C) SiO₃²⁻, D) HCO₃⁻ + SiO₃²⁻ ions on the hydrogen permeation current measured in 3.5% NaCl solution (018VD.002)

Figure 6.12 Hydrogen Permeation transients used for calculating Ck for steel sets (018JL.003)

Figure 6.13 Hydrogen Permeation transients used for calculating Ck for rock bolts (018JL.003)

CHAPTER VII

Figure 7.1 Photographs of I-beam (left) and rock bolt (right) specimens before humidity tests (018VD.004)

Figure 7.2 Photograph of I-beam and rock bolt specimens after 7 days (018VD.004)

Figure 7.3 Photograph of I-beam and rock bolt specimens after 14 days (018VD.004)

Figure 7.4 Photograph of I-beam and rock bolt and specimens after 21 days (018VD.004)

Figure 7.5 SEM evaluation of rock bolt (left) and steel set (right) showing similar corrosion
morphology observed after 21 days of humidity tests. (0018VD.004)

Figure 7.6 A typical SEM-EDS spectrum indicating nature of corrosion product formed on the I-beams and rock bolts after cyclic humidity tests. (018VD.004)

Figure 7.7a Optical micrograph of LCS (0.008%) I-beam showing small amounts of Pearlite embedded in the major ferrite structure. Fig.7.7 b Optical micrograph of MCS (0.44 % C) I-beam showing large amounts of Pearlite leaving out much less ferrite structure compare to LCS(NQA)

Figure 7.8 A Optical micrograph showing inclusions in I-beam (0.08%C) in rolling direction

Figure 7.8 B SEM micrograph of inclusions in YM I-beam. The inclusions are generally of elliptical shape; some more elongated than others

Figure 7.8 C EDS analysis showing extra Mn and S content of the inclusion labeled Spectrum 1(018VD.004)

Figure 7.9 Mass loss profile of fully immersed rock bolt in 1x YM water at room temperature (018AY.001)

Figure 7.10 Mass loss profiles of Rock bolt under fully, partially, and not immersed condition at 75°C (018AY.001)

Figure 7.11 Weight loss of rock bolt and I-beam (steel set) in YM 1x spray environment. Steel set CR=910 μm/yr, Rock bolt =800 μm/yr for this one week exposure at 35°C. (018AY.001)

Figure 7.12 Weight loss of rock bolt and I-beam in YM humid environment. Steel set CR= 6μm/yr, Rock bolt 35 μm/yr for this 21 day exposure in YM 1x water at room temperature. (Comparing these results to the cyclic humidity tests ASTM G-60 test Steel set CR= 1265 μm/yr, Rock bolt 887 μm/yr for this 21 days.) (018AY.001)

CHAPTER VIII

Figure 8.1 X-ray spectra of the precipitates formed over the specimen and cell walls before conducting slow strain rate tests (018AY.003)

Figure 8.2 I-beam specimens broken at 25°C and 85°C by SSRT at Ecorr. Surface appearance is different in each case (018AY.003)

Figure 8.3 (Left) Composition of precipitate layer on I-beam after electromechanical tensile tests using SSRT machine at 25°C showing small amounts of Mn-Mg-Si-Cl scale. (018AY.003)

Figure 8.4 (Right) Composition of the precipitate layer on I-beam tensile specimen after the SSRT experiments. A non-porous, dense scale formed at using 100x waters at 85°C. It can be noted that Fe-Kα and Kβ are not observed due to a thick Mg-Si O layer formation on the surface (018AY.003)

Figure 8.5 Scanning electron micrograph of a porous white scale formed on the I-beam after SSRT tensile test at 25°C showing non-adherent film formation. (NQA)

Figure 8.6 Potentiodynamic polarization curves of I-beam in 100X YM water at 25°C and 85°C, showing passivities (018JL.002)

Figure 8.7 Potentiodynamic polarization scan for LCS I-Beam in 100X YM water at two different temperature. No passivation observed, except some transpassive region at 85°C. (018JL.002)
Figure 8.8 Specimen gauge appearance (right) after SSRT conducted at -550 mV surface potential. The specimen has been corroded during the test, therefore stayed out of evaluation because of its reduced cross section by mechanisms (general corrosion) other than HE or SCC.

Figure 8.9 Load-elongation profile of LCS by SSRT in glycerin as an inert environment reference (018AY.003)

Figure 8.10 Stress as a function of % Elongation for LCS specimens at various potentials in de-aerated 100X YM waters at RT. The numbers represent the applied over potentials on the environmental test specimen in the units of mV. (018AY.003)

Figure 8.11 Current profiles of LCS strained dynamically by SSRT method at 1.6x10^-6/s in de-aerated 100X YM waters with various specimen potentials. The curve of -1200 mV refers to the secondary ordinate, which is on the right hand side. Ag/AgCl electrode was used for all potential measurements (018AY.003)

Figure 8.12 Serrated load-elongation curves due to strain aging effect on the LCS at 85°C. The serrated flow takes place in whole plastic deformation region starting right after the Lüder bands (box A) until the failure point (Box B). (018AY.003)

Figure 8.13 Discontinuous serrated load-elongation curve details at the Lüder plateau and the end of the plastic deformation region. Note that the average frequency of serrations decreased through the failure point. Note that the average frequency of serrations decreased through the failure point. (018AY.003)

Figure 8.14 Stress-strain curve appearance with variation of test temperatures during SSRT of LCS at the strain rate of 1.6x10^-6/s. A close-up view of the shown region is shown in Figure 7.15, revealing different serrated plastic deformation regions resulting from change in test temperatures during the tests. (018AY.003)

Figure 8.15 Correlated $E_{corr}$ change with the serration amplitudes of PLC effect during SSRT in YW water at the strain rate of 1.6x10^-6/s. Just occurred or diminished PLC effect (by examination of the serration amplitude) caused a large amount of potential change at the interface of LCS and the test solution (018AY.003)

Figure 8.16 Serrated stress-strain behaviors of LCS hold at various potentials at 85°C. Strain aging effect (Portevin-LeChatelier Effect) experienced by LCS at 85°C causes these serrated plastic flow behavior because of inclusions such as C, H, and N in the steel (018AY.003)

Figure 8.17 Current profiles of LCS strained dynamically by SSRT method at 1.6x10^-6/s in de-aerated 100X YM waters at 85°C, under various imposed specimen potentials. Potentials are given in reference electrode Ag/AgCl electrode used for all potential measurements. (018AY.003)

Figure 8.18 Significant difference in UTS point and unchanged YP of stress-strain curves carried out at different temperatures (both of the curves belong to -650 mV surface potential). The picture on the right shows the characteristic differences in fracture surfaces at RT and at 85°C failures. (018AY.003)

Figure 8.19 The longitudinal cracks occurred in the gauge at 85°C during strain aging of LCS. All SSRT experiments at 85°C resulted in one or more longitudinal cracks regardless of applied potentials.
Figure 8.20 Secondary cracks of LCS at room temperature (25°C), strained at the rate of 1.6x10^{-6}/s in 100X YM water under the imposed potentials A: $E_{\text{cor}}(-700 \text{ mV})$, and B: 200 mV below $E_{\text{cor}}(-900 \text{ mV})$. Both potentials are of reference Ag/AgCl electrode.

Figure 8.21 SSRT Fracture characteristics of LCS strained at a constant rate of 1.6X10^{-6}/s in air and 100X deaerated YM water at 25°C and 85°C. Columns A, B, and C show mechanical test at RT, environmental test at 25°C, and environmental test at 85°C, with imposed $E_{\text{cor}}(-700 \text{ mV}_{\text{Ag/AgCl}})$. The first row shows half of the fracture surface and the second shows the gauge length portion at the fracture location.

Figure 8.22 SEM fractographs of fracture surfaces of LCS in air (mechanical test) and in 100X deaerated YM waters at 25°C and 85°C. Sample strained at a constant rate of 1.6X10^{-6}/s with the open circuit potential (-700 mV_{Ag/AgCl}).

Figure 8.23 Optical micrograph of transgranular and intergranular cracks in LCS failed by SSRT in YM water at RT. IG and TG shows some intergranularly and transgranularly separated grains respectively.

Figure 8.24 Quasi-cleavage (A) and discontinuous planar cleavage (B) cracking modes of LCS at 85°C

Figure 8.25 Inner wall details of QC modes in LCS failed by SSRT at 85°C. The ridges observed with PLC effect and they showed an average length around 0.4 micron.

Figure 8.26 Measure of ductility by reduction of area values of LCS I-beam under various specimens potentials at room temperature and 85°C (018AY.003)

Figure 8.27 Measure of ductility by % Elongation of LCS under various potentials at room temperature and 85°C. (018AY.003)

Figure 8.28 Measure of ductility by RoF/A obtained with various slow strain rates from 10^{-3}/s to 10^{-7}/s at 25°C and 85°C for LCS under the imposed potential of -700 mV($E_{\text{cor}}$). (018AY.003)

Figure 8.29 Ductility differences of LCS revealed by mechanical tests at RT and 85°C in air with the strain rate 10^{-6}/s. The difference in the rectangular surface areas as a measure of ductility shows the increased embrittlement in the steel due to strain aging, or PLC effect. (018AY.003)

APPENDIX A1

Figure A1-1 Potentiostatically charged samples in XPS machine for Ar+ sputtering

Figure A1-2 XPS Survey spectra of RBBCS in HCO$_3^-$ solution at Active-Passive Transition (018VD.005)

Figure A1-3 XPS Survey spectra of RBBCS in HCO$_3^-$ solution at 2nd Passive Potential

Figure A1-4 XPS Survey spectra of RBBCS in HCO$_3^-$ + SiO$_3^{2-}$ solution at Active-Passive Transition (018VD.005)

Figure A1-5 XPS Survey spectra of RBBCS in HCO$_3^-$ + SiO$_3^{2-}$ solution at 2nd Passive Potential (018VD.005)

Figure A1-6 XPS Survey spectra of RBBCS in SiO$_2^-$ solution at Passive Potential (018VD.005)

Figure A1-7 XPS Survey spectra of RBBCS in HCO$_3^-$ solution at Active- Passive Potential after Ar$^+$ sputtering (018VD.005)
Figure A1-8  XPS Survey spectra of RBCS in HCO$_3^-$ solution at 2$^{nd}$ Passive Potential after Ar$^+$ sputtering (018VD.005)  

Figure A1-9  XPS Survey spectra of RBCS in HCO$_3^-$ + SiO$_2^{2-}$ solution at Active- Passive Potential after Ar$^+$ Sputtering (018VD.005)  

Figure A1-10 XPS Survey spectra of RBCS in HCO$_3^-$ + SiO$_2^{2-}$ solution at 2$^{nd}$ Passive Potential after Ar$^+$ Sputtering (018VD.005)  

Figure A1-11 XPS Survey spectra of RBCS in SiO$_2^{2-}$ solution at Passive Potential after Ar$^+$ Sputtering (018VD.005)  

Figure A1-12  O Is (A) and C Is (B) and Fe(2p) (C) Photoelectron spectra obtained from RBCS polarized at the pre-passive potential marked in Figure. 25 in 3.5% NaCl solution containing 0.5M HCO$_3^-$ (018VD.005)  

Figure A1-13 XPS Spectrum of RBCS polarized at passive potential in 3.5% NaCl solution containing 0.01 M SiO$_2^{2-}$. A. O (1s) B. C (1s), C. Si (2p) D. Fe (2p) (018VD.005)  

Figure A1-14 XPS Spectrum of RBCS polarized at pre-passive potential in 3.5% NaCl solution containing 0.5M HCO$_3^-$ + 0.01M SiO$_2^{2-}$. A. O (1s) B. C (1s), C. Si(2p) and D. Fe (2p) (018VD.005)  

Figure A1-15 XPS Spectrum of RBCS polarized at the passive potential in 3.5% NaCl solution containing 0.5M HCO$_3^-$ + 0.01M SiO$_2^{2-}$. A. O (1s) B. C (1s), C. Si(2p) and D. Fe (2p) (018VD.005)  

APPENDIX A2  

Figure A2-1 Optical micrographs of carbon steel samples exposed to 100x YM water (a) de-aerated 25°C, (b) de-aerated 85°C, (c) aerated 25°C, (d) aerated 45°C and (e) aerated 85°C (018VD.003)  

Figure A2-2 XPS spectrum of Carbon steel recorded after potentiodynamic polarization test in 100X YM water at 25°C (a) Fe(2p), (b) O1s and (c) C1s (018VD.003)  

Figure A2-3 XPS spectrum of Carbon steel recorded after potentiodynamic polarization test in 100X YM water at 45°C (a) Fe(2p), (b) O1s and (c) C1s (018VD.003)  

Figure A2-4 XPS spectrum of Carbon steel recorded after potentiodynamic polarization test in 100X YM water at 85°C (a) Fe(2p), (b) O1s and (c) C1s (018VD.003)  

APPENDIX 3  

Figure A3-1 Polarization of rock bolt in 1x, 10x, and 100x deaerated YM waters at 45°C  

Figure A3-2 Polarization of rock bolt in 1x, 10x, and 100x deaerated YM waters at 65°C  

Figure A3-3 Polarization of rock bolt in 1x, 10x, and 100x deaerated YM waters at 85°C  

Figure A3-4 Polarization of rock bolt in 1x, 10x, and 100x aerated YM waters at 25°C  

Figure A3-5 Polarization of rock bolt in 1x, 10x, and 100x aerated YM waters at 45°C  

Figure A3-6 Polarization of rock bolt in 1x, 10x, and 100x aerated YM waters at 65°C  

Figure A3-7 Polarization of rock bolt in 1x, 10x, and 100x aerated YM waters at 85°C  

xviii
Figure A3-8  Polarization of rock bolt at 25°C, 45°C, 65°C, 85°C in 10x de-aerated YM waters

Figure A3-9  Polarization of rock bolt at 25°C, 45°C, 65°C, 85°C in 100x de-aerated YM waters

Figure A3-10 Polarization of rock bolt at 25°C, 45°C, 65°C, 85°C in 1x aerated YM waters

Figure A3-11 Polarization of rock bolt at 25°C, 45°C, 65°C, 85°C in 10x aerated YM waters

Figure A3-12 Polarization of rock bolt at 25°C, 45°C, 65°C, 85°C in 100x aerated YM waters

Figure A3-13 EIS of rock bolt at 25°C, 45°C, 65°C, 85°C in 1x de-aerated YM waters

Figure A3-14 EIS of rock bolt at 25°C, 45°C, 65°C, 85°C in 10x de-aerated YM waters

Figure A3-15 EIS of rock bolt at 25°C, 45°C, 65°C, 85°C in 100x de-aerated YM waters

Figure A3-16 EIS of rock bolt in 1x, 10x, and 100x de-aerated YM waters at 25°C

Figure A3-17 EIS of rock bolt in 1x, 10x, and 100x de-aerated YM waters at 45°C

Figure A3-18 EIS of rock bolt in 1x, 10x, and 100x de-aerated YM waters at 65°C

Figure A3-19 EIS of rock bolt in 1x, 10x, and 100x de-aerated YM waters at 85°C

Figure A3-20 EIS of rock bolt in 1x, 10x, and 100x aerated YM waters at 25°C

Figure A3-21 EIS of rock bolt in 1x, 10x, and 100x aerated YM waters at 45°C

Figure A3-22 EIS of rock bolt in 1x, 10x, and 100x aerated YM waters at 65°C

Figure A3-23 EIS of rock bolt in 1x, 10x, and 100x aerated YM waters at 85°C

Figure A3-24 EIS of rock bolt at 25°C, 45°C, 65°C, 85°C in 1x aerated YM waters

Figure A3-25 EIS of rock bolt at 25°C, 45°C, 65°C, 85°C in 10x aerated YM waters

Figure A3-26 EIS of rock bolt at 25°C, 45°C, 65°C, 85°C in 100x aerated YM waters

Figure A3-27 Load-Time Profile of LCS in 100x YM water at 85°C, strained at 1.6x 10^3/s

Figure A3-28 Load-Time Profile of LCS in 100x YM water at 85°C, strained at 1.6x 10^4/s

Figure A3-29 Load-Time Profile of LCS in 100x YM water at 85°C strained at 1.6x 10^5/s

Figure A3-30 Load-Time Profile of LCS in 100x YM water at 85°C strained at 1.6x 10^7/s.
(Please note that there were too many data points and plotting routine had problem plotting it.)

Figure A3-31 Load-Time Profile of LCS in 100x YM water at RT, strained at 1.6x 10^3/s

Figure A3-32 Load-Time Profile of LCS in 100x YM water at RT, strained at 1.6x 10^4/s

Figure A3-33 Load-Time Profile of LCS in 100x YM water at RT, strained at 1.6x 10^5/s

Figure A3-34 Load-Time Profile of LCS in 100x YM water at RT, strained at 1.6x 10^7/s.
(Please note that there were too many data points and plotting routine had problem plotting it.)

LIST OF TABLES

CHAPTER III
Table 3.1 Composition of carbon steels used in the present work and standards 20
Table 3.2 Reference YM ground water composition used in the hydrogen permeation experiment 28
Table.3.3 Reference YM ground water composition used in this work 29

CHAPTER IV
Table 4.1 Electrochemical kinetic data obtained from Figure 4.9. (018VD.003) 38
Table 4.2 Binding energy values of Fe(2p), O 1s and C 1s components identified on RBCS in 3.5% NaCl solution containing 0.5M HCO₃⁻ 48
Table 4.3 Corrosion Rates of Rock bolt in Concentrated Deaerated YM Waters. (018AY.002) 54
Table 4.4 Corrosion Rates of Rock bolt in Concentrated Aerated YM Waters. (018AY.002) 55

CHAPTER V
Table 5.1 Summary of corrosion rates obtained from the polarization curves shown in Figure 5.1 in YM water (018JL.002) 66

CHAPTER VI
Table 6.1 Hydrogen permeation parameters obtained from Figure 6.2. (018VD.002) 68
Table 6.2 Electrochemical parameters obtained from Figure 6.9 (018VD.003) 73

CHAPTER VII
Table 7.1 Corrosion rates of Rock bolts and Steel sets Sample 1-5B are Rock bolts and 1-5S are Steel Set I-beam 79

CHAPTER VIII
Table 8.1 SSRT Parameters of LCS strained under various potentials and temperatures in deaerated 100x YM waters. A stereomicroscope has been used for observing the crack appearances. (018AY.003) 108
Table 8.2 SSRT Parameters of LCS strained under various strain rates and temperatures in deaerated 100X YM waters under imposed potential $E_{\text{corr}} (-700 \text{ mV}_\text{Ag/AgCl}).$ (018AY.003) 109

CHAPTER IX
Table 9.1. Rock bolt corrosion rates and the amount material thickness lost due to corrosion in 1, 100, 1000, and 10000 years for rock bolts as determined by electrochemical methods. 115
Table 9.2. Rock bolt corrosion rates and the amount material thickness lost due to corrosion in 1, 100, 1000, and 10000 years for rock bolts as determined by electrochemical methods. 116

XX
APPENDIX A1

<table>
<thead>
<tr>
<th>Table A1-1</th>
<th>Binding energy values of Fe(2p), O 1s and C 1s components identified on RBCS in 3.5% NaCl solution containing 0.5M HCO₃⁻</th>
<th>128</th>
</tr>
</thead>
</table>
I. INTRODUCTION

Yucca Mountain (YM), Nevada, is the proposed repository site for storing high-level nuclear spent fuels and other radioactive materials generated from nuclear power units and national defense programs within the United States [1]. The subsurface structural integrity is very important for storing the canisters in which the radioactive waste is stored. The tunnel reinforcement structural members such as rock bolts, currently, proposed to be made out of medium carbon steels (MCS-0.4%C) and the steel sets (I-beam) are medium of low carbon steels (LCS-0.1%C) have been proposed as candidate materials for the rock bolts (RB) and steel sets (SS) to reinforce the emplacement drifts along the YM tunnel. In this study, Rock Bolt Carbon Steel is designated as RBCS and Steels Sets (I-beam) Carbon Steel as SSCS.

Yucca Mountain is composed of a mile thick sequence of volcanic tuffs and subordinate lavas. The potential repository is located in the lower portion (densely welded tuff) of the Topopah Springs member of the Paintbrush Tuff unit, approximately 300 m below the surface of the mountain and 150 m to 300 m above the static water level. The repository location is in the unsaturated zone of the tuff unit [2], therefore the conditions are oxidizing. Some rainfall is expected in the mountain region is near by the Sierra Nevada mountain range. The preliminary near field investigations in the nuclear repository region are being conducted at the Lawrence Livermore National Laboratory [3].

Rockbolts of medium carbon steel (MCS) and I-beams of low carbon steel (LCS) have been originally suggested as structural materials for reinforcing the emplacement drifts along the repository tunnels in the mountain (Figure 1.1). The unsaturated rock zone (tuff), wherein the potential repository tunnels are located is itself of porous nature, which is likely to permeate ground waters moving downward on to LCS and MCS reinforcement structures, as a worst case scenario. Temperatures in the tunnel are expected to be high enough to cause evaporation of the ground waters resulting a steamy environment, which will increase general and localized corrosion effects on the LCS and MCS. The temperatures after the emplacement [4] over outer surface of the waste canister, and roughly 1 meter away from it, are shown in Figure 1.2, as estimated by D. D. McDonald [4]. If environment is corrosive, it may promote hydrogen evolution, leading to propensity of hydrogen induced cracking. Widely stressed, drifted and cracked rock during the excavations of the tunnel may cause block slipping along preexisting fractures, which would overload the I-beam and rock bolt structural elements. Seismic activities on the other hand may create drifts of tuff zone, further leading cracking of rocks. Thus, the local stress levels in I-beams and rock bolts may go well beyond the conventional maximum allowable level of 1/3 of their yield strength. Considering these additional constraints, combined effect is expected to be more detrimental, causing premature failure of the reinforcement structure by mechanisms such as stress corrosion cracking (SCC) and hydrogen induced cracking (HIC).

It is well known that silicates are progressively used in cooling water systems and potable water pipes to inhibit the corrosion of iron and carbon steels [5-7]. Results indicate that better performance is obtained in the presence of corrosion products as it has high affinity towards hydroxides of iron [6-7]. Several papers were published on the effect of CO\textsubscript{2} on the corrosion of carbon steels in which the effect of HCO\textsubscript{3}\textsuperscript{-}, which forms as a by- product, enhances the formation of FeCO\textsubscript{3} film and decreases the corrosion rate [8-11]. The role of silicate in the presence of bicarbonate has not yet been studied and is included within the scope of present investigation. For this study, the above ions were chosen matching their ratio in YM ground water, and their passivation tendency on carbon steel was examined. The "extrinsic" passive film was characterized using X-ray Photoelectron Spectroscopy (XPS), Impedance Spectroscopy (IS) and Scanning Electron Microscopic (SEM-EDS) techniques.

Consideration of Hydrogen Embrittlement and HIC of Carbon Steels in YM water is equally important aspect. The deleterious effects of hydrogen on the mechanical properties of steels are well known [12-15]. Hydrogen induced cracking (HIC) susceptibility is dependent on diffusivity, solubility and trapping characteristics. This, in turn depends on the microstructural features such as grain boundaries, voids, second phase particles and external factors such as stress and severity of the environment. In recent years, the electrochemical method developed by Devanathan and Stachurski [16] is being widely used to examine the diffusion, trapping behavior of ferrous and non-ferrous materials, and the obtained results have been used to understand the HIC behavior of steels. In the present work, the above technique was used to characterize the corrosion and hydrogen permeation tendencies of two carbon steels RBCS and SSCS proposed for the Yucca Mountain (YM) project. Studies on cathodic protection of steel structures indicate that the formation of calcareous deposits (CaCO\textsubscript{3}) reduced the current requirement for cathodic protection of steel structures and also hydrogen permeation in sea water [17, 18]. Allam et al. [19] reported
a decrease in hydrogen permeation when chloride ions are added to acidic and alkaline environments. It is also well known that MnS inclusions act as preferential sites for crack nucleation as a result of increased hydrogen trapping at those sites [20, 21]. Hence the diffusivity and permeability of hydrogen in RBCS, which has high C, Mn, S and SSCS, which has lower content of the above elements, is an important aspect to study. Further, hydrogen permeation rate was determined using YM repository environment that contains complex anions and cations. The extent of hydrogen absorption by increasing the total YM (1x, 10x, 100x etc.) electrolyte concentration was measured and the effect of various anions, which are considered to be important in deciding the corrosion behavior of carbon steels in YM environment, was also investigated.

![Figure 1.1 Schematic and photograph of the YM tunnel with Steel sets and rock bolts in place. The photos of the YM site (above) and the tunnel (below) were taken from the YM website.](image)

Environmentally assisted cracking studies for the determination of the long-term stability of LCS and MCS in YM environments are of vital importance for the proposed repository site. There have been several studies performed on waste package materials, generally stainless steels, high alloy steels, and Cu, and Ni based alloys [22-24]. The LCS corrosion allowance outer layer of the waste packages was first investigated by Lian and Jones [25] by electrochemical methods (DC polarization techniques) in simulated concentrated J-13 well waters, and low general corrosion performance and pitting behavior of LCS has been reported for both aerated and deaerated simulated repository environments. MacCright and Weiss [26] studied the borehole liners of various carbon steels, in aerated saturated steam of J-13 well reference waters at various temperatures from 50 to 100°C, by weight loss and electrochemical tests. The study reported general corrosion behaviors of cast iron and Cr-Mo alloys, along stress corrosion cracking susceptibilities in J-13 well water, by bent beam specimen (ASTM G39) method. Szklarska-Smialowska, Xia, and Rebak [27] reported stress corrosion cracking (SCC) of X-52 medium carbon steel in dilute aqueous solutions by slow strain rate tests, showing transgranular SCC susceptibilities above and below the corrosion potentials of the MCS in those near neutral solutions. James [28] reported short-term stress corrosion cracking of two different types of corrosion allowance barriers of the same carbon steel (ASTM A27-0.25% C) in a simulated ground water (Hanford Reservation ground waters). The study showed no crack extension in either material that was pre-cracked and statically loaded for various exposure times under simulated repository conditions. There are some studies on environmentally induced cracking susceptibilities in simulated concrete environments for eutectoid steels and Al-Mg alloys by slow strain rate tests [29-30], which revealed that SCC processes are associated
with hydrogen action, or a hydrogen uptake occurs during SCC. Hydrogen embrittlement is well known [31-34] in steels; however, there is not any detailed work on hydrogen embrittlement of subsurface structural carbon steel in the aqueous underground YM repository environment. Thus, environmentally induced cracking of rock bolt and I-beams steels by electro-mechanical methods are important. Also, there is no study reported on strain aging, or Portevin LeChatelier effect that can occur with variety of carbon steels under overloads, and causes embrittlement in any hot aqueous environment. If it combines with the other factors like HE and SCC, then the effect becomes more deleterious.

The main aim of this work is to report corrosion behavior of the rock bolts and steel sets furnished from Yucca Mountain site by using standard ASTM “Immersion Type” methods as well as “Electrochemical and Electro-mechanical” giving SCC and HIC susceptibilities of these steels. The SCC tests were performed on the I-beam using a SSRT machine with the sample in an electrochemical cell, and a Potentiostat was used to vary the potentials. We also investigated an important phenomenon of the “Dynamic Strain Aging Effect” and its temperature and potential dependencies in the simulated YM repository environments in details. General corrosion rates were determined on these carbon steels by electrochemical methods such as “linear polarization” and “Impedance spectroscopy”, and weight loss measurements via standard Laboratory Immersion and cyclic humidity tests.

1.1 References for Introduction
2. DOE from viewgraph package of the Department of Energy, Yucca Mountain Site Characterization Project office, XSECTBWCX SECTIONS/9/14/92(1992)
II. BACKGROUND AND THEORETICAL ASPECTS

Corrosion phenomena are very well known in steels, and have been the subject of numerous investigations [1-7]. Corrosion of metal in aqueous environments is entirely electrochemical in nature, as it is governed by anodic and cathodic reactions that occur at the metal electrolyte interface. Anodic reactions can cause dissolution of metals while cathodic reactions cause compound formations from the dissolved species in the electrolyte. Thus, metals usually lose weight because of their deterioration, while additional insoluble products may precipitate in the electrolyte. Therefore, these electrochemical reactions also change the chemical composition of the reacting environment, which may influence further degradation, or deceleration of the weight loss of metals. Metallic forms are of higher Gibbs energy as compared to compounds or ores, and have a tendency to lower the energy [8]. It is necessary for metals to absorb and store energy when they leave their original natural compounds; this energy in turn will be released by corrosion even at the room temperatures in a corrosive environment. The amount of free energy increased during metallization process varies from metal to metal; it is relatively high for some metals such as magnesium or iron, and relatively low for noble metals such as gold or platinum. Consequently, magnesium and iron corrode faster than gold and platinum [9]. In some cases, metals have a tendency to return to their original compounds. For example, the most common iron ore, hematite, is an oxide of iron ($\text{Fe}_2\text{O}_3$). The energy required to convert iron ore to metallic iron is released when the iron corrodes to form the same compound.

2.1. Electrochemical Corrosion Mechanism

Two types of reactions occur electrochemically at the metal-electrolyte interface. One of them is anodic (oxidation) reaction, which is dissolution of metallic form into an ionic form at the interface, with the release of valence electrons in to the metal. It is transformation of electrically neutral metal atoms into discrete ions. These ions may remain in solution or react to form insoluble corrosion products. The anodic reaction (oxidation) of a metal $M$ is generally expressed by the following equation:

$$M = M^{n+} + ne^-$$  \hspace{1cm} (2.1)

where, $n$, represents the valence of the metal, the number of electrons released by metal from its outermost shell, which can be used by a cathodic reaction occurs over the same metal surface. Cathodic reactions (reductions) form compounds at cathodic sites of metal by consuming electrons, either released internally by anodic reactions, or supplied by an external source, or both. There are two fundamental cathodic reactions in neutral ground waters. If the environment is aerated, the cathodic reaction (reduction of oxygen) will be in the form of:

$$\text{O}_2 + 2\text{H}_2\text{O} + 4e^- = 4\text{OH}^-$$  \hspace{1cm} (2.2)

If the water is deaerated and no other side reactions then the cathodic reaction (reduction of deaerated water) at metal solution interface is given by:

$$2\text{H}_2\text{O} + 2e^- = \text{H}_2 + 2\text{OH}^-$$  \hspace{1cm} (2.3)

If the pH of ground water electrolyte is low, then the cathodic reaction (evolution of hydrogen) at the existence of extra $\text{H}^+$ ions would be in the following form:

$$2\text{H}^+ + 2e^- = \text{H}_2$$  \hspace{1cm} (2.4)

It is possible to have any of these reactions for carbon steel-ground water corrosion systems depending upon the potentials over the steel, and the pH values of environment. Ions in electrolytes can move and carry charges, anions move from cathodic to anodic regions, and cations move in the opposite direction in an ionically conductive electrolyte. The absence of any one of them stops the electrochemical corrosion reactions.

The extrapolation of the anodic and cathodic linear regions of the curve gives the corrosion current density ($I_{corr}$), which is inversely proportional to the corrosion rate. The hypothetical cathodic and anodic polarization curves for electrodes show active and passive behaviors as seen in Figures 2.1 and 2.2 [9b]. The corrosion rate can be determined as follows:
\[ CR = 3.27 \times 10^{-3} \frac{I_{corr} EW}{\rho} \]  

(2.4a)

where,  

- \( I_{corr} \) = Corrosion Current Density (A/cm²)
- \( EW \) = Equivalent weight of the metal
- \( \rho \) = Density of the metal (g/cm³)

2.2. Corrosion of Steel in Water

Corrosion processes in steel due to ground water interactions are electrochemical in nature. Therefore, the mechanisms are anodic and cathodic reactions for corrosion of steel in water. Metallic Fe in anodic region oxidize to ferrous Fe\(^{2+}\) ions by the reaction in the form of:

\[ \text{Fe} = \text{Fe}^{2+} + 2e^- \]  

(2.5)

This reaction is balanced by the reduction of dissolved oxygen to hydroxyl ions (OH\(^-\)) via consuming the electrons released by the oxidation as given in Equation 2.2. Then the product of anodic reaction Fe\(^{2+}\) and the hydroxyl ions (OH\(^-\)) formed by the cathodic reactions will react to form ferrous hydroxide precipitate Fe(OH)\(_2\):

\[ \text{Fe}^{2+} + 2\text{OH}^- = \text{Fe(OH)}_2 \]  

(2.6)

Since the YM water would likely be aerated with approximately 10 ppm dissolved oxygen [9c], it would be possible to represent the overall reactions for the corrosion system of interest as follows:

\[ 2\text{Fe} + 2\text{H}_2\text{O} + \text{O}_2 = 2\text{Fe(OH)}_2 \]  

(2.7)

The corrosion mechanism of steel in neutral waters can be illustrated as shown in Figure 2.1a.

2.3. Faraday's Law

The free energy change of a corrosion process in terms of the potential difference and the amount of transported charge is known as Faraday’s Law:

\[ \Delta G = -nFE \]  

(2.8)

where, \( F = 96,494 \) coulombs/mole, \( E \) is the measured potential, and \( n \) is the number of electrons transferred in the corrosion reaction [10]. An expression for penetration rate “\( r \)” (penetration per unit time) of a corroding metal can be derived from Faraday’s law as given in the following equation:

\[ r = 0.129 \frac{a}{n.D} \]  

(2.9)
The penetration rate \( 'r' \) in Equation 2.9 is in the units of mills/year (mpy) when current density is \( I \) (\( \mu A/cm^2 \)), density \( D \) (g/cm\(^3\)), and the atomic weight \( 'a' \) (g/mol). Consequently, it is possible to calculate the penetration rate equivalent of a current density measured from corrosion reaction of a metal by Equation 2.9.

### 2.4. Nernst Equation

Considering a reaction with reactants A and B, and products C and D, as in the following:

\[
A + B = C + D
\]

Then Nernst equation for this particular reaction can be expressed as:

\[
AG = AG^\circ + RT \ln \left[ \frac{[C][D]}{[A][B]} \right]
\]

(2.10)

(2.11)

where, \( R \) is the gas constant which equals to 8.3143 J /mol K, \( T(K) \) is temperature. The symbol (\(^\circ\)) represents standard state parameters at 298 K and at the pressure of 1 atmosphere. The terms in the square brackets represent the concentrations of the species in the solution expressed in molarities (mol per liter). Nernst equation may also be written by substituting Faraday’s free energy expression as follows:

\[
E = E^\circ - \frac{RT}{nF} \ln \frac{[products]}{[reactants]}
\]

(2.12)

The electrode potential \( E \) changes as a function of concentrations of the participating substances. Therefore, this formula can be used to construct equilibrium potential-pH diagrams, also called Pourbaix diagrams [11].

### 2.5. Pourbaix Diagrams

Pourbaix used the Nernst equation (Equation 2.12) to develop potential-pH diagrams for a variety of metals considering all possible equilibrium reactions in water. Pourbaix diagram for iron, for all dissolved species at electrolyte activity of \( 10^{-6} \) g-equiv/L, is given in Figure 2.2. Three main regions in the Pourbaix diagram describe the cases in which corrosion, immunity, and passivity occur. The hatched regions in Figure 2.2 show soluble products formed in a wide range of acidic conditions, and a narrow range of alkaline conditions, in which corrosion takes place. Between these two regions, an insoluble film forms giving rise to passive region. The third region, immunity, shows that the metal is thermodynamically stable and neither corrodes nor passivates. Pourbaix diagrams provide a strong thermodynamic basis for understanding corrosion reactions for the metals of interest. However, it does not take into account the kinetics of reactions and how contaminated the water is. In practice, the corrosion processes are usually taking place in contaminated aqueous environments and they are deviating from the thermodynamics.
2.6. Polarization

The difference between the potentials of an electrode with and without current (measured in the external circuit via counter electrode) is called polarization. Polarization may also be referred to the departure from equilibrium, or to over potentials. Positive over potentials are called anodic polarization, whereas negative over potential are called cathodic polarization. Evans [12] introduced a method to represent the relationship between potential and current for a corroding metal in an environment, introducing a linear Tafel shown in Figure 2.3 (in A and B), where the horizontal axis represents the logarithm of the current. The intersection of the anodic and cathodic curves represents the condition where the rates of those two reactions are equal, and no net current flows through the external circuit in between anode and cathode. At this point, all of the electrons released by anodic reactions are consumed by the cathodic reactions. Therefore, the potential at the intercept of the cathodic and anodic curves defines the corrosion potential \( E_{\text{corr}} \), and it will not change its value as long as the environmental conditions effective on reactions are the same. There are two types of polarizations effective on controlling the electrochemical reactions [9]; activation and concentration polarizations, and can occur simultaneously or individually at any time for any given corrosion system. Activation polarization is a type of reaction control that comes inherently from the reaction, such as limited speed of electron transfer in a certain metal, or temperature of the metal effective on the reaction. On the other hand, concentration polarization is caused by concentration changes of the species in bulk solution at metal-solution interface. They wait for a reaction to be involved because of rapid depletion of species at metal surface along low diffusivity of electrolyte. Thus, the reaction rate cannot exceed a certain value, which is associated with the limiting current density. The limiting current density is the highest current density possible for a given metal-environment reaction due to diffusion limitation of the reaction particle in the electrolyte [13-14]. The polarization plot representing the concentration controlled rate is given in Figure 2.3 (in B) in which \( i_{\text{corr}} \) value is equal to the limiting current in this particular reaction control.

In the case of 'activation polarization', the relationship between polarization and reaction rate can be given in terms of Tafel constants \( \beta_a \) and \( \beta_c \) [15], which are the slopes of the anodic and cathodic linear regions on the semi-logarithmic polarization plot.

\[
\eta_a = \beta_a (\log i_{\text{corr}} - \log i_a)
\]  

(2.13)
\[ t_e = \beta_a (\log i_c - \log i_{\text{corr}}) \]  

(2.14)

where \( i_a \) and \( i_c \) are the equilibrium current densities for anodic and cathodic reactions respectively. The limiting current density is an important quantity as it is related to the concentration polarization. It is inversely proportional to the thickness of the diffusion boundary layer \( \delta_i \) [16], which can be expressed as:

\[ i_L = \text{constant} \]  

(2.15)

For a cathodic process, the concentration polarization is given in reference [25],

\[ \eta_c = 0.059/z \log c_e / c_0 = 0.059/z \log (1-i/i_L) \]  

(2.16)

where, \( c_e \) is the concentration on an electrode, \( c_0 \) is bulk solution concentration, \( i \) is applied current density, \( i_L \) is limiting current density, \( z \) is the number of exchange electrons.

2.7. Polarization Resistance

The determination of the corrosion rate by polarization method has been widely accepted because of their reliability and fast data acquisition as compared to classical long-term corrosion testing methods based on weight loss measurements [17]. Polarization resistance is defined as the slope of the \( E = f(I) \) curve, given in Figure 2.3C, which is a typical plot of electrode potential vs current in the linear axis. The slope is inversely proportional to the corrosion rate, or \( i_{\text{corr}} \) [15]. Therefore, the corrosion rate can be calculated using the equation:

\[ i_{\text{corr}} = B/R_p \]  

(2.17)

where, \( R_p \) represents the polarization resistance. \( B \) is the proportionality constant obtained from the Tafel constants \( \beta_a \) and \( \beta_c \) as given by the Stern-Geary equation [16] given below:

\[ B = \beta_a \beta_c / [2.3(\beta_a + \beta_c)] \]  

(2.18)

The anodic and cathodic reaction plots are shown in the same polarization plot [13]. Hypothetical Evan’s diagrams are the Tafel constants, \( \beta_a \) and \( \beta_c \) slopes of two linear regions on the semi-logarithmic polarization plot, may be obtained by potentiodynamic or galvanodynamic scans using a Potentiostat. A modern Potentiostat can analyze polarization curves \( E \) vs. \( \log(I) \), and gives the polarization resistance values. In some cases, potentiodynamic scans are favored over galvanodynamic ones, or vice versa, depending on the resistance of test solution which always has negative effect on measured currents.

2.8. Electrochemical Impedance Spectroscopy

Impedance spectroscopy is another method for calculating the corrosion rate of metals in aqueous environments. We can obtain the polarization resistance by applying a sinusoidal voltage of small amplitudes to the working electrode in an extensive frequency range [18-20]. The response in the circuit to every applied alternative voltage with different frequency is a sinusoidal current with different amplitude, and a phase shift relative to the input signal. The ratio of the applied and resultant signals through the circuit gives the impedance \( Z \):

\[ Z = \Delta E / \Delta I = Z_r - iZ_c \]  

(2.19)

The impedance \( Z \) is a complex quantity, so it has real and imaginary components as opposed to a real resistance. The ‘Nyquist Plot’ shown in Figure 2.4 is obtained by plotting the imaginary part and the real part of complex \( Z \) as \( y \) and \( x \) axes respectively.

It is useful to consider a hypothetical ‘equivalent circuit’, in order to realize the variations of the electrochemical impedance with changing frequencies. A combination of common circuit elements can behave in a similar manner like a corroding electrode in an electrolyte [21-22]. The equivalent circuit proposed by Randles has been found to have a wide application in many electrochemical systems [19]. Figure 2.4 shows the equivalent circuit of Randles.
type. In case of steel and YM water interface, we can employ the same equivalent circuit in order to analyze the electrochemical IS data.

Figure 2.3. A: Corrosion potential and rate (I_{corr}) under activation control, B: Corrosion potential and rate under concentration control. C: Linear portion of polarization curve at low overvoltage near E_{corr}. 
The resistance $R_o$ in the equivalent circuit represents the solution and the corrosion product film. $R_t$ (charge transfer resistance) and $C_{dl}$ (double layer capacity) both represent the corroding interface. $R_t$ determines the rate of the corrosion reaction as it is the measure of electron transfer across the surface. Under an activation-controlled systems $R_t$ is always equivalent of $R_p$, the polarization resistance. As the $R_t$ can be measured precisely from the intercept of semicircle with the real axis of Nyquist plot, this value can be substituted in the Stern-Geary equation to calculate the corrosion current density and the corrosion rate. The Stern-Geary equation will take the form as in the following:

$$i_{corr} = \left[\beta_a \beta_c/2.3 (\beta_a + \beta_c)\right][10^6][1/R_t] \mu A/Cm^2 \quad (2.20)$$

where, $\beta_a$, $\beta_c$ are anodic and cathodic slopes in the polarization plot ($E$ vs $\log I$). In practice $R_t$ and $C_{dl}$ are non-linear elements. Their numerical value depends on the magnitude of the applied voltage. This difficulty can be overcome by considering the response of the electrochemical cell to a sinusoidal voltage of a single frequency, $\omega$, and small enough amplitude for the non-linearity of the cell to be negligible. Figure 2.4 shows the behavior of the equivalent circuit in terms of a Nyquist plot. The horizontal axis in Figure 2.4 represents the real part of the cell impedance i.e. resistive component, and the vertical axis the imaginary component, i.e. the capacitive reactance. At high frequencies (typically more than 10 kHz) $C_{dl}$ conducts easily and shorts out $R_t$ effectively. Therefore, only the film resistance $R_o$ remains effective. As the frequency decreases $C_{dl}$ conducts less and less and the response typically follows a semicircle. At low frequencies or as a DC voltage is approached, the capacitor stops to conduct and the cell impedance becomes the sum of $R_t$ and $R_o$. In practice, the above situation (depressed semicircle) cannot be easily observed because of the activation controlled corrosion rate and the complications due to diffusion effects that are usually present. In order to model those effects, it is necessary to include an additional circuit element $W$, in series with $R_t$. This element is called Warburg impedance, which represents the concentration and diffusion related processes. By adding the Warburg impedance to the Randies circuit the complex plain response in Figure 2.4 changes from the depressed semi-circle to the gray curve denoted ‘$W$’, representing increased amounts in concentration controlled processes. In addition the Bode plot is represented in the Figure 2.5 with equivalent circuit.

### 2.9 Passivation in Metals and Alloys

If the corrosion product is insoluble and adheres to the metal surface, it forms a very thin protective film on the metal surface, causing “passivity” because of it’s significant effect on decreasing the current density, as lowering the corrosion rate. A typical appearance of passivity on a hypothetical polarization diagram is given in Figure 2.6, showing the passive region with the passive current density. If there were no passivity, a steady increase in current would occur with increasing over-potentials as shown by the dashed line in Figure 2.6. The passivity due to film formation is of two types in general [22-23], such as chemical passivity and precipitation related mechanical passivity. Chemical passivity occurs due to a thin and dense semi-conducting oxide film that adheres strongly onto
metal surfaces. It is a type of coating, in which certain anodic and cathodic reactions form mainly metallic oxides with high adhesive forces. This type of passivity moves the working electrode potential strongly to the positive directions, to more noble values. Passivity by precipitation or mechanical passivation is the decrease in corrosion rate by accumulation of insoluble solid salts, already available in the solution, onto metal surfaces. These precipitates do not only form at the interface, and also in the electrolyte due to temperature and concentration effects and deposited over the specimen leading to significant decrease in corrosion rates. The scale built up on the surface is a very thick salt layer but porous in nature, and most of the time it is not electrically conductive at all. Higher temperatures and concentrations increase the activity of aqueous environments and lead to more precipitation.

2.10. Pitting

Pitting is a type of localized corrosion that occurs on the passive surfaces of metals exposed to a corrosive environment [24]. The passivity of metal i.e. the thin film formation is one of the requirements for pitting to occur over the metal surface. Another main factor for pit formations is the high chloride content of the environment [25]. Pitting initiates by preferential attacks of aggressive ions, especially of chlorides in certain electrochemical conditions [26]. Then, it starts to grow at an increasing dissolution rate to propagate through the metal while the other parts of the surface are still passive. Physical defects over the passive film such as cracks or pores also allow
the pitting initiation and growth on the metal surface [27]. Pitting initiation has been observed at certain electrode potentials for particular alloy-environment systems. This "critical pitting potential" is a function of the temperature as well as concentration of aggressive ions in the environment [28]. Initiation and growth rate of pitting also depend on the properties of the passive film and crystal orientation of the metal grain on which pitting occurs. Particularly, the grain boundaries, inclusions, and heterogeneities are common sites where pits initiate. Generally, pitting can cause sudden unexpected failures, because of its localized nature. In localized corrosion, the dissolution takes place at an anode of preferably small surface area while cathodic areas are much larger. Then the exchanged current between anodic and cathodic reactions will cause more current density in the anodic areas due to that large surface area difference. Therefore, the corrosion rate becomes significantly high resulting in a rapid dissolution and failure of metals and alloys. When a passive metal is under stress in an aggressive environment, it becomes more perilous, and more rapid failures become imminent due to local strain at the crack tip initiated by pitting. However, there are certain metal-environment systems that experience these types of failures, which will be topic of the stress corrosion-cracking phenomenon.

2.11. Hydrogen Permeation Studies

Hydrogen diffusion and trapping characteristics were determined and compared for the steel sets and rock bolts using the classical Devanathan and Stachurski's electrochemical permeation technique. The above technique has been widely used to calculate the diffusivity and also to classify the role of traps and their effect on hydrogen diffusivity. In general, traps are classified as reversible or irreversible depending on their binding energies. The contribution of traps on the diffusivity can be obtained by successive permeation transients on the same sample. Usually, during the first permeation transient, all the reversible and irreversible traps are filled and during the second permeation transient, irreversible traps are ineffective and only reversible and lattice sites are effective on diffusivity. Hydrogen permeation studies are performed on flat and thin specimens by electrochemical charging with hydrogen.

A model plot showing the variation in hydrogen permeation with time is shown in Figure 2.7. This shows two permeation transients, which will be plotted separately to determine material property such as permeation rate, Effective Diffusivity, Solubility and density of trapping sites for RBCS and SSCS.

The hydrogen permeation rate \( J_w L \) (mol H cm\(^{-1}\) s\(^{-1}\)), effective diffusivity \( D_{\text{eff}} \) (cm\(^2\) s\(^{-1}\)) and solubility \( C_0 \) (ppm) were calculated using the following equations:

2.11.1 Analysis of Hydrogen Permeation Rate \( J_w L \) (mol H cm\(^{-1}\) s\(^{-1}\))

\[
J_w L = \frac{I_{poo} L}{nF} \tag{2.21}
\]

Where \( J_w \) is the steady-state flux, \( L \) is the specimen thickness in (cm), \( I_{poo} \) is the steady-state permeation current density in A/cm\(^2\), \( n \) is the number of electrons transferred, \( F \) is the Faraday's constant (96485 Coulombs/mol.) and \( L \) is the specimen thickness.

2.11.2 Analysis of effective diffusivity \( D_{\text{eff}} \) (cm\(^2\) s\(^{-1}\))

The steady state hydrogen permeation flux \( (J_{ss}) \) is given as [6]

\[
J_{ss} = \frac{I_{ss}/A}{F} = \frac{D_l C_0}{L} \tag{2.21a}
\]

Where, \( I_{ss} \) = steady state atomic hydrogen permeation current (\( \mu \)A),
\( A = \) Exposed area of specimen in the oxidation cell (cm\(^2\)),
\( C_0 = \) Sub-surface concentration of atomic hydrogen at the charging side of the specimen (mol/cm\(^3\))
\( D_l = \) Lattice Diffusion Coefficient of Atomic hydrogen (cm\(^2\)/s)

The effective Diffusion Coefficient can be calculated based on the elapsed time \( t_{ss} \) at \( J(t)/J_{ss} = 0.63 \) [6],

\[
D_{\text{eff}} = \frac{L^2}{6t_{ss}} \tag{2.22}
\]
Where \( t_\ell \) is the lag time at \( J(t)/J_{ss} = 0.63 \) and \( L \) is the thickness of the specimen (cm).

### 2.11.3 Solubility (\( C_o \) ppm)

Subsurface concentration of atomic hydrogen at the charging side of the specimen (Solubility) is given as [6]

\[
C_o = \frac{J_{\infty}L}{D_{eff}}
\]  

(2.23)

### 2.11.4 Density of Trapping (\( cm^3 \))

The density of trapping sites was calculated as

\[
N = \frac{C_o D_L}{3D_{eff}}
\]  

(2.24)

Where \( C_o \) is the hydrogen concentration measured from the permeation transient of the respective steels, \( D_L \) is the lattice diffusion coefficient \((7.2 \times 10^{-5} cm^2/s)\) and \( D_{eff} \) is the effective diffusion coefficient of the respective transients.

![Graph showing hydrogen permeation transients](image)

Figure 2.7. Actual Hydrogen permeation transients obtained from Devanathan and Stachurski Cell to calculate material property of RBCS (018VD.010 File: 514rockboltmaha.xls)

### 2.12 Environmentally Induced Cracking

Environmentally induced cracking (EIC) is one of the most important forms of failures caused by the localized corrosion. It causes catastrophic brittle failure, which can occur in a wide variety of metals and alloys in their specific environments [29]. Normally, the tensile forces have no effect on corrosion of metals. However, a specific corrosive environment coupled with these forces leads to a sudden brittle cracking failure on metal structures. There are various types of environmentally induced failures for metals; such as stress corrosion cracking, hydrogen induced cracking, and corrosion fatigue cracking are the ones in which electrochemical corrosion effects are involved [30-32]. Unexpected brittle failures occur during EIC with all the types above, however their cracking mechanisms are quite different from each other. In general, when an initiated crack penetrates through the metal, roughly as normal to the load direction, the effective cross section gets smaller. Failure results when the narrowed cross section does not hold up with the external load any more. Environmental cracks are generally not noticeable by normal visual examination before cracking occurs. Optical or scanning microscopic analysis can be used to determine the failure mode and the type of corrosion cracking. There are two main modes of cracking in
polycrystalline metals, such as inter-granular and trans-granular cracking. The grains are always intact, and ruptures occur along the grain boundaries when the cracking is inter-granular. Individual grains split apart without regard to the grain boundaries, in trans-granular cracking mode. Mostly, there is one or another mode that occurs with in a particular corrosion cracking in a specific environment, but in some cases both of the modes appear together, depending on the environmental conditions, such as pH or temperature [33]. Stress corrosion cracking and hydrogen embrittlement are expected environmental effects on carbon steel and ground water systems. However, the degree of susceptibility to any environmental cracking will depend on the existing ions in waters, environmental conditions, and strain rates. Whereas passive film formation on the metal surface leads to SCC, hydrogen in water, transformed to atomic hydrogen in some processes, leads to hydrogen induced cracking [34]. These two major environmental failures are main subjects of this work and will be discussed in details within the next section.

2.12.1 Stress Corrosion Cracking

Stress corrosion cracking (SCC) is an environmentally induced cracking of a metal caused by the combined effects of tensile stress and a corrosive environment specific to the metal [34-36]. Only certain combinations of alloys and environments will result in severe SCC. For instance, stainless steels crack in chloride environments but not in ammonia. To the contrary, brass cracks in ammonia but not in chloride environments. SCC is experienced in a wide variety of metals and environments that have one common surface feature: alloys/metals undergo SCC always show some types of corrosion product film on their surfaces [36-37]. The existence of film or passivation is one of the main elements for SCC to occur. Crack initiations on passive films are of two types such as electrochemical and mechanical. Film rupture by applied tensile stress or static stress allows mechanical initiation for pitting. Chemically induced pitting occurs in those films that are intact, in the absence of excessive stresses put upon them. In both cases, initiated pits create anodic sites that result in rapid dissolution of the metal. SCC reveals unique crack surface patterns, which can easily be examined by even the naked eye, whereas the surface of metal is attacked very little, when highly localized cracks propagate through the metal. In general, a number of secondary cracks in a necked region may be observed, extended parallel to the main crack. The crack tips generally branch and appear sharp, and propagate approximately normal to the applied load. There is always a reduction in the effective gauge cross section without losing too much ductility, or gaining brittleness. Specimen surface potentials play significant role in SCC to occur. In general, there are two different potential regions, in which SCC occurs predominantly, as illustrated on the polarization diagram in Figure 2.8. These susceptible potential regions around the potentials called \( E_{\text{prot}} \) and \( E_{\text{pit}} \) create the right electro-mechanical conditions for SCC to occur severely between metal and its specific environment. Because both regions are of transpassive nature, it may not require a fully passive thick film for SCC to occur for most of the systems, as one can conclude from Figure 2.8.

2.12.2 Mechanism of SCC

There are a number of proposed SCC mechanisms such as film rupture model, active path inter-granular model, corrosion tunnel model, tarnish rupture model, and film induced cleavage model. In the most general case a surface film is necessary for pit formation, or rupture or tarnish to create an active path for corrosion during straining. However, there are only two competitive events at the tip of a propagating crack, with any model mentioned above. One is the tensile stress causing plastic deformation to produce fresh un-filmed metal at the crack tip. The other one re-passivation or new film formation process, which restricts the anodic or cathodic reactions between metal and solution. If re-passivation occurs too rapidly, the localized corrosion would be insufficient to cause further crack growth, and SCC will not occur. If re-passivation is too slow, the corrosion attack will occur all over the metal, causing pitting rather than cracking. Therefore the relationship between the fresh surface creation rate and the re-passivation rate is of critical importance in any model proposed. Constant strain rate tests with certain rates that are able to control this mechanical factor and to create the required repetitive passivation-re-passivation steps, lead to severe SCC for certain alloys in their specific environments. Figure 2.9 shows how the crack travels through the metal during straining, and passivation and re-passivation events.

2.12.3 Hydrogen Embrittlement

Hydrogen induced cracking (HIC) is an other type of environmentally assisted cracking which occurs in hydrogen gas rich environments, or in environments where hydrogen evolution takes place by cathodic electrochemical reduction reactions. If a metal is mechanically tested in a hydrogen-involving environment or it is cathodically charged during testing, or charged with hydrogen prior to mechanical testing, its mechanical properties are generally
degraded [38-40]. This degradation can take a number of different forms. When a smooth cylindrical tensile specimen is tested in hydrogen bearing environment, its elongation and reduction of area at failure is diminished. Yield strength and ultimate tensile strength are generally not affected with hydrogen embrittlement of the metals [41]. There are various proposed mechanisms such as hydride model, pressure model, surface adsorption model, and de-cohesion model. The pressure model states that hydrogen in the metal lattice could reach super large saturations as the result of cathodic charging and forms bubbles of gas in there. These bubbles then could create strain on the lattice and cause failure [38]. This model may be valid only for highly saturated environments because it was already proven that even much smaller pressures of hydrogen could cause premature failures [42]. If metal has nonmetallic inclusions, then these anodic sites become voids, and hydrogen gas accumulates at the site increasing the pressure to cause internal rupture. Therefore, the model may also be valid for metals with nonmetallic inclusions.

Figure 2.8. General susceptible potential regions to stress corrosion cracking around $E_{prot}$ and $E_{pits}$ on the potentiodynamic polarization diagram. (Non-Q for information only)

Figure 2.9. The sequence of events occurring at a propagating crack tip during SSRT.
A: Passive surface prior to pitting, or brittle film fracture due to straining.
B: Pitting or cracking, exposing the fresh metal to the electrolyte.
C: Dissolution and re-filming of exposed surface, but yet another crack.
D: Continuation of the processes. (Non-Q for information only)

The surface adsorption model proposes the idea that hydrogen adsorbs on the crack tip surface and lowers the surface energy. Hence, it lowers the required force for a fracture to occur. The de-cohesion model expresses that hydrogen enters the lattice and causes chemical bonds to be weakened, leading to premature failure [43-44]. The hydride model proposes brittle hydride formation that can easily be cracked, however there are many hydrides that
do not undergo hydrogen embrittlement [38]. Some of the proposed mechanisms above would be appropriate to explain certain failures; however, none of them have general applicability. It is possible for a metal in a hydrogen-bearing environment to undergo all or some of these mechanisms above.

2.12.4. Strain Aging- Portevin LeChatelier Effect

Strain aging, or Portevin-LeChatelier (PLC) effect occurs in most metals at various temperatures during straining, generally at slow rates. It manifests itself through complex deformation behaviors, such as serrated flow stress and negative strain rate sensitivity of the stress. The PLC effect is more the rule rather than the exception in metals that involve solute inclusions [45-47]. The plastic deformation region of stress-strain curves show a serrated flow behavior, as the result of PLC. The serrated curve given in Figure 2.10 illustrates the behavior of a carbon steel during strain aging effect, with its characteristic Luder band plateau onset of plastic deformation. Serrations due to the PLC effect occur in different types of shapes such as type B, type C etc., depending on where the actual dislocation activities take place in the effective specimen gauge. Experimental results (serration shape analysis) in the literature showed that in carbon steel C type PLC bands were observed in general, which took place at random places of specimen gauge by activation of fully aged dislocations through local stresses that were created by dislocation-inclusion interactions [45]. The most widely accepted explanation for the strain aging effect is called diffusion-assisted obstruction of dislocation motion. If the solute (such as carbon, hydrogen, and nitrogen) mobility becomes comparable to the dislocation mobility, then the solutes pile up around the dislocations, prohibiting the smooth transitions between the saturated and enriched parts of the alloy, and cause slow and fast deformation regimes. There are many other proposed mechanisms, but none of them so far explained the issue with reasonable and ample enough physical support and evidence [48]. Therefore, it requires further research and investigations to explain of why serrations occur.

Carbon steels are well known to be more sensitive to dynamic strain aging or the PLC effect because of their high carbon content. These metals also easily permeate hydrogen, which may interact with carbon or nitrogen solute inclusions, and allow all solute atoms to interact with dislocations [49]. In carbon steels, the PLC effect is observed in a temperature range where the mobility of carbon atoms is relatively close to the imposed dislocation velocity [50-51]. In general, the PLC effect induces an increase in flow stress, ultimate tensile strength (UTS) and work hardening rate, and decreases the ductility of metals that corresponds to a reduction in elongation, effective gauge cross section, strain rate sensitivity coefficient, and fracture toughness.

2.13 References for Background and Theoretical Section

III. EXPERIMENTAL

3.1 Materials and Specimen Preparation

The rock bolts (0.44%C, medium carbon steel) and the steel sets I-beam (0.08%C, low carbon steel) were furnished from the Yucca Mountain site. The other alloying elements that are important for the corrosion properties are listed in Table 3.1. The low and medium carbon steels with different C, Mn and S content were used in the present investigation furnished by US-DOE, Yucca Mountain site. The low carbon steels were in the form of a large I-beam to provide ground support reinforcement. The medium carbon steels were in form of rock bolts with a hollow core. The chemical composition of the above steels is given in Table 3.1. Photographs of original rock bolts carbon steel (RBCS) and section of the I-beam steel set carbon steel (SSCS) obtained from YM repository site are shown in Figure 3.1. The electrodes were polished up to 600 grit SiC papers, cleaned in distilled water followed by acetone. For polarization measurements, disk specimens were machined from low carbon steel to yield electrodes of area 0.95cm². These electrodes were mounted in epoxy resin with one end soldered to a copper wire for electrical connection. The other side was subsequently polished using 600 grit SiC paper and finally cleaned in distilled water and acetone. For polarization and impedance studies, disks were cut from RBCS rods and SSCS to yield electrodes of area 0.8cm². These electrodes were mounted by using cold-setting resin, with one side soldered to a copper wire.; the other side was subsequently polished on SiC paper down to grade 800 and finally cleaned in distilled water. Electrochemical Polarization, Impedance Spectroscopy, hydrogen permeation measurements-rectangular specimens were machined with size 80x 10x 1.5mm from both the rock bolt and I-beams and are shown in Figure 3.2. Also shown are tensile test specimens of the steel sets for stress corrosion cracking and hydrogen embrittlement in Figure 3.2.

The chemical composition of YM rock bolt-carbon steel (RBCS) and steel set-carbon steel (SSCS) obtained from the YM site for present research is given in Table 3.1. The chemical composition of SSCS was compared with ASTM A-36, and that of RBCS with ASTM A-29, A-108, A-311 and they were in compliance with the standards.

3.2 Cell Design and Experimental Set-Up for Electrochemical Tests

A schematic of a one-liter flask of Pyrex brand glass, shown with the set-up of electrochemical experiments in Figure 3.3, was used as the test cell of both polarization resistance and electrochemical impedance measurements. A disk shape lid constructed out of 2 cm thick Teflon to seal the cell by means of o-ring, was held in place by compression clamps. A tapered Teflon plug with two

<table>
<thead>
<tr>
<th>ASTN Standards (AISI/UNS)</th>
<th>YM Carbon steels</th>
<th>Elements (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Steel Sets (SSCS)</td>
<td>C</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>ASTM A-36</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.44</td>
</tr>
<tr>
<td></td>
<td>ASTM A-108/A-29/A-311 (1144/G11440)</td>
<td>0.4-0.48</td>
</tr>
</tbody>
</table>
Figure 3.1 A. Rock bolts (shown with arrows) from YM site (B) Steel set (I-beam 8") from YM site (C) A cross section at xx in Figure B. (Non-Q for information only)

Figure 3.2. Photographs of the specimens prepared from the rock bolts and I-beam shown in Figure 3.1. Specimens prepared for (A) Potentiodynamic and EIS tests are shown in the top left photograph, (B) Electromigration are shown in top-middle photograph, (C) Immersion experiments are shown in top right photograph, (D) Stress corrosion cracking and hydrogen embrittlement studies in bottom left photograph (I-beam), and (E) For YM water or salt spray tests in the bottom right photograph.
holes were machined for the middle opening of the lid, in which cylindrical receptacles for specimen and a Luggin probe were placed in the chamber. Several other receptacles on the lid sealed the entire cell elements via threaded o-ring fittings. The cell design was based on the design of Jones and Paul [1] and met ASTM Standard Specification, G5. A tapered Teflon stopper constructed for the larger central hole of the lid held both the specimen and Luggin probe in close proximity, as shown in Figure 3.3. The distance between the probe tip and the specimen surface was maintained constant using a small Teflon block spacer in between them. It did not block the interface since only the edge of the epoxy mold leaned against the spacer set on the probe. The probe and specimen holder set-up was designed to provide a desired distance of 1 mm in all cases, to eliminate any probe distance effect on the entire potentiodynamic polarization or impedance experiments.

A more detailed schematic of the overall arrangement is shown in Figure 3.4. In this, cylindrically shaped working electrodes (test specimens) were mounted in epoxy with their 1 cm$^2$ bottom surface area and electrical connection wire protruded out. A large (~10 cm$^2$) platinum sheet sealed to a glass capillary was used as a counter electrode to provide good conductivity in the electrolyte. The Luggin probe tip and Ag/AgCl reference electrode were connected via the test solution (YM water) in the probe, without using a salt bridge. Continuously purged gas (nitrogen or oxygen) in the sealed cell maintained constant pressure above the solution, and formed a tall column (8-10 cm) of solution bridge inside the probe, which connected the Luggin tip and the reference electrode. Therefore, the reference electrode was able to be placed well above the solution level, outside the cell. Thus, the set-up avoided excessive heat on the reference electrode, by means of the temperature gradient created along the solution bridge in the probe.

An auto tune proportional integral-differential (PID) temperature controller (Ace Glass, Love controls series 32A) along with an electric mantle heater (Glass-Col TM812) that surrounded the cell maintained the desired test temperatures from 25°C to 85°C at any value to an accuracy of ± 0.1 °C. An end sealed thin glass capillary was used as thermo-well to hold the thermocouple sensor in the solution. A fritted glass capillary was used for continuous aeration/de-aeration of the solution throughout the experiments with the rate of 150 ml/min. The fritted region with a surface area of ~4 cm$^2$ supplied appreciable aeration and de-aeration for the test solutions. A water-cooled glass reflux condenser was used to minimize the loss of test solution by evaporation at elevated temperatures. The outlet of the reflux condenser was connected to an oxygen trap to avoid aeration/de-aeration fluctuations in the electrolyte.
The overall construction required no complicated glass blowing while it already met the designations approved by ASTM Standard, G5.

A-Platinum counter electrode  
B-Specimen-working electrode  
C-Reference electrode  
D-Fritted glas purging element  
E-Heating mantel  
F-Water cooled condenser  
G-Oxygen trap  
H-Flowmeter  
I-Temperature controller  
J-Potentiostat  
K-Oxygen gas for aeration  
L-Nitrogen gas for de-aeration

Figure 3.4. Experimental set-up for potentiodynamic linear polarization and impedance spectroscopy.

3.3. Electrochemical Impedance Spectroscopy

The electrochemical impedance spectroscopy (EIS) was performed at the corrosion potentials (open circuit potentials) of the test specimens using the same cell set-up and the same software as used in the polarization studies, which is introduced in Figure 6. Polarization resistance values can be determined from the real axis intercepts of the obtained semicircles of Nyquist plots of the impedance scans. Please see Figure 3.5 for polarization curve and the point A through E and the corresponding Nyquist plots in Figure 3.6. These tests will be used to determine the electrochemical interface leading to activation and passivation events on the carbon and other steel surfaces during polarization experiments. In general, impedance $Z(\omega)$, may be expressed in terms of real, $Z'(\omega)$ and imaginary $Z''(\omega)$, components.

$$Z(\omega) = Z'(\omega) + Z''(\omega)$$  \hspace{1cm} (3.1)

The Stern-Geary equation (see section II) provides a direct relationship between the steady state corrosion current and the resistance across the interface, which can be expressed as follows:

$$i_{corr} = \frac{\beta_a \beta_c}{2.303(\beta_a + \beta_c)} \left[ \frac{1}{R_p} \right]$$  \hspace{1cm} (3.2)

where, $\beta_a$ and $\beta_c$ are the Tafel constants for the anodic and cathodic partial reactions, respectively and $R_p$ is the polarization resistance. Polarization resistance is given by the difference of the measured impedance at sufficiently low and high frequencies:
Gamry Potentiostats were used for Impedance spectroscopy analysis (ASTM G106). Nyquist and Bode plots will be obtained for rock bolt steels in YM environment at different concentrations of ionic salts (1x to 500x). To understand the effect of applied potentials on the passivation tendency, and its influence on the impedance change, experiments were conducted at different potentials by fixing the electrode potential potentiostatically. Influence of temperature was also determined at different temperatures (45, 65 and 85°C). Representative plots obtained in our laboratory showing the effect of impedance changes at different potentials applied on the carbon steel electrode exposed to 3.5% NaCl solution with different anions are shown in Figures 3.5 and 3.6.

\[ R_p = |Z(j\omega)_{a\rightarrow c} - |Z(j\omega)_{i\rightarrow c}| \]  

(3.3)

Figure 3.5. Polarization behavior of carbon steel in 3.5% NaCl + silicate + bicarbonate + sulfate, pH = 8 (018VD.003 file: 224nac3.5nas0.01nah0.5sul0.2pd.xls)

Figure 3.6. Nyquist plots showing the impedance changes on Carbon Steel in 3.5% NaCl + silicate + bicarbonate + sulfate at different potentials shown in Figure 3.5 at points A, B, C, D, and E at pH = 8. (018VD.009 File: impedance v potential.doc)

3.4 Environmentally Assisted Corrosion Tests

3.4.1 Stress-Corrosion Cracking and Hydrogen Embrittlement Tests:

A screw-driven SSRT universal machine (United STM-10ES) along its software and a Gamry Potentiostat (DC-105) were used for environmental cracking susceptibility determinations for I-beams. A schematic of the experimental set up is given in Figures 3.7. Also, details of the experimental cell and the set-up are given in Figure 3.8 and 3.9. All SSRT of I-beam (low carbon steel) were carried out with 100X simulated YM water at two different temperatures such as 25 °C and 85 °C; these will be followed for the rock bolts, studies yet to be performed. The simulated waters were conditioned (de-aerated) by purging nitrogen gas for at least one hour before specimen immersion. Then, freshly prepared wet-ground specimens with a 600-grit emery paper finish were immediately installed into the cell through the top and bottom central necks using o-ring compression fittings. The conditioned de-aerated 100X YM water were transferred to the test cell within 10 to 15 seconds without exposing it to air for too long. The cell openings are then closed quickly by threaded o-ring fittings and neck joints, which holds the entire elements of the cell sealed. The installation of the cell on to the universal joints of the SSRT machine did not exceed a total of 4-5 minutes after finishing the specimen preparation. By this rapid installation, possible oxygenation of the de-aerated conditioned test solution, subject to effect the open circuit potential of the LCS by letting excessive oxygen in to the cell, should be prevented. After setting the temperature controller to the desired test temperature, open circuit potential monitoring with the Gamry Potentiostat is started. From previous experience, the open circuit potential (E_{corr}) will stabilize around -700 mV_{Ag/AgCl} while the temperature will have already reached to the desired values to an accuracy of ±0.1 °C. De-aeration by purging nitrogen gas into the test solutions was continuous throughout the tests at a flow rate of 150 ml/min. Then, the conditioned specimens in the test solutions were charged for
approximately 45 minutes by imposing the desired potentials via potentiostatic method, until the current values were stabilized prior to monitoring stress-strain curves and currents.

Figure 3.7. Experimental set-up for environmental cracking, such as SCC and HIC, and strain aging determination [2].

The SSRT test is started with appropriate strain rates ranging from $10^{-3}$/s to $10^{-7}$/s. During these tests, the changes over the test solutions and specimens were examined, and recorded. After reaching the failure stress of the specimens, the cell was disassembled and the pH changes of the test solutions were recorded. Specimens were washed with distilled de-ionized water, and acetone and alcohol, and retained to carry out scanning electron microscopy (SEM), energy dispersive spectral (EDS) analysis, optical microscopy, and reduction of area measurements.

3.5 Scanning Electron Microscopic (SEM-EDS) Studies

A Field Emission Hitachi scanning electron microscope (FE-SEM), Hitachi S-4700, with 1.5 nm resolution and operated between 15 to 20 keV was used for these studies. An Oxford INCA Energy 2000 energy dispersive system (EDS) system was used for X-ray microanalyses to characterize the corrosion products. The corrosion morphologies of I-beam or rock bolts, as a result of the incorporation of the above YM ions in the electrolyte and the change in electrode potential, were examined in this SEM in the secondary-electron imaging mode. The concentration of ions at the localized pit was analyzed by EDS. The SEM was normally operated at a voltage of 20keV.

3.6 Optical Microscopy

Corrosion morphology of the RBCS samples after electrochemical experiments was also observed under Olympus Optical Microscope (OM) equipped with digital cameras.

3.7 X-ray Photoelectron Spectroscopy (XPS)
XPS analysis was performed on RBCS surfaces by additions of different ions using a physical Electronics Quantum 2000 scanning ESCA microprobe at Pacific Northwest National Laboratory (PNNL), Richland Washington. The samples of 0.8 cm$^2$ were polished using SiC paper and passivated at pre-passive and passive potentials for 30 minutes. The changes in chemical compositions were analyzed using XPS. Spectra were generated using an X-ray source operated at 1486.7 eV and using an Ar K$_{α}$ X-ray source with a energy of 58.7 eV resulting in a full width at half-maximum (FWHM) value of 1.15 eV for the Ag (33d$_{5/2}$); spectrum. The ion gun was operated with an Ar$^{+}$ at an energy of 5 kV and the ion gun filament current in 25 mA, corresponding to an etching rate of 8.6 nm/min. The collected data were referenced to an energy scale with binding energies for Cu 2p$_{3/2}$ at 932.67 eV, Cu 3p$_{3/2}$ at 75.14 eV.

Figure 3.8 (A) Photographs of the SSRT Universal Testing Machine showing the specimen in position held between pull rod made for YM project specimens, and glass electrochemical cell. (B) Detailed photo of the electrochemical cell with electrical connections. (C) Close up of the specimen and heater rod.

Figure 3.9. (Left) A typical Potentiodynamic scan plot showing anodic and cathodic regions for the YM 100x water. The SCC/HE tests were conducted at Ec Orr and other potentials. Two examples, at which SCC curves were obtained (at -620 and -680 mV; potentials above the Ec Orr) are shown in this diagram. (Non-Q for information only) (Right) Schematic of the electrochemical cell with the electrodes and sample.

A. Cylindrical Specimen-working electrode, B. Platinum Counter Electrode, C. Ag/AgCl Reference Electrode, D. Luggin Probe, E. Quartz Immersion Heater, F. Fritted End Purging Capillary, G. Electrolyte, H. Water Cooled Condenser, I. Specimen Holder, J. O-Ring seal with Threaded Joints, K. Thermocouple
3.8 Hydrogen Permeation Experiments

Hydrogen permeation experiments were performed in a system with two compartments separated by carbon steel membrane as introduced by Devanathan-Stachursky. Hydrogen was charged galvanostatically at an applied cathodic current density of 1mA/cm$^2$ and the anodic side of the specimen was fixed at a potential of +0.28 V with respect to Silver-Silver Chloride (Ag-AgCl) to enable the oxidation of atomic hydrogen that diffused through the steel membrane. The electrolyte on the charging and the oxidation sides of the cell was de-aerated 0.1N NaOH. De-aeration was done by purging N$_2$ gas for one hour prior to the experiment and was continued until the end of the experiments. The anodic side of the membrane was electroplated with Ni to avoid corrosion. To enhance the hydrogen absorption, 10mg of arsenic trioxide (As$_2$O$_3$) was added in the charging cell as a hydrogen recombination poison. Effect of trapping was investigated by recording a second permeation transient immediately after the first transient. To calculate the critical hydrogen concentration, a third permeation was obtained after completing the second transient at an applied current density of 5mA/cm$^2$ using 1N H$_2$SO$_4$ solution. The calculation of $C_k$ was performed according to the method proposed by Pressouyre et al. [3]. The depth of the crack was measured after completing the third transient by diametrically cutting the specimen followed by metallographic polishing and etching. To compare the uptake of hydrogen, using simulated YM groundwater, permeation experiments were performed by using YM ground water as charging environment instead of 0.1N NaOH. The simulated 1x YM ground water composition was prepared in the laboratory by adding appropriate chemicals to distilled water is listed in Table 3.2; the electrolyte concentration was varied by increasing the dissolved ionic concentrations of 1x, 10x and 100x.

![Figure 3.10. Schematic of Devanathan-Staruchi cell showing the two compartments for permeation of hydrogen. This experiment requires two potentiostats.](image)

![Figure 3.11. A photograph of Hydrogen Permeation cell at UNR used for this work.](image)
3.9 Weight Loss Measurements

The experimental setup to measure the corrosion rate of the above steels using weight loss measurements are shown in Figure 3.12, using reference ground water composition used in all the experiments are in Table 3.2. The species used in this work is shown in Table 3.3. The top specimen marked A is not immersed and is in the humid air. The middle specimen is partially immersed (marked B) and third specimen is fully immersed (marked C). Oxygen gas is purged continuously.

Table 3.2. Reference YM ground water composition used in the hydrogen permeation experiment. (018AY.001 File: YM Sim(III).xls)

<table>
<thead>
<tr>
<th>Dissolved salts</th>
<th>Weight (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na(^+)</td>
<td>88.69</td>
</tr>
<tr>
<td>SiO(_2)(^-)</td>
<td>56.22</td>
</tr>
<tr>
<td>Ca(^{2+})</td>
<td>101.22</td>
</tr>
<tr>
<td>K(^+)</td>
<td>19.50</td>
</tr>
<tr>
<td>Mg(^{2+})</td>
<td>17.0</td>
</tr>
<tr>
<td>HCO(_3)(^-)</td>
<td>176.50</td>
</tr>
<tr>
<td>Cl(^-)</td>
<td>129.08</td>
</tr>
<tr>
<td>F(^-)</td>
<td>0.91</td>
</tr>
</tbody>
</table>

A-Non-immersed specimen  
B-partially immersed specimen  
C-Fully immersed specimen  
D-fritted glass purging element  
E-Plug specimen holder  
F-Thermowell  
G-Water cooled condenser  
H-Flowmeter  
I-Oxygen trap  
J-Oxygen gas for aeration  
K-Nitrogen gas for de-aeration  
L-Temperature controller  
M-Heating mantle

Figure 3.12. Laboratory setup at UNR used to perform dipping immersion tests to measure corrosion rates by measuring weight loss of the coupons after corrosion experiments.
Table 3.3 Reference YM ground water composition used in this work. (018AY.001 File: YM Sim(III).xls)

<table>
<thead>
<tr>
<th>YM Dilute water composition (1x)</th>
<th>mg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCl$_2$.2H$_2$O</td>
<td>196</td>
</tr>
<tr>
<td>MgCl$_2$.6H$_2$O</td>
<td>100</td>
</tr>
<tr>
<td>CaSO$_4$.2H$_2$O</td>
<td>210</td>
</tr>
<tr>
<td>MgSO$_4$.7H$_2$O</td>
<td>50</td>
</tr>
<tr>
<td>NaF</td>
<td>2</td>
</tr>
<tr>
<td>NaHCO$_3$</td>
<td>200</td>
</tr>
<tr>
<td>KHCO$_3$</td>
<td>50</td>
</tr>
<tr>
<td>Na$_2$SiO$_3$.9H$_2$O</td>
<td>210</td>
</tr>
</tbody>
</table>

These experiments were conducted as per ASTM G31 procedure. Carbon steel coupons of size 25x13x0.5mm were machined from the rock bolt and were polished down to 600 grade SiC papers and subsequently cleaned in acetone followed by de-ionized water. The experiment was performed at ambient temperature at open environment for a period of 110 days. The mass loss was converted into corrosion rate using the following formula:

$$\text{Corrosion rate, CR} = K \cdot (W/A) \cdot T \cdot D$$

(3.4)

where, $K = \text{constant (8.76 x 10}^7 \text{ for } \mu \text{m/year}), T = \text{time of exposure in hours}, A = \text{area in cm}^2, W = \text{mass loss in gms},$ and $D = \text{density in g/cm}^3$.

Corrosion rate of the rock bolt was also measured at 75°C under aerated conditions and the effect of immersion conditions (fully immersed, partially immersed and above the electrolyte level) was also tested at this temperature.

3.10 Salt Spray Test

This test was performed as per ASTM B-117 except the electrolyte which is 1x YM water and the test was carried out for a period of 7 days. Coupons of sizes 76x127x0.8 and 10x127x0.8 mm were machined from steel sets and rock bolts and was cleaned as per ASTM B-117 procedure for running the test. Test was conducted at external facility at National Exposure Testing (NET), Columbus/Sylvania, Ohio. The experimental set up used for carrying out this test is shown in Figure 3.13 (a). The photograph of the equipment and the condition of the samples before and after the experiment are also shown in Figure 3.13 (b and c).

3.11. Cyclic Humidity Tests

These tests were performed at MATCO Associates, Pittsburg, PA using standard cyclic humidity apparatus as per ASTM standard. Photograph of the equipment was not taken but a sketch is shown in ASTM standard.

3.12. References for the Experimental Section

Figure 3.13. Salt spray testing at NET, Ohio Columbus a) Photograph of the equipment b) Sample conditions before experiment and C) after experiment.

IV. ELECTROCHEMICAL CORROSION RESULTS ON ROCK BOLTS

4.1 Summary of Electrochemical Corrosion Results of Rock Bolts

Corrosion behavior of the YM rock bolts are presented in this section. We start with passivation behavior of Yucca Mountain Repository rock bolt carbon (RBC) steel in deaerated 3.5%NaCl solution containing SiO$_2^-$ and HCO$_3^-$ ions was investigated by Potentiodynamic Polarization, Electrochemical Impedance Spectroscopy, Scanning Electron Microscopy, and X-ray Photo-electron Spectroscopic methods. Polarization results indicate that combinations of silicate and bicarbonate anions decrease the passive current density and raise the pitting potential. XPS results indicate the enrichment of silica at passive potential and a mixed FeCO$_3$ and silica film at lower potentials. This change in film composition was responsible for the changes in corrosion rate at lower and higher potentials. XPS results also support the thermodynamic data with regard to the occurrence of second oxidation peak observed in the polarization curves to be due to the oxidation of FeCO$_3$ to Fe$_2$O$_3$.

4.2 Polarization studies on Rock Bolts From YM Project Site

4.2.1 Effect of Deaeration on Passivation of Carbon Steel in IX YM water

Oxygen plays a vital role in passivation behavior. Experiments were carried out to study this effect by purging Nitrogen in YM water solution for 30, 40, 60 minutes and with continuous deaeration. It can be seen that passivity increases with increase in nitrogen purging time as shown in Figure 4.1. It can also be observed that deaeration for a longer period of time results in the formation of a more stable film due to the decrease in oxygen content in the electrolyte. There was little change in the initial cathodic curve possibly due to low ionic conductivity of the solution.

![Figure 4.1 Effect of Deaeration on passivation of RBCS in 1X YM water solution.](018VD.009 File: effect of deaeration on passivation.doc)

Passivating ions such as silicates and bicarbonates are present in YM water which are very important in determining the corrosion rate of rock bolt carbon steel in YM environment. A systematic study was performed to understand the influence of silicate and bicarbonate ions on the passivation of the RBCS with and without Chloride ions, and the results are presented in the following sections.

4.2.2 Effect of Silicate Ions in DI water

The effect of addition of silicate ions (0.005 to 0.025 M) on the polarization behavior of RBCS in DI water is shown in Figure 4.2. It was observed that the corrosion rate (CR) measured in terms of corrosion current density ($I_{corr}$)
remained unchanged with slight decrease in corrosion potential \( (E_{corr}) \) when silicate concentration is increased. The pitting potential \( (E_{p}) \) increased with higher silicate ion concentration. These results indicate that the increase in silicate ion level improves the passivity of RBCS to some extent although the corrosion rate did not vary significantly.

4.2.3 Effect of Bicarbonate Ions in DI water

The effect of addition of bicarbonate ions in DI water was also studied by potentiodynamic scans, as shown in Figure 4.3. In case of bicarbonate ions, \( I_{corr} \) increases with increase in molar concentrations. Passive current density \( (I_p) \) was also increased with increase in bicarbonate concentration. It was also observed that a stable passive film was formed with increase in bicarbonate concentration from 0.5 M to 1 M, but an unstable film was formed in 0.1 M bicarbonate solution.

![Figure 4.2. Molar Effect of Silicate ions on the RBCS. (018VD.010 Files: 0.01M: 610si0.01watpd.xls; 0.025M: 611si0.025watpd.xls; 0.005M: 613si0.005watpd.xls)](image1)

![Figure 4.3. Molar effect of bicarbonate ions on \( I_{corr} \) and \( I_p \) of RBCS. (018VD.010 Files: 0.1M: 615bi0.1watpd.xls; 0.5M: 601bi0.5watpdR1.xls; 1M: 620bi1watpd.xls).](image2)
4.2.4 Interaction of Silicate and Bicarbonate ions in (0% NaCl) DI water

Polarization curves obtained from RBCS in water and the effect of HCO$_3^-$ and SiO$_3^{2-}$ ions are shown in Figure 4.4. These curves, in general, reveal that the added ions enhanced the passivation tendency of carbon steel to different extents. In the absence of these ions i.e. in DI water, carbon steel did not show any passivity. The anodic polarization curves for carbon steel in the presence of HCO$_3^-$ ion exhibit an active-to-passive transition behavior. At potentials more anodic than the active-to-passive transition, the sharp current decrease is due to the formation of FeCO$_3$ film by dissolution-precipitation mechanism according to the following reaction:

$$\text{Fe} + \text{HCO}_3^- \rightarrow \text{FeCO}_3 + \text{H}^+ + 2e^- \quad (4.1)$$

It was observed that $I_{corr}$ in the presence of bicarbonate ions is the highest and in presence of silicate ions is the lowest, while $I_{corr}$ for combined ions (bicarbonate and silicate) is in between. From Figure 4.4 it is observed that the $I_{corr}$ values are close to each other; hence silicate ions have very less effect on $I_{corr}$ values in DI water.

The polarization resistance ($R_p$) is given as:

$$R_p = \frac{\beta_a \beta_c}{2.3 I_{corr} (\beta_a + \beta_c)} \quad (4.2)$$

From the above equation polarization resistance ($R_p$) is inversely proportional to $I_{corr}$. The same trend was observed in impedance spectroscopy that showed the highest $R_p$ value for silicate ions, lowest for bicarbonate ions and intermediate value of $R_p$ for combined ions as shown in Figure 4.5. These results are in accordance with the results shown by polarization results.

Figure 4.4. Potentiodynamic Polarization Curves of RBCS in Water (A) No additional ions (B) 0.01M SiO$_3^{2-}$ (C) 0.5M HCO$_3^-$ (D) 0.5M HCO$_3^-$ + 0.01M SiO$_3^{2-}$. (018VD.010 Files: A: 629DIwater; B: 610si0.01watpd; C: 601bi0.5watpdR1; D: 602bi0.5si0.01watpd.xls)

4.2.5 Effect of Bicarbonate Ions in Presence of 3.5 % NaCl

The polarization behavior of RBCS in 3.5 % NaCl solution with different bicarbonate concentration (0.1 to 1 M) is shown in Figure 4.6. It was observed that $I_{corr}$ increased significantly with increasing bicarbonate concentration and pitting potential ($E_{pit}$) also increased with concentration. At higher bicarbonate concentration (0.5 and 1M), a second oxidation peak was noted and that caused the increase in passivity of RBCS. This implies that there is a change in oxide film at lower and higher potentials. By comparing Figures 4.5 and 4.6 it indicates that addition of bicarbonate increased the corrosion rate of RBCS with and without chloride ions. However a drastic decrease in pitting potential was observed in chloride solution.
4.2.6 Effect of Chloride Ions in Presence of 0.5 M HCO$^-$

The chloride ions play an important role in passivation of RBCS in bicarbonate media, and the effect of chloride ions was further studied on the corrosion behavior of RBCS for fixed bicarbonate content. In this study it was found that the effect of chloride ions, ranging from 0 to 3.5%, to bicarbonate ions (0.5 M) reduces the passivity range from 1.5 V to 0.4 V of the rock bolt, as shown in Figure 4.7. The passive current density ($I_p$) increased with the increase in chloride concentration. These results indicate that chloride ions have a strong depassivation effect in bicarbonate solution. The pitting potential reduced by the addition of 1.7 % NaCl but did not show any significant effect with further increase in chloride concentration.

4.2.7 Effect of Silicate Ions in Presence of 3.5 % NaCl

The polarization behavior of RBCS at two silicate concentrations added to 3.5 % NaCl is shown in Figure 4.8. It can be observed that an increase in silicate content decreased the $I_{corr}$ value some extent and the passive current density ($I_p$) also reduced in the rock bolts. However, the Epit value did not vary much.

The same trend was observed in impedance spectroscopy that showed highest $R_p$ value for silicate ions, lowest for bicarbonate ions and intermediate value of $R_p$ for combined ions as shown in Figure 4.9. While comparing the passive current density ($I_p$), the same trend was observed between these two ions except that significant reduction in $I_p$ was measured when silicate was added to bicarbonate (25 to 8.9 μA/cm$^2$). This means that silicate ions provide better inhibitive effect at higher potential than at lower potential in the presence of bicarbonate ions. The pitting potential ($E_{pit}$) measured for HCO$^-$ ions alone and when combined with SiO$^2-$ ions was higher as compared to SiO$^2-$ alone although the corrosion rate for SiO$^2-$ was found to be less compared to HCO$^-$ ions and the combined ions. In the case of bicarbonate ions, active dissolution was observed at low potentials and the sharp current decrease thereafter was due to the formation of FeCO$_3$ film because of dissolution-precipitation mechanism according to the following reaction [9]:

$$\text{Fe} + \text{HCO}_3^- \rightarrow \text{FeCO}_3 + \text{H}^+ + 2e^- \quad (E^\circ = -0.735 \text{V SCE}) \quad (4.3)$$

As the standard potential reported for the above equation is close to the $E_{corr}$ value measured in the present case, FeCO$_3$ formation on RBCS is thermodynamically favorable. Furthermore, comparison of the $b_c$ values from Table 4.1 indicates that, it was much less for bicarbonate than silicate. This shows that the cathodic reaction rate was high in the former than in the latter. That could be possible due to the partial dissolution of FeCO$_3$ forming a dissolved...
complex of Fe as Fe (CO$_3$)$_2^{2-}$ at lower potentials as proposed by Burstein et al. [1]. As a result of this, the corrosion rate of RBCS is more due to the addition of bicarbonate ions.

Figure 4.6. Molar Effect of Bicarbonate ions in presence of 3.5% NaCl. (018VD.010 Files: 1M: 631bi1na3.xls; 0.5M: 605bi0.5na3.5watpd.xls; 0.1M: 606bi0.1na3.5watpd.xls)

Figure 4.7. Effect of chloride ions in presence of 0.5M bicarbonate ions. (018VD.010 Files: 0%: 601bi0.5watpdR1.xls; 1.7%: 603bi0.5na1.7watpd.xls; 3.5%: 605bi0.5na3.5watpd.xls)
The absence of passivity in this case confirms that the passive behavior of RBCS was due to the salt film formed in chloride media. However, $E_{pa}$ was found to be much less when compared to the values obtained in the presence of the above ions. Further more, the polarization curves obtained for RBCS with $\text{HCO}_3^-$ and $\text{HCO}_3^- + \text{SiO}_3^{2-}$ reveals a secondary oxidation peak at -400mV in addition to the large anodic peak at -580mV. Many researchers have discussed the occurrence of the second anodic peak for iron and steel in bicarbonate media. A detailed study was carried out by Thomas et al. [2] for pure iron at pH 11.3 and they attributed this to the oxidation of FeCO$_3$ to form hydrated ferric oxide according to the following reaction:

$$2\text{FeCO}_3 + 3\text{H}_2\text{O} = \text{Fe}_2\text{O}_3 + \text{CO}_3^{2-} + 6\text{H}^+ + 2\text{e}^-$$  \hspace{1cm} (4.3)
Figure 4.10. Nyquist Curves of RBCS in 3.5% NaCl (A) 0.01M SiO$_3^{2-}$ (B) 0.5M HCO$_3^-$ (C) 0.5M HCO$_3^-$ + 0.01M SiO$_3^{2-}$.

Table 4.1. Electrochemical kinetic data obtained from Figure 4.9. (Determined using the polarization method discussed in Chapter 2 from 018VD.010 Rock bolt polarization.doc).

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>$E_{corr}$ (mV)</th>
<th>$i_{corr}$ (μA/cm$^2$)</th>
<th>$\beta_a$</th>
<th>$\beta_c$ mV/decade</th>
<th>$E_{pit}$ (mV)</th>
<th>$i_p$ (μA/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No ions</td>
<td>-854.2</td>
<td>2.57</td>
<td>-</td>
<td>128.9</td>
<td>-365.0</td>
<td>1.2</td>
</tr>
<tr>
<td>0.01M SiO$_3^{2-}$</td>
<td>-771.3</td>
<td>4.46</td>
<td>-</td>
<td>133.3</td>
<td>-364.3</td>
<td>2.6</td>
</tr>
<tr>
<td>0.5M HCO$_3^-$</td>
<td>-762.5</td>
<td>15.19</td>
<td>117.1</td>
<td>77.45</td>
<td>-253.8</td>
<td>25.18</td>
</tr>
<tr>
<td>0.5MHCO$_3^+$</td>
<td>-747.0</td>
<td>11.71</td>
<td>128.9</td>
<td>84.05</td>
<td>-236.3</td>
<td>8.94</td>
</tr>
<tr>
<td>0.01MSiO$_3^{2-}$</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The standard potential of the above reaction reported was between -0.19 to -0.3V in 1 M sodium carbonate. Similar result was reported by John Sticksma et.al. [3] for dual phase steel in open environment and by Jelinek et al. [4] for mild steel in de-aerated chloride solutions. In the present case, the potential corresponding to the second oxidation peak was slightly lower than the value reported by them. That could be due to the change in concentration of bicarbonate (0.5M) used in this work. It is also possible that the secondary anodic peak could be due to the
oxidation of atomic hydrogen, which is absorbed at lower potential. This can happen due to the reduction reaction of bicarbonate ions and also by classical hydrogen evolution reaction as given below [1]:

\[ 2 \text{HCO}_3^- + 2e = \text{H}_2 + \text{CO}_3^{2-} \quad (E^o = -0.856) \]  
\[ 2\text{H}^+ + 2e = \text{H}_2 \quad (E^o = -0.5V \text{ at pH 8.5}) \]  

Comparison of the standard potential values, \( E^o \), indicate that the second reaction was more favorable than the first one as has been proposed by Burstein et al. [1]. To ascertain the possible cause for the secondary anodic peak, additional experiment was performed by cathodically polarizing the RBCS at -1.2V for 30 minutes and then the polarization scan was started. This was to enhance the hydrogen absorption on RBCS, the obtained polarization curve is shown in Figure 4.12. For comparison, the polarization curve measured without cathodic charging is also shown.

![Figure 4.11. Polarization behavior of RBCS in plain water (018VD.009 File: Polarization behavior of RBCS in plain water.doc).](image)

It can be seen that both curves are similar, and there was no significant increase in current at the second oxidation peak due to cathodic charging. Hence the secondary anodic peak may be attributed to the oxidation of FeCO\(_3\) to Fe\(_2\)C\(_3\) as has been proposed [1, 3, 4]. To further understand the decrease in passivation current density due to the addition of silicate ions with bicarbonate ions and the possible change in oxide film after second anodic peak, impedance spectroscopy and photoelectron spectroscopic analysis were performed.

### 4.3 Impedance Spectroscopy Results on Rock bolts

Impedance spectra were recorded at different potentials marked on the polarization curves (P1 to P4) as shown in Figure 4.13. Nyquist and Bode plots recorded for RBCS in presence of 0.5M HCO\(_3^-\), are shown in Figure 4.14. Nyquist plot displays a single capacitive semicircle in the measured frequency range at \( E_{\text{corr}}(P1) \) (Figure 4.14A). At pre-passive potential, impedance spectra leads to the emergence of another capacitive loop in low frequency region (P2) (Figure 4.14B). This loop bending towards the negative real part is directly related to the negative slope of the polarization curve in this region and is attributed to the pre-passivation process reported for iron dissolution [31, 32]. This is due to the adsorption of iron hydroxide and iron carbonate at active passive transition. These films are expected to form thermodynamically at that potential given in equations 4.2 and 4.3. With further increase in the potential, the low frequency semicircle transformed into a straight line indicative of Warburg component (P3) (Figure 4.14C) and again transformed into a capacitive loop at -290mV (P4) (Figure 4.14D). A porous FeCO\(_3\) film is likely to be formed on the surface and pitting may take place primarily at areas that are not covered by the film.
This indicates that the kinetics of the dissolution processes is limited by the diffusion of the oxidation products. Moreover the resistance corresponding to the high frequency semicircle increases with increase in potential towards noble direction due to the passivation process.

Similar plots obtained for RBCS in chloride media containing 0.5M HCO$_3^-$ + 0.01M SiO$_3^{2-}$ at the same potentials are shown in Figure 4.15. No significant change in the shape of the spectra was observed in this case except an increase in the resistance of the film at all the measured potentials as seen from the values of X-axis corresponding to high frequency semicircle. Close observation of the spectra shows that the increase in resistance $R_p$ was much pronounced especially at higher potentials for 0.5M HCO$_3^-$ + 0.01M SiO$_3^{2-}$ (Figures 4.15C and 4.15D), than the resistance values observed in 0.5M HCO$_3^-$ (Figure 4.15C and 4.15D). This indicates that silicate along with bicarbonate increased the polarization resistance of the film and was significant at higher potentials. These results support the polarization results discussed in the above sections.

Additionally, the evolution of impedance spectra with respect to potential changes reveals that, at the pre-passive potential, the low frequency phase angle maxima shifted to high frequency side as seen from the Bode diagrams and that indicates the on-set of localized corrosion process at the pre-passive potential. This could be due to the incomplete passivation of carbon steel at that potential. It is also well known that, this potential region is more susceptible for stress corrosion cracking as there is incomplete passivation. The obtained polarization resistance also was very less than the values measured at rest of the potential ranges. The Bode diagrams shown in Figures 4.14 and 4.15 further show that the phase angle maxima was relatively high. This again suggests that, the film formed on carbon steel in presence of bicarbonate + silicate was more capacitive. The broad phase angle maxima observed in the latter case further indicate that silica provides strong barrier film to the anodic dissolution of steel in chloride media [34]. This is further evident from the Bode plots recorded for rock bolt 0.44%C carbon steel in 3.5% NaCl solution containing only 0.01M SiO$_3^{2-}$ (Figure.4.16). The high value of phase angle maxima and absolute impedance shows pure capacitive behavior indicating that silicate ions plays an important role in improving the passive film resistance.

4.4 Surface Characterization by Optical, Scanning Electron Microscopy, and X-ray Photoelectron Spectroscopy

4.4.1 Optical Characterization of the Corrosion products

Rock bolt samples were potentiostatically polarized for 30 minutes to study film formation at pre-passive potential and at second passive potential. The current observed was decreasing at charged potential which suggest the formation of stable film. The potentials chosen from polarization curves are shown in Figure 4.17. The effect of HCO$_3^-$ and SiO$_3^{2-}$ is observed from the optical images taken after polarizing the samples at different potentials as shown in Figure 4.18. The images of 1mm$^2$ area of the samples are shown in Figure 4.21 and 4.22(SEM image), which depict growth of pits when potential is increased in potentiodynamic scans in presence of HCO$_3^-$ and SiO$_3^{2-}$ ions individually. However silicate additions to bicarbonate exert a strong passivation effect as seen from these micrographs.

4.4.2 SEM-EDS Results

The morphology of the steel samples was observed at pre-passive, passive potentials and after polarization scan as shown in the SEM micrographs in Figure 4.19. The morphologies of the samples demonstrate the increase in polarization resistance due to silicate addition with bicarbonate shown in Figures 4.18 and 4.19. In the presence of 0.5M HCO$_3^-$, large numbers of pits were seen at the pre-passive potential (Figure 4.18A). The pits were found to be active and growing with increase in anodic potential. The presence of Mn and S rich inclusions was identified by EDS analysis (Figure 4.18B). After crossing the pitting potential the pits grew too much larger size and were covered by porous carbonate film (Figure 4.18C). As a result of this, the passive current density remained high, as seen from polarization results (Figure 4.10). When silicate ions were added with bicarbonate, the sample surface was found to be smooth and very few pits were seen, as shown in Figure 4.20 at all potentials. The EDS analysis at the localized pits shows significant amount of silica deposited in the pits. This indicates that silicates were found to deposit preferentially at the defective sites of the film and controlled the growth of the pits (Figure 4.20 A-C). As a result of this the film resistance increased and the passive current density decreased. The SEM results also indicate the lower pitting potential observed for RBCS in the presence of 0.01M SiO$_3^{2-}$. At passive potential, the surface was
Figure 4.12. Potentiodynamic polarization plots of RBCS in 3.5% NaCl solution containing 0.5M HCO₃⁻ (a) No pre-charging and (B) Hydrogen pre-charged for 30 minutes at -1.2 V, showing virtually no difference in the scans (top). (018VD.009 File: Effect of hydrogen charging on passivation.doc) – Top.

Figure 4.13. Potentials chosen from polarization curves of RBCS using 0.5M HCO₃⁻ and 0.5M HCO₃⁻ + 0.01M SiO₃²⁻ to perform impedance spectroscopy shown in Figure 4.14 and 4.15 (bottom). (018VD.010 Files: 0.5M+0.01M: 604bi0.5na3.5si0.01watpd.xls; 0.5M: 605bi0.5na3.5watpd.xls) – Bottom.
Figure 4.14. Impedance spectra measured for RBCS in presence of 0.5 M HCO₃⁻ added to 3.5% NaCl solution at potentials (A) Ecorr (B) -580mV (C) -375mV and (D) -290mV marked as P1, P2, P3 and P4 in Figure 4.12 (018VD.001 Files: A: 524bi0.5na3.5imp B: 524bi0.5na3.5imp585 C: 524bi0.5na3.5imp375 D: 524bi0.5na3.5imp295).
Figure 4.15. Impedance spectra measured for RBCS in presence of 0.5M HCO$_3^-$ + 0.01M SiO$_2^2-$ added to 3.5% NaCl solution at potentials (A) $E_{corr}$ (B)-580mV and (C)-375 mV and (D)-290mV marked as P1, P2, P3 and P4 in Figure 4.12 (018VD.001 Files: A: 522bi0.5si0.1cl3.5is2ndset B: 522bi0.5si0.1cl3.5is2nd-580 C: 522bi0.5si0.1cl3.5is2nd-400 D: 522bi0.5si0.1cl3.5is2nd-280)
Figure 4.16. Bode plots measured for RBCS in presence of 0.01M SiO$_2$$^-$ added to 3.5% NaCl solution at potentials (a) $E_{corr}$ (b) -550mV on the polarization curve (018VD.001Files: A: 526si0.01na3.5 B: 526si0.01na3.5-550)

Figure 4.17. Potentials Chosen from polarization curves in case of 0.5M HCO$_3^-$ and 0.5M HCO$_3^-$ + 0.01M SiO$_2$$^-$ to perform SEM (Figures 4.19 to 4.21), Optical Images (Figures 4.18) and XPS spectra (also included in Appendix of this chapter). (018VD.010 Files: 0.5M+0.01M: 604bi0.5na3.5si0.01watpd.xls; 0.5M: 605bi0.5na3.5watpd.xls)
Figure 4.18. Optical images of 1 mm of RBCS in HCO$_3^-$ solution (A) Active- Passive Transition (B) Passive Potential (C) After Potentiodynamic Scans

Figure 4.19. SEM morphology of the samples observed after impedance experiments in presence of 0.5M HCO$_3^-$ added to 3.5% NaCl solution (A) Pre-passive (P2) (B) Passive (P4) and (C) after potentiodynamic polarization and the corresponding EDS spectra also shown (018VD.004 File: site5spec3.doc)
Figure 4.20. SEM morphology of the samples observed after impedance experiments in presence of 0.5M HCO$_3^-$ + 0.01M SiO$_2^-$ added to 3.5% NaCl solution (A) Pre-passive (P2) (B) Passive (P4) and (C) after potentiodynamic polarization and the corresponding EDS spectra also shown (018VD.004 Files: A: site1spec4.doc B: Ysite4spec1.doc C: site9spec1.doc)
completely covered by oxide film and the enrichment of silica at the few localized pits created by sulfur rich inclusions (Figure 4.21A). Further increase in polarization beyond the pitting potential caused micro-cracks on the film that was porous in nature. As a result of these changes, corrosion was enhanced due to the diffusion of chlorides, which was the cause of pitting (Figure 4.21B).

4.4.3 XPS Studies

The composition of the anodic oxide film formed on RBCS in 3.5% NaCl solution containing 0.5M HCO$_3^-$, 0.01M SiO$_2^{2-}$ and 0.5M HCO$_3^-$ + 0.01M SiO$_2^{2-}$ ions was analyzed by XPS. The change in the nature of oxide with depth was analyzed by Argon ion sputtering. To understand the change in composition of the oxide film at different potentials the specimens were held at the pre-passive (P1) and at second passive (P4) potentials in the above electrolytes as shown in Figure 4.17.

XPS survey spectra were taken before sputtering and after Ar$^+$ sputtering over the samples. These samples were sputtered with Ar$^+$ at low rate initially to study the film morphology. The sputtering rate was increased after removal of the initial oxide layer. Samples at active-passive transition potential in only bicarbonate media have shown enrichment of Carbon, Oxygen and Iron on the surface, while in combined bicarbonate and silicate media it has shown additional silica enrichment on the surface as illustrated in Figures 4.24; also see Appendix A-1 Figures A-1 to A-13).

Iron peaks were observed in XPS survey spectra for all the samples after Ar$^+$ sputtering which shows that base metal was reached after different sputtering cycles (see Appendix A-1, Figures A-12 - A-15).
4.4.4 Passivation in NaCl solution containing 0.5M HCO$_3^-$ of Rock Bolts

A typical XPS depth profile spectra of RBCS polarized in the above electrolyte for 30 minutes at -0.580 V (pre-passive) of Fe(2p), O(1s) and C(1s) is shown in Figures 4.23. The rest of these depth profiles for other conditions are shown in Appendix ( shows and -0.30 V (passive) respectively. At pre-passive potential (Figure 4.23 c), the Fe (2p)$_{3/2}$ spectra exhibit two peaks at 711 and 707.6eV, corresponding to metallic and oxide components. For the specimen polarized at the passive potential, no significant change in binding energy values corresponding to Fe(2p) spectra was noted. However, the XPS spectra recorded prior to Ar ion sputtering did not show iron in any form on the electrode surface at the passive potential. Based on the asymmetry of the oxide peak observed at the two potential levels, it may be suggested that Fe may exist in Fe$^{2+}$ and or Fe$^{3+}$ oxidation states. The dominance of the metallic peak after removing the initial oxide layer reveals that the film is considerably thinner at passive potential than that formed at pre-passive potential.

The O (1s) spectra exhibit a broad peak for the sample polarized at the pre-passive potential. Based on the asymmetry of the peak, two peaks could be easily identified at 532.6 and 530.8eV indicating two oxide components. However, at passive potential only single peak at 532.6eV was observed and with sputtering another shoulder peak at 530.8eV was seen. Again, comparison of O (1s) intensity at all sputtering depths clearly shows that the oxide film was found to be thin at the passive potential. The C(1s) spectrum recorded for the samples polarized at the respective potentials display two peaks at 284.6 and 289.5eV respectively. It is well known that the peak corresponding to 284.6eV is due to hydro-carbon contamination and the higher energy peak is assigned to carbonate species. With respect to the nature of the passive film, the presence of Fe(2p), O(1s) and C(1s) peaks at 711, 532.6 and 289.4eV respectively and confirms the presence of FeCO$_3$. The binding energy values obtained in the present work are compared with the reported values for FeCO$_3$ given in Table 4.2.

Table 4.2 Binding energy values of Fe(2p), O 1s and C 1s components identified on RBCS in 3.5% NaCl solution containing 0.5M HCO$_3^-$ [17-21] (Non-Q for corroboration only, except for last row which is an average value of peaks from 018VD.005)

<table>
<thead>
<tr>
<th>Fe(2p$_{3/2}$)</th>
<th>O(1s)</th>
<th>C(1s)</th>
<th>Data source</th>
</tr>
</thead>
<tbody>
<tr>
<td>710.9</td>
<td>530.9</td>
<td>290.3</td>
<td>Ref. 17</td>
</tr>
<tr>
<td>710.3 ± 0.2</td>
<td>531.8 ± 0.2</td>
<td>289.3 ± 0.1</td>
<td>Ref. 18, 19</td>
</tr>
<tr>
<td>710.2</td>
<td>531.9</td>
<td>289.4</td>
<td>Ref. 21</td>
</tr>
<tr>
<td>711</td>
<td>532.6</td>
<td>289.5</td>
<td>018VD.005 (avg. value)</td>
</tr>
</tbody>
</table>

These values are in agreement with the reported values for FeCO$_3$ [17-21] except that the O(1s) value was 0.6eV higher than the reported values indicating that the FeCO$_3$ may be in hydrated form. Hence the oxide layer formed at pre-passive potential mostly consists of FeCO$_3$ and some hydrated iron oxide, which was observed as a shoulder peak at 530.8eV (Figure 4.23a). The presence of O(1s) and C(1s) peaks at 532.6 289.5eV confirms the presence of only carbonate (CO$_3^{2-}$) as there was no Fe component on the initial oxide film (Figure 4.23b). This indicates that the FeCO$_3$ film formed at pre-passive potential transformed into CO$_3^{2-}$ film at passive potential. This could be possible due to the oxidation of FeCO$_3$ film to ferric oxide as explained in the polarization results. The absence of Fe peak at higher potential could be attributed to the preferential dissolution of Fe from carbonate at high oxidation potentials. The XPS results obtained in the present work confirm the previous findings with regard to the change in the oxide film, which was observed as a secondary oxidation peak in the polarization curves.

4.4.5 Passivation in 3.5% NaCl solution containing 0.01M SiO$_2^{2-}$ Ions

Figure 4.24 shows the XPS components of Fe (2p), O (1s) and Si (2p) from the RBCS exposed to chloride solution containing 0.01M SiO$_2^{2-}$ ions. A small Fe peak was noted at 711eV, which shifted to the lower energy side (710.6eV) upon sputtering corresponding to the Fe(2p)$_{3/2}$ energy level. The appearance of the metallic peak is clear from the peak at 707.2eV, whose intensity increased with sputtering depth. A small Fe peak corresponding to the initial oxide layer indicates the presence of some other component on the electrode surface. O(1s) spectra reveal the presence of two components, one at 532.5eV and another at 531.3eV. With increase in sputtering the intensity of the higher binding energy peak decreased and the intensity of the lower energy peak increased.
Figure 4.23. Photoelectron spectra obtained from RBCS of O 1s (A), C 1s (B), Fe(2p) (C) and depth profile of the specimen (D) polarized at the pre-passive potential marked in Figure 4.16 in 3.5% NaCl solution containing 0.5M HCO$_3^-$ (018VD.005 File: Bi-A-P Transition Profile and Spectra.ppt)
Figure 4.24. Depth Profile of (A) Pre-passivated (B) Passivated Films obtained from XPS analyses of RBCS of O 1s (A) and C 1s (B) and Fe(2p) (C) polarized at the pre-passive potential marked in Figure 4.16 in 3.5% NaCl solution containing 0.5M HCO$_3^{-}$. (018VD.005 File: Bi-Si-2P Profile and Spectra.ppt)

Si (2p) signal was identified at 103.3eV and with sputtering an energy shift towards lower values (102.6eV) was observed. Comparison of the binding energy values of Si (2p) at 103.3eV and O (1s) at 532.5eV and the weak iron oxide peak shows the presence of silica on the outer oxide layer [5-8]. The lower binding energy values of O (1s) and Si(2p) peaks noted after argon ion sputtering suggest the presence of silicates in the form of iron silicate layer. Reported results also indicate that silicates are converted to silica with increase in degree of polymerization, which was indicated by the progressive increase in binding energy values [5]. The higher binding energy values observed for the outer layer confirms the presence of silica. In this case also the broad oxide Fe (2p) peak is attributed to the presence of both high and lower valence oxides (Fe$^{2+}$ and Fe$^{3+}$). Notably the oxide film formed on RBCS in presence of silicates is much thicker compared to the film formed in presence of bicarbonates, which is evident from the intensity of the O(1s) and Fe(2p) signals and also by comparing the depth profiles in HCO$_3^{-}$ and SiO$_2^{-}$.

4.4.6 Passivation in 3.5% NaCl Solution containing 0.5M HCO$_3^{-} + 0.01M$ SiO$_2^{-2}$ Ions

XPS spectra measured from RBCS samples polarized in 3.5% NaCl solution containing 0.5M HCO$_3^{-} + 0.01M$ SiO$_2^{-2}$-ions at the same potentials measured in 0.5M HCO$_3^{-}$ solution are shown in Appendix. The Fe(2p)$_{3/2}$, O 1s, C 1s and Si (2p) spectra exhibits peaks at binding energy levels of 713.2, 536, 289.2 and 107eV respectively for the sample polarized at the pre-passive potential. With increase in sputter depth, these peaks were shifted to 711, 533, 285 and 103.5eV respectively. The latter binding energy values mentioned after sputtering the initial oxide layer confirm the presence of Fe and Si containing species mostly as silica and hydrated iron oxide. Between these two components
Si contribution was found to be more as the intensity of Si (2p) peak was more when compared to that of Fe (2p) oxide peak. The C(1s) peak at 289eV for the initial oxide layer can be assigned to carbonate species. The increase in binding energy values for Fe(2p) 3/2, O(1s), C(1s) peaks could be due to the association of carbonate species with both Fe and Si compounds. Fe and Si may exist as FeCO₃ and silica based on the binding energy values reported in the literature.

At the passive potential, Fe (2p) 3/2, O(1s), C(1s) and Si (2p) photoelectron spectra were identified at 710.4, 533, 285.8 and 103.8eV respectively. The C(1s) peak was found to be broad which could be easily de-convoluted into an additional peak at 289.2eV indicating carbonate species. The Fe oxide signal was virtually absent for the initial oxide layer whose intensity increased with sputtering after which the metallic Fe signal progressively increased. The absence of Fe oxide signal demonstrates that the initial oxide peak could be due to mostly silica and some carbonate layer. This was based on the binding energy values of O(1s) and Si(2p) values at 533 and 103.8eV. With sputtering the intensity of Si(2p) signal deceased and a small shoulder peak at 531.4 eV in the O(1s) peak was seen. This suggested that the inner layer consisted of silica and hydrated iron oxide. Comparison of the O(1s) and Fe(2p) peaks measured for the samples polarized at pre-passive and passive potentials shows that the oxide film is comparatively thick at the lower potential than at higher potential, which was similar to the film formed in bicarbonate containing chloride solution. Here the oxidation of FeCO₃ to hydrated iron oxide was seen, similar to the case found in solution containing only bi-carbonate. However the carbonate contribution in the oxide film was found to be minimum compared to silica, which suggests that silicates get adsorbed preferentially on the oxidized iron surfaces and protect further oxidation of Fe. This was seen from the flat Fe oxide peak irrespective of the sputtering depth.

4.5 Effect of Temperature and YM Water Concentration on Rock bolts

4.5.1 Corrosion Behavior in Deaerated Environments by Polarization

In order to reach a stabilized $E_{corr}$ before conducting the potentiodynamic polarization scans, specimens were held in the simulated test waters for two hours. Non of the corrosion forms observed on the rock bolt specimens during this period in the de-aerated YM waters. Corrosion rates of rock bolt have been determined for de-aerated 1X,10X, and 100X concentrated simulated YM waters at the temperatures 25°C, 45°C, 65°C, and 85°C by employing linear polarization methods [9,10]. Polarization curves obtained with this method, especially for the 1X waters at high temperatures (85°C), showed some noise due to low ionic conductivity of the electrolyte [10]. However, the software was capable of smoothing out this noise before the conventional $R_p$ values for the corrosion rates were calculated. General corrosion rates for the deaerated waters were determined to be between 35 μm/year and 168 μm/year in the temperature interval from 25°C to 85°C. The polarization curves for 1X deaerated YM water given in Figure 4.25 show the differences in both cathodic and anodic branches of the curves for various water temperatures.

Linear portions of the cathodic branches (Tafel lines) of the polarization curves intercepted various current density values ($I_{100}$) at their corrosion potentials ($E_{corr}$), within an increasing order from 25°C to 85°C. Increasing temperatures reduced the curvatures in the anodic regions at the passive states. The curving in the passive region became almost a vertical straight line for 85°C, suggesting the dissolved oxygen involvement with the system was the least in this particular temperature [11]. In general, when the temperatures approach to the boiling points, dissolution of oxygen becomes as less as 0.08 ppm [12] for deaerated waters. Pitting potentials (PP) decreased with increasing temperatures from 25°C to 65°C, but increased again at 85°C. This effect may have been caused by inhibition of the chloride attacks on the metal [13], possibly by the formation of extra cations at ~85°C to combine and form compounds with Cl⁻ ions. That is also consistent with the observed salt precipitates, which occur more at higher temperatures. The details of the ionic species and precipitations can be seen in in stress corrosion cracking section. Pitting rates after the pitting potentials were similar for each temperature because the slopes of the curves after pitting remained alike, as laying parallel to each other. The corrosion potentials ($E_{corr}$), or open circuit potentials for each studied temperature appeared approximately the same, around -760 mV. The reactions in the de-aerated waters were controlled by activation polarization within the studied potential range because the potentials of cathodic regions at each studied temperature changed linearly with current densities.

51
There was no significant difference in the corrosion behavior of different ionic concentrations of YM waters; the $I_{\text{corr}}$ values at $E_{\text{corr}}$ were fairly close to each other at each of the studied temperatures as shown in Figure 4.26. The trend of the rates is not observable clearly on the potentiodynamic polarization curves in this case, for those different ionic concentrations. However, electrochemical impedance spectroscopy (EIS) revealed a better trend for those different concentrations, as given in Figure 4.32, and Figure 4.33. The corrosion rate calculations from measured polarization resistance ($R_p$) values confirmed the increased corrosion rates with increasing concentrations from 1X to 100X, but only slightly. Penetration rates determined by linear polarization method for various de-aerated concentrations YM waters are given in Table 4.3. The reduced data calculated from the polarization curves showed rate increase with increasing temperatures for deaerated 1X, 10X and 100X YM waters as given in Figure 4.27 At lower temperatures, there was a slight rate difference associated with concentrations at 25°C, however it was not that pronounced at 45°C, 65°C and 85°C.

Pitting is observed in almost the entire temperature range for all deaerated waters. PP values at 25°C resulted in approximately the same value for the 10X and 100X YM water, however it was slightly higher for the 1X, as expected. Linear portions of the cathodic branches (Tafel Lines) of the polarization curves intercepted various current density due to the lesser Cl ionic content, in this case. The precipitate films that have been formed at higher temperatures on the specimens were colorless and clear. The pits were nearly round in shape and uniformly distributed all over the specimen surface which could be attributed to its uniform thickness and homogeneity. The appearance of the specimen after polarization scanning is given in Figure 4.29A and Figure 4.30, showing film formation on the surface and pitting, respectively.

4.5.2. Corrosion Behavior in Aerated Environments by Polarization

Potentiodynamic polarization tests for rock bolt of MCS in aerated concentrated YM waters showed much higher corrosion rates than in de-aerated waters. The rates extended from 120µpy to 1000µpy within the studied temperature range. Penetration rate values for aerated YM waters calculated by linear polarization are given in Table 4.4. The rate results for each temperature also given in Figure 4.27, in a form of plot. Since the aeration is maintained by purging with oxygen, and the experimental cells are sealed well against leaks, these high values are expected for MCS in those oxygenated, extremely corrosive environments. These rates are the upper limits because
the test solutions are intentionally purged by oxygen to create highly oxidizing conditions. This design always establishes a high but credible corrosion penetration rate for conditions subject to change. The corrosion rate trend with respect to temperatures for aerated 1X and 10X waters were similar to the de-aerated waters: The rates increased with increasing temperatures in both, aerated and de-aerated waters. However, aerated 100X water showed a totally different behavior than 1X and 10X waters. The test with aerated 100X water also resulted in some corrosion product on the specimens subject to preconditioning at 45 °C, prior to the experimental scans. This observation suggests that 100X water of 45°C was the most severe corrosive environment for MCS rock bolt. Potentiodynamic scans showed that the rates increased from 25°C to 45°C, and then decreased at 65°C, and decreased further at 85 °C having its lowest value, as given in Figure 4.28. The shape of the 100x corrosion rate curve was refined with more experiments at different temperatures to determine the apex.

Further experiments confirmed that the rate is the highest at −45°C. It was also observed that the clearness of 100X water started to decrease at 55°C and continued till 85°C, with increasing precipitate layers on the specimen and the cell walls. Consequently, the decreased rates for aerated 100X YM waters at elevated temperatures were caused by these precipitate layers. Similar behavior in YM J-13 reference well waters (with similar ionic content but more dilute than YM water) have been observed for low carbon steel with studies done earlier by T. Lian [12]. The precipitate scales were white in color and relatively thicker and smoother than the films formed in deaerated waters, as can be seen from Figure 4.29. The pitting that occurred with 100X waters was mostly observed at the temperatures of 65°C and 85°C. The appearance of these pits formed in aerated hot waters is shown in Figure 4.31. The aligned oval-shape-inclusions in the given micrograph are the sites where the corrosion has just started. The light gray section is the precipitation layer over the metal, dark gray is the rock bolt itself, and the white spots are the salt islands, which are mainly responsible for the pitting. One can conclude that the resulted pitting in the aerated hot waters may create susceptibility for the material to stress corrosion cracking in the similar environments, according to the pitting necessity models. However, the scale is sooty, and easily removable. Also, the requirement for passivity on MCS is not met at all in this environment, as it was shown in the polarization curves earlier. All of the raw data for potentiodynamic polarization experiments along with the electrochemical impedance spectroscopy runs for rock bolt are shown in Appendix A3.

4.5.3 Corrosion Behavior by Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) was conducted to confirm the rate change trends determined by the linear polarization method, as a complementary technique carried out at open circuit potential $E_{corr}$. EIS showed that it has greater sensitivity [14,15] for the electrolytes of even lower conductivity, compared to the polarization techniques. The results of EIS experiments for de-aerated waters at the temperature range from 25°C to 85°C are shown in the Nyquist plot, in Figure 4.32. The results of EIS experiments for de-aerated waters conducted at $E_{corr}$ potential values also showed increased corrosion rates with increased temperatures. Therefore, the corrosion rate trends were determined to be the same as the ones obtained by the polarization technique given in Figure 4.25. The polarization resistance $R_p$ is represented with the diameters of the depressed semicircles, which is inversely proportional to $I_{corr}$, and therefore also to the corrosion rates. Corrosion rate estimations from the determined $R_p$ values obtained from the semicircles of Nyquist plots supported the polarization tests results closely as given in Figure 4.32. EIS also confirmed the corrosion rate trend obtained for various concentrations of YM water by the linear polarization technique at RT. The EIS trend for various concentrations of YM waters at room temperature is given in Figure 4.33 for comparison with that of the polarization trends. More polarization and impedance curves will be given in Appendix A3, which show corrosion rate trends for rock bolt at the rest of the temperatures and concentrations.

4.6 References for Results on Corrosion of Rock bolts

Figure 4.26. Potentiodynamic polarization curves for rock bolt at 25°C in various deaerated simulated YM waters, such as 1X, 10X, and 100X. (018VD.010 File: rock bolt polarization.doc)

Table 4.3. Corrosion Rates of Rockbolt in Concentrated Deaerated YM Waters. (I_corr and corrosion rates determined using the polarization method discussed in chapter 2 from data 018AY.002 Files: 1xnrti, 1x45iii, 1x65i, 1x85ii, 10xnrti, 10x45i, 10x65i, 10x85ii, 100xnrti, 100x45i, 100x65i, 100x85ii)

<table>
<thead>
<tr>
<th>Concentration (times)</th>
<th>Temperature (°C)</th>
<th>I_corr (A/cm²)</th>
<th>Corrosion Rates (mpy) (µpy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>3.8x10^-5</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>6.0x10^-5</td>
<td>2.7</td>
</tr>
<tr>
<td></td>
<td>65</td>
<td>1.0x10^-5</td>
<td>4.7</td>
</tr>
<tr>
<td></td>
<td>85</td>
<td>1.3x10^-5</td>
<td>6.3</td>
</tr>
<tr>
<td>10X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>3.0x10^-6</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>5.5x10^-6</td>
<td>2.3</td>
</tr>
<tr>
<td></td>
<td>65</td>
<td>1.0x10^-5</td>
<td>4.6</td>
</tr>
<tr>
<td></td>
<td>85</td>
<td>1.4x10^-5</td>
<td>6.4</td>
</tr>
<tr>
<td>100X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>4.5x10^-6</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>6.0x10^-6</td>
<td>2.7</td>
</tr>
<tr>
<td></td>
<td>65</td>
<td>1.0x10^-5</td>
<td>4.5</td>
</tr>
<tr>
<td></td>
<td>85</td>
<td>1.5x10^-5</td>
<td>6.7</td>
</tr>
</tbody>
</table>

*mpy=mils/year, and µpy=micrometers/year
Table 4.4. Corrosion Rates of Rockbolt in Concentrated Aerated YM Waters. ($I_{\text{corr}}$ and corrosion rates determined using the polarization method discussed in chapter 2 from data 018AY.002 Files: 1xorti, 1x045i, 1x065ii, 1x085ii, 10xorti, 10xo45iii, 10xo65i, 10xo85i, 100xorti, 100xo45i, 100xo65i, 100xo85i)

<table>
<thead>
<tr>
<th>Concentration (times)</th>
<th>Temperature (°C)</th>
<th>$I_{\text{corr}}$ (A/cm²)</th>
<th>Corrosion Rates (mpy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1X</td>
<td>25</td>
<td>1.1x10⁻⁵</td>
<td>4.9</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>2.8x10⁻⁵</td>
<td>12.6</td>
</tr>
<tr>
<td></td>
<td>65</td>
<td>5.6x10⁻⁵</td>
<td>24.8</td>
</tr>
<tr>
<td></td>
<td>85</td>
<td>1.0x10⁻⁴</td>
<td>45.0</td>
</tr>
<tr>
<td>10X</td>
<td>25</td>
<td>1.2x10⁻⁵</td>
<td>5.4</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>3.5x10⁻⁵</td>
<td>16.0</td>
</tr>
<tr>
<td></td>
<td>65</td>
<td>6.6x10⁻⁵</td>
<td>30.0</td>
</tr>
<tr>
<td></td>
<td>85</td>
<td>9.4x10⁻⁵</td>
<td>42.0</td>
</tr>
<tr>
<td>100X</td>
<td>25</td>
<td>2.0x10⁻⁵</td>
<td>9.0</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>3.9x10⁻⁵</td>
<td>18.0</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>4.5x10⁻⁵</td>
<td>20.0</td>
</tr>
<tr>
<td></td>
<td>55</td>
<td>3.3x10⁻⁵</td>
<td>15.0</td>
</tr>
<tr>
<td></td>
<td>65</td>
<td>2.3x10⁻⁵</td>
<td>10.3</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>1.8x10⁻⁵</td>
<td>7.9</td>
</tr>
<tr>
<td></td>
<td>85</td>
<td>1.7x10⁻⁵</td>
<td>7.6</td>
</tr>
</tbody>
</table>
Figure 4.27. Temperature effect on corrosion rates of rock bolt in simulated deaerated concentrated YM waters. (Summarized data from Table 4.3)

Figure 4.28. Temperature effect on corrosion rates of rock bolt in simulated aerated concentrated YM waters. (Summarized data from Table 4.4)
Figure 4.29. Specimen surface appearances after polarization scanning. Left: De-aerated 100X waters, Right: Aerated 100X waters which is sooty and easily scratched by hand. (NQA)

Figure 4.30. Transparent scale formation and pitting over rock bolt in deaerated 100X YM waters.

Figure 4.31. Precipitate formation and pitting over rock bolt in aerated 100X YM waters. Oval inclusions appear as the initiation site for the pitting.
Figure 4.32. Nyquist Plot for MCS rock bolt in de-aerated 1X YM water at various temperatures. [16] (Non-Q for corroboration only)

Figure 4.33. Nyquist Plot for MCS rock bolt in deaerated water at RT for various concentrations. [16] (Non-Q for corroboration only)


V. ELECTROCHEMICAL CORROSION RESULTS OF STEEL SETS

5.1 Summary of Polarization studies on I-Beams from YM Project Site

The electrochemical corrosion behavior of steel set (I-Beam) made of low carbon steel was determined by using simulated Yucca Mountain (YM) ground water by varying the electrolyte concentration and temperature under aerated and deaerated conditions. Earlier corrosion studies on low carbon steel were studied for corrosion allowance multi-barrier waste container using J-13 ground water [1-3]. Lian et al. [1] reported very low corrosion rates of low carbon steel in the simulated J-13 well water. Their EDS analyses indicate that their low corrosion rates are due to possible enrichment of sulfur species at low temperatures, and silicates at high temperatures. Thompson et al. [2] used 1020 carbon steel and examined the effect of various ions on carbon steel corrosion performance using potentiodynamic polarization experiments. According to them, solution pH, chloride and bicarbonates are important in deciding the life-time of the multi-barrier waste package material. Brossia et al. [3] examined general and localized corrosion behavior of carbon steel at different chloride and carbonate concentrations; emphasizing the role of chloride to bicarbonate ratio on temperature. In this present work, we have examined the low carbon steel in simulated YM ground water environment, which has high concentrations of bicarbonate, calcium, sulfates, magnesium and chlorides. The objective of the present investigation is to identify the environmental condition that is most susceptible towards corrosion performance of low carbon steel and to characterize the nature of corrosion products formed on steel using electrochemical and surface analytical methods.

The results show that in deaerated conditions, the corrosion rate is low in the order of 0.6 to 4.5mpy (mils/yr), between 25 to 85°C, respectively. However, in aerated conditions the measured rates are expectedly very high, in the order of 3-55 mpy in the above mentioned temperature levels. The rates initially increased up to 45°C, and a decreasing trend was observed with further increase in temperature from 65 to 85°C. The maximum corrosion rate occurred at 45°C (54.5mpy). The low corrosion rates observed in all deaerated conditions, and in aerated solutions at higher temperatures were due to the preferential adsorption of Mg-species on the steel surface, as identified by XPS analyses. The results also indicate possible localized corrosion behavior of carbon steel in aerated conditions up to 45°C.

5.1.1 Aeration and Deaeration Effects on YM I-Beam

Polarization plots of carbon steel measured in deaerated and aerated YM electrolytes (1x, 10x and 100x) are shown in Figures 5.1A and B. These plots indicate that carbon steel exhibits a weak passivation behavior, in deaerated electrolytes and active dissolution in aerated electrolytes measured at different temperatures and electrolyte concentrations. In deaerated electrolytes, the increases in electrolyte concentration improved the passivity, and also increased the pitting potential (E_{pit}) in Figures 5.1 (a-c). In aerated conditions, the increased electrolyte concentrations did not improve the passivity as shown in Figure 5.2 (a-c), except at the most concentrated electrolyte (100x) and at higher temperature, 85°C. The measured corrosion potential (E_{corr}) was found to be lower in deaerated conditions as compared to aerated conditions. This is due to the presence of oxygen in aerated electrolytes that polarized the potential of steel to its pitting potential (E_{pit}) and leads to active dissolution at E_{corr}. The corrosion rates obtained from polarization curves are summarized in Table 5.1. The above table indicates the low corrosion rate of carbon steel in deaerated conditions which varied from ~0.6 to 4.5mpy in de-aerated conditions and was found to be significantly higher in aerated conditions (~ 3 to 55mpy).

5.1.2 Effect of Temperature on Polarization Behavior of I-beam

In general, increase in temperature increased the corrosion rate slightly, in deaerated conditions for all electrolyte concentrations. This can be possibly attributed to the increase in cathodic reactions due to reduction of ions on the electrode surface as seen from the shift in cathodic current densities in Figures 5.1(a-c). In aerated conditions, between 25 and 85°C, the corrosion rate initially increased up to 45°C, and thereafter the rate decreased from 45 to 85°C for all electrolyte concentrations. The decrease in cathodic current densities at higher temperatures indicates possible oxygen reduction reactions.

5.1.3 Effect of Electrolyte Concentrations on Polarization Behavior of I-beam

In deaerated conditions, the increase in electrolyte concentration, from 1 to 10x, increased the corrosion rate. Further increases, to 100x decreased the corrosion rate. In aerated conditions, the rates initially increase with electrolyte concentration between 25 and 45°C and then decrease at higher temperatures (65 and 85°C). The increase in corrosion rate at lower temperatures is due to the increase in cathodic reaction rates and at higher...
temperatures the reduction of such reaction leads to decrease in corrosion rates. These results indicate the effect of higher electrolyte concentrations in reducing the corrosion rate of steel.

5.1.4 Electrochemical Impedance Spectroscopy (EIS) on I-beams

Impedance spectra recorded for carbon steel in 100xYM solution, under aerated and deaerated conditions are shown in Figures 5.3 and 5.4, in Nyquist and Bode representations. The impedance values are measured as the diameter of the semicircle along the x-axis indicates higher resistance at 25°C (Figure 5.3a) than that measured at 85°C (Figure 5.3b).

![Figure 5.1 A. (Left) Polarization plots of I-beam measured in deaerated (nitrogenated) YM solutions (a) 1x, (b)10x, (c) 100x (A, B,C,D indicates temperatures 25°C, 45°C, 65°C and 85°C respectively). (018JL.002 Files: A.A: Joshpdib25Cym1xn1 A.B: Joshpdib45Cym1xn1 A.C: Joshpdib65Cym1xn1 A.D: Joshpdib85Cym1xn1 B.A: Joshpdib25Cym10xn1 B.B: Joshpdib45Cym10xn1 B.C: Joshpdib65Cym10xn1 B.D: Joshpdib85Cym10xn1 C.A: Joshpdib25Cym100xn1 C.B: Joshpdib45Cym100xn1 C.C: Joshpdib65Cym100xn1 C.D: Joshpdib85Cym100xn1)

![Figure 5.1 B. (Right) Polarization plots of I-beam measured in aerated (oxygenated) YM solutions (a) 1x, (b)10x, (c) 100x (A, B,C,D indicates temperatures 25°C, 45°C, 65°C and 85°C respectively). (018JL.002 File: A.A: Joshpdib25Cym1x01 A.B: Joshpdib45Cym1x01 A.C: Joshpdib65Cym1x01 A.D: Joshpdib85Cym1x01 B.A: Joshpdib25Cym10x01 B.B: Joshpdib45Cym10x01 B.C: Joshpdib65Cym10x01 B.D: Joshpdib85Cym10x01 C.A: Joshpdib25Cym100x01 C.B: Joshpdib45Cym100x01 C.C: Joshpdib65Cym100x01 C.D: Joshpdib85Cym100x01)
This decrease in resistance values observed in deaerated conditions indicates the increasing tendency of corrosion when the electrolyte temperatures are increased. In aerated environments, very low resistance was observed at 25°C (Figure 5.4a) and further decreased at 45°C (Figure 5.4b) followed by an increase in resistance value at 85°C (Figure 5.4c) indicating higher corrosion resistance. These results are in agreement with the polarization results (in Figures 5.1 and 5.2) showing that the measured corrosion rates increased slightly with increase in temperature in deaerated conditions. However, the behavior is different in aerated conditions at higher temperatures as shown Figures 5.3 (b). The corresponding Bode plots exhibit a single phase angle maxima at lower temperature (25°C) while two phase angle maxima was observed at higher temperatures (85°C). The occurrence of two phase angle maxima shows that the passivation of carbon steel is similar to the impedance behavior of coated electrodes [4]. Comparison of Figures 5.3b and 5.4b further demonstrate that diffusion process are dominant in the later, which is seen as a Warburg diffusion tail in the low frequency region of the spectrum. This shows that the film formed on carbon steel in the aerated conditions are more porous compared to the film formed in deaerated conditions, at these corresponding temperatures. To further understand the nature of film formed on carbon steel in deaerated and aerated environments, surface analysis of the samples were performed by optical and X-ray Photoelectron Spectroscopy (XPS). For these analyses, samples were held at passive potential (200mV above E_{corr}) at 25 and 85°C, for deaerated conditions. However, in the case of aerated conditions the samples were analyzed directly after completion of potentiodynamic experiments at 25, 45 and 85°C.

5.2 Characterization of the surface products by Optical Microscopy
The surface morphologies of the samples observed after polarizing the samples in deaerated 100x YM water at temperatures 25 and 85°C smooth surface without any localized corrosion at the above temperature levels (see Figure A2-1, A and B in Appendix A2). However, the carbon steel samples observed after potentiodynamic polarization experiments, in aerated solutions, show localized corrosion at 25 and 45°C (see Figure A2-1,C to D in Appendix A2). The sample treated at 85°C shows similar morphology as that observed in deaerated conditions. Formation of (black) precipitates at higher temperatures (see Figure A2-1 E in Appendix A2). These results further indicate that the increased corrosion rates in aerated environments compared to deaerated environments.
Figure 5.3. Impedance plots recorded on carbon steel in aerated 100x YM water at (a) 25°C, (b) 45°C and (c) 85°C (018JL.002 Files: A: Joshzib25CymlOOxol01 B: Joshzib45CymlOOxol01 C: Joshzib85CymlOOxol01)

5.3 X-ray Photoelectron Spectroscopy of the I-beam Specimens after corrosion

The nature of corrosion product formed on carbon steel surfaces in aerated and deaerated 100x YM water, treated at different temperatures, was examined by depth profile analyses through argon ion sputtering and are shown in Figure 5.4 (a-c). These data show that the corrosion product film for carbon steel tested in aerated YM electrolytes at 25 and 45°C are primarily the base metal oxides with a small amount of carbon in the outer layer of the product. However, the sample treated at 85°C exhibits enrichment of Mg species. For the samples treated in deaerated environment, the corrosion products are mostly Mg rich (at 25 and 85°C). These results also show that Si species are found to increase at higher temperatures, in addition to Mg. Porous precipitate scales were evident from micrographs shown in Figure 5.5 d and e.
The XPS spectra obtained for carbon steel in aerated conditions treated at 25 and 45°C (100x YM water) in Figure A2-2, in Appendix A2, show presence of Fe (2p), O1s and C1s. Peaks with binding energies 710.5eV and 707.2eV for Fe 2p3/2 spectra indicated the oxidized and metallic Fe components. The intensity of metallic signal increased with increase in sputtering depth. Three component peaks were evident in the O1s spectra. The higher binding energy (BE) peak at 534.2eV and 531.2eV was attributed to CO$_3^{2-}$ and OH species while the lower BE peak at 530.6eV assigned to O$^2$ species. The peak with binding energy at 288.5eV for C1s spectra confirms the presence of CO$_3^{2-}$ species for the outer layer of the corrosion product film [5,6]. The presence of Fe(2p) at 710.5eV, O1s peak at 534.2eV and C1s peak at 288.5eV confirms the formation of FeCO$_3$ on the outer layer of the corrosion product while the inner layers were mostly oxides/hydroxides of Fe species [5-8]. Increase in temperature to 45°C did not change the chemistry of the corrosion product film as seen at 25°C and the representative Fe(2p), O1s and C1s spectra are shown in Figure A2-3. The intensity of CO$_3^{2-}$ peak is less at this temperature than that formed at lower temperature (25°C).

Figure 5.4. Depth Profile analyses of carbon steel as a result of polarization in 100x YM water at different temperatures. Spectra a, b and c are oxygenated. (018VD.007 File: XPS Depth profile.doc).

Figure 5.5 Depth Profile analyses of carbon steel as a result of polarization in 100x YM water at different temperatures under nitrogenated conditions; spectra d and e. (018VD.007 File: XPS Depth profile.doc) The carbon steel polarized in aerated electrolyte at 85°C exhibit Fe(2p), Mg(1s) and O1s peaks (These can be seen in Appendix 2, figure A2-4). Comparing the results in Figure 5.4 (e), this depth profile analyses shows, Mg(1s) peak is
more intense compared to the base metal component. The presence of O1s peak at 533.2eV and Mg(1s) peak at 1304eV confirms that Mg is in hydrated form as Mg(OH)₂ [9-11]. However, the shift in binding energy value of the as-received surface may probably due to the oxidation of the outer hydrated layer upon exposure to air. This is also seen from the slight shift in BE of Mg(1s) peak for the as received layer. In all the deaerated environments, Mg was found to be mostly in Mg(OH)₂ form similar to that shown for aerated conditions at 85°C (Appendix 2, Figure A2-4); the corresponding spectra are not shown here, as they are similar in nature.

Variations of corrosion rate with temperature, at different electrolyte concentrations, are summarized in Figures 5.6 and 5.7. The reported results [1] using J-13 water are also included to compare our results, in the same plot. This shows that the measured corrosion rates are significantly higher in the simulated water in the present work as compared to reference 1. Lian et al. [1], and MacCright and Weiss [1a] work was very good and pioneering work on corrosion of steels using YM water electrolytes and environment. The differences in corrosion rates may be attributed to the differences in ionic concentrations of the simulated waters [1]; the electrolyte used in present work contains more chlorides and sulfates as compared to J-13 well-water. But the HCO₃⁻ content is much higher, as a well-known [12-13] important controlling species in corrosion of steel as it forms carbonates with Fe and Ca. Interestingly, such species were not identified in the present work in aerated conditions, except at 25 and 45°C. The absence of such species in the deaerated conditions and in aerated electrolyte at 85°C could be attributed due to the less Fe²⁺ ion concentration, as seen revealed from XPS analyses (compare Figures 5.4 (c) to 5.5 (e)).

It is interesting to note that CaCO₃ product scales were not identified in any of the samples, in spite of the high Ca content present in this YM waters. We know that such scale formation is important in controlling the corrosion of steel structures in marine environments [13, 14]. Significant Mg(OH)₂ precipitate film was noted in the present work, although they are minor species of the present water composition. The preferential formation of such species could be due to the high pH existing in the 100x concentrated YM water due to the higher content of carbonates.

Figure 5.6. Corrosion rates of I-beam as a function of temperature and electrolyte concentration in deaerated condition. Results of Lian et al. [1] are included. (Summarized information from Table 5.1; Lian et al. curve Non-Q, for corroboration only)
Figure 5.7. Corrosion Rates of I-beam as function of temperature and concentration in aerated conditions. Results of Lian et al. [1] are included. (Summarized information from Table 5.1, Lian data Non-Q for corroboration only)

Table 5.1. Summary of corrosion rates of I-beam obtained from the polarization curves shown in Figure 5.1 in YM water. \( I_{corr} \) and corrosion rates calculated using the polarization method detailed in chapter 2 from data 018JL.002 Files: Joshpdib25Cym1x1n1, Joshpdib45Cym1x1n1, Joshpdib65Cym1x1n1, Joshpdib85Cym1x1n1, Joshpdib25Cym10xn1, Joshpdib65Cym10xn1, Joshpdib45Cym10xn1, Joshpdib85Cym10xn1, Joshpdib25Cym100xn1, Joshpdib65Cym100xn1, Joshpdib45Cym100xn1, Joshpdib85Cym100xn1, Joshpdib25Cym1x01, Joshpdib65Cym1x01, Joshpdib85Cym1x01, Joshpdib25Cym10x01, Joshpdib45Cym10x01, Joshpdib65Cym10x01, Joshpdib85Cym10x01, Joshpdib25Cym100x01, Joshpdib65Cym100x01, Joshpdib85Cym100x01

<table>
<thead>
<tr>
<th>Temp °C</th>
<th>( I_{corr} ) (( \mu A/cm^2 ))</th>
<th>C.R ( \mu m/y )</th>
<th>C.R mpy</th>
<th>( I_{corr} ) (( \mu A/cm^2 ))</th>
<th>C.R ( \mu m/y )</th>
<th>C.R mpy</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>18.44</td>
<td>216.01</td>
<td>8.50</td>
<td>3.63</td>
<td>42.52</td>
<td>1.674</td>
</tr>
<tr>
<td>45</td>
<td>94.24</td>
<td>1103.88</td>
<td>43.46</td>
<td>3.879</td>
<td>45.466</td>
<td>1.79</td>
</tr>
<tr>
<td>65</td>
<td>79.73</td>
<td>933.96</td>
<td>36.77</td>
<td>4.529</td>
<td>53.040</td>
<td>2.088</td>
</tr>
<tr>
<td>85</td>
<td>29.96</td>
<td>351.028</td>
<td>13.82</td>
<td>5.41</td>
<td>63.50</td>
<td>2.50</td>
</tr>
<tr>
<td>Oxygenated (10x)</td>
<td></td>
<td></td>
<td></td>
<td>Oxygenated (10x)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>31.58</td>
<td>370.08</td>
<td>14.57</td>
<td>5.596</td>
<td>65.53</td>
<td>2.58</td>
</tr>
<tr>
<td>45</td>
<td>65.66</td>
<td>769.11</td>
<td>30.28</td>
<td>5.812</td>
<td>68.07</td>
<td>2.68</td>
</tr>
<tr>
<td>65</td>
<td>32.68</td>
<td>382.82</td>
<td>15.07</td>
<td>6.02</td>
<td>70.51</td>
<td>2.78</td>
</tr>
<tr>
<td>85</td>
<td>13.86</td>
<td>162.78</td>
<td>6.39</td>
<td>9.39</td>
<td>110.01</td>
<td>4.331</td>
</tr>
<tr>
<td>Oxygenated (100x)</td>
<td></td>
<td></td>
<td></td>
<td>Oxygenated (100x)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>67.8</td>
<td>794.26</td>
<td>31.27</td>
<td>1.306</td>
<td>15.30</td>
<td>0.602</td>
</tr>
<tr>
<td>45</td>
<td>118.2</td>
<td>1384.55</td>
<td>54.51</td>
<td>2.686</td>
<td>31.46</td>
<td>1.239</td>
</tr>
<tr>
<td>65</td>
<td>7.03</td>
<td>82.35</td>
<td>3.24</td>
<td>5.47</td>
<td>64.26</td>
<td>2.53</td>
</tr>
<tr>
<td>85</td>
<td>6.06</td>
<td>70.99</td>
<td>2.79</td>
<td>4.674</td>
<td>54.76</td>
<td>2.146</td>
</tr>
</tbody>
</table>

5.4 References for the Polarization Results of I-Beams

(1) T. Lian and D.A. Jones, Corrosion 55 (1999), p.1012
(3) C.S. Brossia and G.A. Cragno, Corrosion, 56, 2000, p.505-514
(6) V. Deodeshmukh, A. Venugopal, D.Chandra, J. Daemen and D.A. Jones, S. Lea and M. Engelhard, communicated to Corrosion Sci.,
(10) P. Stefanov, Vacuum, 47 (1996), p.1107
(15) Herbert Feitler, Materials Performance, August 1975, p.33
VI. HYDROGEN PERMEATION RESULTS OF ROCK BOLTS AND STEEL SETS

6.1 Summary of Hydrogen Permeation Results

The electrochemical hydrogen permeation method has been used to investigate hydrogen transport, trapping characteristics of low (0.08%C) and medium carbon (0.44%C) steels proposed for the Yucca Mountain (YM) repository environment. Medium carbon steel was more resistant towards Hydrogen Induced Cracking (HIC) than low carbon steel as the critical hydrogen concentration (C_k) was found to be higher (36.15ppm) than low carbon steel (8.13ppm). The presence of high C, Mn and S increased the density of trapping sites in medium carbon steel and improved the HIC resistance. The measured diffusivity of medium carbon steel was lower than that of low carbon steel due to increased absorption of hydrogen at irreversible sites in medium carbon steel. Hydrogen concentration values obtained for carbon steels in YM ground water electrolytes indicate that increased electrolyte concentration decreases the uptake of hydrogen. X-ray diffraction analyses show that, the corrosion products formed on carbon steel surfaces as a result of hydrogen charging was found to be CaCO_3 and that caused the decrease in hydrogen permeation and corrosion rate.

6.2 Diffusion and Trapping

The permeation transients obtained for SSCS and RBCS are shown in Figure 6.1. Figure 6.2 represents the obtained permeation transients in terms of normalized flux (J/J_0) and dimensionless time (τ = Dt/L^2), where D is the lattice diffusion coefficient for pure iron (7.2x10^-5 cm^2/s), t is the time and L is the thickness of the carbon steel membrane. The parameters obtained from the resulting transients are listed in Table 6.1. Depending on the trapping, the permeation transient displaces to larger τ (Normalized Time = Dt/L^2) values. The larger the displacement of τ value, the higher the effect of trapping. It is evident from Table 6.1 that there is a significant change in the first and second transient especially for the RBCS. This is attributed to the higher Mn, C and S present in that steel, which caused substantial delay in the hydrogen transport. As a result of this, the second transient moved to larger τ values. However, for SSCS, the first and second transient lie close together indicating that lattice hydrogen transport was dominant. The hydrogen diffusivity was almost four times higher for SSCS than RBCS. The values in Table 6.1 show that the number of trapping sites calculated was much higher for RBCS than SSCS due to the higher concentration of C, Mn and S in RBCS. The solubility (Subsurface concentration) was also higher for RBCS than SSCS, while permeability was lower in RBCS.

The hydrogen permeation rate (J_0L) (mol H cm^\(-1\) s^\(-1\)), effective diffusivity (D_{eff}) (cm^2 s^\(-1\)) and solubility (C_0) (ppm) and density of trapping sites (N) were calculated using the equations explained in theoretical section.

Table 6.1. Hydrogen permeation parameters obtained from Figure 6.2. (Permeability, Diffusivity, Solubility and density of trapping sites calculated using methods detailed in chapter 2.11 using data 018VD.010)

<table>
<thead>
<tr>
<th>Carbon steel</th>
<th>Transient</th>
<th>Permeability (J_0L) mol/cm.s x 10^11</th>
<th>Effective Diffusivity (cm^2/s) x10^-7</th>
<th>Solubility (Co) (ppm)</th>
<th>Density of Trapping Sites (N) x 10^21/cm^3</th>
</tr>
</thead>
<tbody>
<tr>
<td>SSCS</td>
<td>1st</td>
<td>5.94</td>
<td>5.18</td>
<td>114.7</td>
<td>3.2</td>
</tr>
<tr>
<td></td>
<td>2nd</td>
<td>5.54</td>
<td>7.43</td>
<td>58.3</td>
<td>1.5</td>
</tr>
<tr>
<td>RBCS</td>
<td>1st</td>
<td>2.65</td>
<td>1.64</td>
<td>161.6</td>
<td>14.2</td>
</tr>
<tr>
<td></td>
<td>2nd</td>
<td>3.20</td>
<td>2.42</td>
<td>132.2</td>
<td>7.9</td>
</tr>
</tbody>
</table>

6.3. Effect of Cold Work on Hydrogen Permeation

Effect of cold work on hydrogen permeation in SSCS was examined for the SSCS by straining the tensile sample up to 80% of yield strength value. Subsequently the gage length portion of the sample was positioned in the charging cell and the experiment was carried out. The load vs. elongation curve obtained for SSCS and the obtained permeation transients are shown in Figure 6.3. Since there was no appreciable delay in the time, the reversible trapping effect by dislocations do not play significant role.
Figure 6.1. Hydrogen permeation transients for carbon steels in 0.1M NaOH solution (Time of zero indicates the beginning of cathodic charging. (0.18VD.010 Files: Steel Sets: 121steelnaohpd.xls; Rock Bolt: new rock bolt calculations.xls).

Figure 6.2. Normalized Hydrogen permeation transients for carbon steels in 0.1M NaOH solution (0.18VD.010 Files: Steel Set: calculations steel sets.xls; Rock Bolt: new rock bolt calculations.xls).
6.4. Hydrogen permeation in Simulated YM water

The hydrogen permeation transients obtained for I-beam carbon steel membranes as a result of exposure to simulated YM water is represented in Figure 6.4.

Figure 6.3  Load-Elongation curve for SSCS I-beam sample. (018VD.009 File: Elongation for ibeam.doc).

Figure 6.4. Effect of Cold Work on hydrogen permeation of I-beam steel SSCS I-beam in 0.1 M NaOH. (018VD.010 File: 1st transient: 123Naohyshpd.xls; 2nd transient: 123Naohyshpda.xls).
These transients demonstrate that the uptake of hydrogen decreases when the electrolyte concentration is increased. The hydrogen permeation current density ($i_p$) decreases from 3 to $0.5 \mu A/cm^2$. It is also noted that once the steady state is achieved there is no further decrease in current indicating the absence of voids at the charging current density of $1mA/cm^2$. The variation in potential with time at the hydrogen charging side observed during the experiment shows that the potential was more negative and fluctuated between -4V to -3V for 1x electrolyte concentration as shown in Figure 6.6.
However, the potential shifted to noble direction when the dissolved ionic concentration is increased (10x and 100x) and was observed to be stable. The attainment of noble potential indicates the build up of oxide/scale on the carbon steel surface that was believed to provide barrier effect to diffusion of atomic hydrogen. X-ray diffraction analysis of the deposits formed as a result of hydrogen charging reveal that the by-product was predominantly CaCO$_3$ when exposed to 100x and 10x solution concentrations as shown in Figure 6.7.

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

Figure 6.7. X-ray diffraction pattern showing the deposition of CaCO$_3$ scale on SCS after cathodic hydrogen charging experiments, A) 100x and B) 10x YM electrolyte. (018VD.009 scale formation from hydrogen.doc).

Such scales could not be found in 1x electrolyte due to the lower concentration of ionic salts. Insufficient formation of scales did not provide complete protection and as a result of this the hydrogen absorption was found to be higher. The precipitation of CaCO$_3$ scales occurs through the following reactions (6.1) and (6.2). It can be noted that the resulting permeation transient for 100x concentration reveals a hump initially, followed by reduction of current. This is attributed to the formation of thick scale in that electrolyte concentration.

In order to study the film formation on cathodic side in hydrogen permeation experiment, impedance spectroscopy was carried out on the film formed at the cathodic area before and after hydrogen charging. Impedance spectra were taken for 100 x YM water before starting the experiment and was also taken after completion of experiment, which is shown in Figure 6.8. Nyquist plot taken before hydrogen charging showed depressed semicircle with lower polarization resistance ($R_p$) value. Nyquist plot taken after hydrogen charging for about 12 hrs shows higher $R_p$ value, which implies formation of film after hydrogen charging. The effect of electrolyte concentrations on the
anodic and cathodic polarization behaviors of SSCS is shown in Figure 6.9. The electrochemical parameters of interest measured from the curves are given in Table 6.2.

![Figure 6.8: Nyquist plots during hydrogen permeation experiment for SSCS in 100x YM water before and after Hydrogen Charging](018VD.006 File: 803umlOxl2hr.xls)

Polarization curves obtained for RBCS show similar behavior to that of steel sets carbon steel in YM water. Potentiodynamic scans for the RBCS in YM water is shown in Figure 6.10. The results show that with increase in electrolyte concentration the passivation tendency of carbon steel increases. The passive current density is decreased and the width of the passive region is increased. The corrosion rate ($i_{corr}$) was found to decrease from 9.34 to 4.01 ($\mu$A/cm$^2$) in 1x to 100x electrolyte concentrations and the measured corrosion potentials ($E_{corr}$) was slightly negative for 100x electrolyte.

Table 6.2 Electrochemical parameters obtained from Figure 6.9 (Information summarized from figure 6.9)

<table>
<thead>
<tr>
<th>Electrolyte concentration</th>
<th>$E_{corr}$ (mV)</th>
<th>$i_{corr}$ ($\mu$A/cm$^2$)</th>
<th>$\beta_a$ (mV/decade)</th>
<th>$\beta_c$ (mV/decade)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1x</td>
<td>-705</td>
<td>9.34</td>
<td>80</td>
<td>170</td>
</tr>
<tr>
<td>10x</td>
<td>-710</td>
<td>7.56</td>
<td>86</td>
<td>180</td>
</tr>
<tr>
<td>100x</td>
<td>-720</td>
<td>4.01</td>
<td>90</td>
<td>190</td>
</tr>
</tbody>
</table>

The change in the anodic and cathodic Tafel slopes demonstrate that they tend to increase with increase in electrolyte concentration indicating that the ionic species act as mixed inhibitor. As the result of this the corrosion rate decreased and the passivation tendency enhanced when the electrolyte concentration is increased. The above results show that the formation of CaCO$_3$ on carbon steel surface provides barrier effect to the diffusion of hydrogen on carbon steel and hence increases its resistance towards hydrogen induced cracking in the YM environment.

6.5. Effect of Anions on Hydrogen Permeation in 3.5% NaCl Solution

Although the corrosion product formed is predominantly CaCO$_3$, a question arises as to what is the role of silicate on the corrosion and hydrogen permeation on carbon steel. Previous work performed [1] and [2] using YM water environment indicate the enrichment of silicate as silica on carbon steel surface at ambient...
Figure 6.9. Polarization behavior of I-beam SSCS in simulated YM water with increasing electrolyte concentrations A) 1x, B) 10x and C) 100x (018VD.010 Files: 1X: steel1x.xls; 10X: steel10ym.xls; 100X: steel100ym.xls).

Figure 6.10. Polarization behavior of rock bolt RBCS in simulated YM water with increasing electrolyte concentrations A) 1x, B) 10x and C) 100x (018AY.010 Files: 1X: Rock1x.xls; 10X: 202ym10xr4pdcxl.xls; 100X: 619ym100xwatpd.xls).
temperature. As a result of this the corrosion rate decreased and passivation enhanced. In the present work, silicate could not be identified by XRD due to its lower concentration as compared to Ca content in the electrolyte solution. Hence to understand the role of silicate experiments were performed in 3.5% NaCl solution in which specific quantities of HCO$_3^-$ and SiO$_3^{2-}$ ions were added individually and then in combined form. In order to match their content in 100x electrolyte and their hydrogen uptake tendencies were compared.

The results show that the permeation current was higher for HCO$_3^-$ followed by SiO$_3^{2-}$ as shown in Figure 6.11.

![Graph showing hydrogen permeation in bicarbonate and silicate environment in 3.5% NaCl solution](image)

**Figure 6.11.** Effect of A) no added ions B) HCO$_3^-$, C) SiO$_3^{2-}$, D) HCO$_3^-$ + SiO$_3^{2-}$ ions on the hydrogen permeation current measured in 3.5% NaCl solution (018VD.010 Files: A: 505nac3.xls; B: 505bi0.5nac3.xls; C: 507si0.01nac3.xls; D: 508bi0.5si0.01nac3.xls).

The combination of these two ions shows a decreasing permeation current indicating that the film formed in presence of these two ions imparts higher resistance as compared to only one type of ions alone. Interestingly the permeation current was much lower in the base solution than in the presence of above ions. It is reported that iron oxide provides a strong barrier effect and hence stops the permeation of hydrogen [3,4]. Further, in chloride environment formation of salt film together with oxides of iron provides corrosion protection of steel. Hence the decrease in hydrogen permeation in chloride solution can be attributed to the salt film formation. Allam et al. [5] also reported the decreasing permeation current when chloride ions were added to the acidic and alkaline environments. However, in the present case, when the ions are added to chloride solution the nature of oxide film is modified and the resistance of the oxide was reduced. As a result of this the hydrogen permeation current increased as compared to its value for chloride solution only. The increase in permeation current to HCO$_3^-$ can be attributed due to the complex formation of Fe as Fe(CO$_3$)$_2^{2-}$ as proposed by Burstein et al [6]. As a result of this, the corrosion rate of carbon steel increased due to addition of bicarbonate addition. Furthermore, the hydrogen over potential for Si is high compared to Fe [7,8]. Hence, hydrogen evolution tendency of carbon steel decreased when silicate is added to chloride solution.

To summarize, we conclude that the silicate ions when added with bicarbonate ions reduced passive current density of RBCS significantly due to the preferential adsorption of silicate at the defects or pits on the passive film. This is observed from polarization and microscopy results. However, its effect was found to be less at low anodic polarization due to the complex formation of bicarbonate with Fe. The evolution of impedance spectra with respect to potential changes closely reflects above changes occurring on RBCS as seen through polarization plots. The corrosion morphology of the pits observed under SEM reveals that the pits are active at all potentials due to
bicarbonate addition. As a result of this the corrosion rate remains high. However the pits formed are inhibited by silicates improving the passivation process. XPS results indicate the surface enrichment of silica on the carbon steel surface at higher potentials and a mixed silica and FeCO$_3$ at lower potentials. XPS results provide evidence for the change in the oxide film after the second oxidation peak seen in the polarization plots. Second oxidation peak is due to the oxidation of iron carbonate to carbonate. The presence of high C, Mn and S content increased the density of trapping sites in RBCS. As a result of this, diffusivity obtained was much lower and hydrogen content was found to be higher indicating that the hydrogen induced cracking tendency of this steel is more when compared to SSCS. The formation of CaCO$_3$ deposit reduced the hydrogen permeation and corrosion rate of carbon steel when the electrolyte concentration was increased. HCO$_3^-$ in combination with SiO$_2^-$ imparts good protection against hydrogen permeation in chloride solution as compared to that for any of these ions alone.

6.6. Critical Hydrogen Concentration
The critical hydrogen concentration was calculated using the data in tables 6.1 and 6.2. This yield values of 8.13 ppm for steel sets and 36.15 ppm for rock bolts.

![Figure 6.12](0018JL.003 file: ibeam1) Hydrogen permeation transients used for calculating $C_h$ for steel sets.

![Figure 6.13](0018JL.003 File: rbolt1) Hydrogen Permeation used to calculate $C_h$ for rock bolts.
6.7. References for Hydrogen Permeation Section

VII. GENERAL CORROSION RESULTS OF YM I-BEAMS AND ROCK BOLTS

7.1 Summary of Humidity, Fog Tests, and Immersion Tests

Conventional or modified ASTM long-term tests such as ASTM G-31 (Immersion Tests), ASTM G-85 (modified YM water spray, rather than salt water spray), Humidity tests, and ASTM G-60 (Cyclic Humidity) test performed on the YM Rock Bolt and I-beam specimens showed reasonable agreement with electrochemical short-term tests. Data points (for example, CH-887 indicates cyclic humidity corrosion rates of 887 µm/year) for these experiments have been incorporated in the summary section, Figures 1 (a and b). Further research on the new materials using these established methods would allow selection of better steels for the rock bolts and I-beam used for the YM subsurface reinforcements.

Modified YM water spray Fog Tests were conducted using 1x YM water for I beams and rock bolt specimens, and the corrosion rate was calculated from the measured weight loss. (Normally, salt is added to the water for this ASTM B-117 test, but in this experiment, we just used the 1x YM water for the spray to determine its effect.) The measured CR for low (0.08%) carbon steel I-Beams was ~818 µm/yr and for medium (0.44%) carbon rock bolt steel was ~729 µm/yr.

Cyclic Humidity tests on carbon steel rock bolts and I-beams using ASTM G-60 method. The corrosion rates were measured from the mass losses. Simulated 1x YM waters were used for these tests. The results show that the corrosion rate of rock bolt was ~887 µm/yr, as compared to steel sets ~1265 µm/yr.

Humidity tests (85%) were conducted using 1x YM water for I beams and rock bolt specimens and the corrosion rate was calculated from the measured weight loss using pure water without any addition of YM ions in the water. The measured CR for low (0.08%) carbon steel I-Beams was 4.17 µm/yr and for medium (0.44%) carbon steel was 30.54 µm/yr.

Immersion or Dipping Tests were conducted at room temperature and at 75°C. The room temperature experiments showed a CR (Rock bolts) ~ 45 µm/yr for 107 day exposure in nitrogenated environment; which is comparable with the results of electrochemical tests for YM 1x deaerated waters. The 75°C immersion experiments, in oxygenated condition, showed three different rates depending on position of the sample in the YM 1x waters; (a) fully immersed CR= 200 µm/yr (b) Exposed to Humid air and not dipped, the CR= 510 µm/yr, and (c) 960 µm/yr for 500 hours exposure. The 75°C immersion has the second highest rate. In this case, the concentration cell effect is still dominant because of the beads of water accumulated over the specimen, again creating preferential anodes and cathodes. However, this effect is less pronounced resulting at lower corrosion rates compared to that of the half immersion. Fully immersed specimen showed a rate of nearly 200 µm/yr., which matches closely with the potentiodynamic polarization results of the same environment. 5°C in the aerated 1x YM water revealed higher corrosion rates than the ones at 25°C, as similar to the results of electrochemical experiments. Mass loss results of a total of 500 hour exposure period

7.2. Cyclic Humidity Test on Rock Bolt (RB) and Steel Set (SS) as per at MATCO Associates in Pittsburgh, PA

The experiments for effect of cyclic humidity on corrosion rate were performed on rock bolt and steel set samples at MATCO Associates according to ASTM G-60 procedure using 1x Yucca Mountain (YM) electrolyte for the duration of 21 days. The humidity cycle was varied from 100% to 50% humidity in a test chamber held to constant temperature (52°C). At the end of 21 days, the mass loss of the coupons were measured and the corrosion rate CR was calculated using the following equation

\[
\text{Corrosion rate} = \frac{K \times W}{A \times T \times D}
\]

where, K is a constant [3.45 x 10^6 (mpy) and 8.76 x 10^7 (µm/y)]
T = time of exposure in hours
A = area in cm^2
W = mass loss in grams
D = density in g/cm$^3$

The calculated corrosion rates (C.R) (average of five specimens) are shown in Table 7.1.

Table 7.1. Corrosion rates of Rock bolts and Steel sets Sample 1-5B are Rock bolts and 1-5S are Steel Set I-beam.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$W_1$ (gm.) Initial</th>
<th>$W_3$ (gm.) Before Stripping</th>
<th>$W_3$ (gm.) After Stripping</th>
<th>Surface Area Cm$^2$</th>
<th>Corrosion Rate mpy</th>
<th>Corrosion Rate $\mu$m/yr</th>
</tr>
</thead>
<tbody>
<tr>
<td>1B</td>
<td>46.4598</td>
<td>46.7273</td>
<td>44.2707</td>
<td>33.44</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2B</td>
<td>46.3740</td>
<td>47.3990</td>
<td>44.8572</td>
<td>33.44</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3B</td>
<td>46.4060</td>
<td>47.2271</td>
<td>44.4643</td>
<td>33.44</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4B</td>
<td>46.0240</td>
<td>46.8169</td>
<td>43.2194</td>
<td>33.44</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5B</td>
<td>45.5866</td>
<td>47.1851</td>
<td>44.4000</td>
<td>33.44</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>230.8504</td>
<td>235.3554</td>
<td>221.2116</td>
<td>167.2</td>
<td>49.8</td>
<td>1264.92</td>
</tr>
<tr>
<td>Total Weight Loss ($W_1-W_3$)</td>
<td>9.6388</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1S</td>
<td>11.1941</td>
<td>11.7610</td>
<td>11.2971</td>
<td>11.04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2S</td>
<td>11.7185</td>
<td>11.9055</td>
<td>11.3681</td>
<td>11.04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3S</td>
<td>11.7614</td>
<td>12.1415</td>
<td>11.0979</td>
<td>11.04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4S</td>
<td>11.5813</td>
<td>11.4227</td>
<td>11.4526</td>
<td>11.04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5S</td>
<td>11.9427</td>
<td>11.8807</td>
<td>10.7520</td>
<td>11.04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total B</td>
<td>58.198</td>
<td>59.1114</td>
<td>55.9677</td>
<td>55.2</td>
<td>34.9</td>
<td>886.46</td>
</tr>
<tr>
<td>Total Weight Loss ($W_1-W_3$)</td>
<td>2.2303</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

It can be seen from these results in the above table that, the corrosion rate of rock bolts was higher (1264.92$\mu$m/yr.) than that of I-beam (886.46$\mu$m/yr.). Figure 7.1 shows the photographs of the samples before exposure to the environment and Figure 7.2 to 7.4 represents the photographs of the samples observed after 7, 14 and 21 days respectively.

Figure 7.1. Photographs of I-beam (left) and rock bolt (right) specimens before humidity tests.

Figure 7.2. Photograph of I-beam and rock bolt specimens after 7 days.
The above figures indicate that the extent of corrosion increased with exposure time. Characterization of the corrosion morphology using SEM showed similar nature of corrosion. The surface morphologies are shown in Figure 7.5, and EDS spectra of the corrosion product is shown Figure 7.6. In general, the spectrum of the corrosion product shows SEM-EDS X-ray peaks of Fe, Ca, Cl, C and O, as expected; and there was not much difference between these rock bolt and I-beam samples.

7.3. General Corrosion Behavior of Rock Bolts and I-beam

General corrosion behavior of carbon steels in concentrated Yucca Mountain (YM) Waters carried out by three different classical rate determination methods, such as simple laboratory immersion (dipping) testing, salt spray (fog or environmental chamber testing), and linear polarization method will be presented in this section. The potentiodynamic polarization curves will be given for various temperatures and concentrations along the electrochemical corrosion rate results. Also, complementary electrochemical impedance spectroscopy results will be reported. Preliminary microstructure analysis of I-beam and rock bolt will be given prior to the analysis results of EDX (electron dispersive X-ray spectra) and X-ray diffraction carried out on the corrosion product surface films, and the results of optical microscopy will be presented, as focused on microstructures and pitting behavior of those steels in aerated and de-aerated hot YM water environments.
7.4. Metallographic Evaluations

The time, for etching both of the specimens properly, was roughly twice as much longer for the I-beam specimen compared to that of rock bolt, with a 2% freshly prepared Nital solution used for the both steels. Optical microscopy of the low carbon I-beam steel I-beam and the medium carbon rock bolt steel rock bolt showed quite dissimilar microstructures as shown in Figures 7.5A and 7.5B, respectively. An Olympus optical analyzer along with a Sony DP2 camera was used to take both micrographs at 700X linear magnification under the same illumination. I-beam specimen with 0.08 weight % carbon I-beam content revealed approximately 85% Ferritic and 15% Pearlite grains as shown in Figure 7.5A, that appear in lighter (grayish) and darker colors respectively. The Pearlite grains in the I-beam that formed out of lamellar structures also appeared to be aligned in a certain direction, suggesting that it was cold or hot rolled. The rock bolt micrograph, to the contrary, showed more Pearlite structures approximately 65% along 35% ferrite structure, as shown in Figure 7.5. The MCS rock bolt’s (C=0.44 wt %), Pearlite content much higher than that of LCS I-beam. This 0.36 wt. % carbon content difference caused these different microstructures of LCS and MCS. Micro-hardness tests conducted with a Shimadzu model optical micro-hardness tester revealed significant differences between the hardness of Pearlite and Ferrite structures as expected. Vickers hardness numbers were calculated out of diagonal measurements of diamond indentations, as 374 and 270 for Pearlite and Ferrite grains respectively. Several micro-hardness tests were carried out at different regions of many individual Pearlitic grains in order to investigate the probable involvement of Bainite in the Pearlite structures. However, all of the tests conducted over different domains of individual grains revealed the same Vickers number given above, showing no other harder or softer sub-structure involvement in those Pearlite grains.

The determined differences between the microstructures of these two types of carbon steels are expected to affect their general and localized corrosion performances in the concentrated YM waters. In general, increased carbon content increases general corrosion rates due to the galvanic effects among various individual grains.

![Figure 7.5](image1.png)

Figure 7.5. SEM evaluation of rock bolt (left) and steel set (right) showing similar corrosion morphology observed after 21 days of humidity tests.

![Figure 7.6](image2.png)

Figure 7.6. A typical SEM-EDS spectrum indicating the nature of corrosion products formed on the I-beams and rock bolts after cyclic humidity tests. (018VD.009 File: SEM-EDX.doc).
Figure 7.7. Optical micrograph of LCS (0.008%) I-beam showing small amounts of Pearlite embedded in the major ferrite structure. 7.7. Optical micrograph of MCS (0.44 % C) I-beam showing large amounts of Pearlite leaving out much less ferrite structure compare to LCS.

Figure 7.8 A. Optical micrograph showing inclusions in I-beam (0.08%C) in the rolling direction.
Figure 7.8 B. SEM micrograph of inclusions in the YM I-beam. The inclusions are generally of elliptical shape; some more elongated than others.
Figure 7.8 C. EDS analysis showing extra Mn and S content of the inclusion labeled Spectrum 1. (018VD.004 File Ysite3spec1.doc).

Optical micrographs of I-beam specimen, polished by successive 1, 0.3, 0.05 micron diameter alumina powders, revealed inclusions of elongated elliptic shapes which extended in a certain direction as shown in Figure 7.8. The EDS analysis of the inclusions by a cold field emission scanning electron microscope (Hitachi, Model S-4700) revealed high peaks of manganese and sulfur in the analysis plot given in Figure 7.8 C. According to the EDS results they are most probably MnS nonmetallic inclusions, as commonly found in variety of carbon steels.

7.5. Corrosion Rates by Basic Lab Immersion Tests
Simulated test solutions were totally colorless and clear prior to the specimen dipping. Corrosion rates determined by the basic immersion corrosion tests for rock bolt were in close agreement with the rates determined by the electrochemical tests. Determined mass loss results of 107 day exposure period at room temperature given in Figure 82
7.9. Test solution of this particular test was neither aerated, nor de-aerated by any gas purging; it was exposed to the ambient air only. The weight loss measurements revealed penetration depth of about 45 micron/year for the fully dipped rock bolt coupon specimen. This value is comparable with the results of electrochemical tests for YM 1x deaerated waters. It is well known, that corrosion rates by electrochemical polarization tests always result in larger values than that of weight loss measurements. This is particularly true when fresh unexposed surfaces are used in the electrochemical experiments. The results would be then as low as the weight loss results, if the surfaces had already been exposed and had already some corrosion products on them. Therefore, one should take the electrochemically measured rates as conservative upper bounds.

Laboratory immersion tests carried out at 75°C in the aerated 1X YM water revealed higher corrosion rates than the ones at 25°C, as similar to the results of electrochemical experiments. Mass loss results of a total of 500 hour exposure period of laboratory immersion test are given in Figure 7.10, as normalized. Partially immersed specimens
in aerated waters had the highest rates with a CR of 960 μm/yr. Because the concentration cell effects causes higher rates, these values were already expected for the aerated environments. There is differential aeration between the solution and the air in the cell, so more oxygen reduction occurs at the upper part of the specimen, while more dissolution occurs in the immersed part. As a result, the created preferential anodes and cathodes created by half immersion revealed higher corrosion rate. Non-immersed specimens (above the water level, in the humid portion of the cell) had a CR of 510 μm/yr as the second highest rate. In this case, the concentration cell effect is still dominant because of the beads of water accumulated over the specimen, again creating preferential anodes and cathodes. However, this effect is less pronounced resulting in lower corrosion rates compared to that of the half immersion. Fully immersed specimen showed a rate of nearly 200 μm/yr, which matches closely with the potentiodynamic polarization results of the same environment.

7.6 Corrosion Rates by YM Water Spray and Humid Environment Tests

Experimental results showed that corrosion rates of rock bolt and I-beam were fairly close to each other at 35°C in sprayed 1X YM waters. Exposure results given in Figure 7.11 show the mass loss after a seven-day exposure period. Penetration rates were around ~814 μm/yr and ~970 μm/yr for rock bolt and I-beam respectively. These values are in close agreement with the partial immersion test rates, the rates with the most severe position for the coupon specimens. They are close to the polarization tests rates of the aerated waters as well. R. Daniel MacCright et al. [3] reported corrosion rates ~ 452 μm/yr for gray cast iron and 749 μm/yr for 1020 carbon steel in aerated 1x J-13 well waters, by electrochemical linear polarization method. The carbon content of 1020 steel is relatively close to the presently studied material MCS rock bolt, but J-13 reference waters are more dilute in ionic content compared to the YM water. The same study showed lower corrosion rates, around 450 μm/yr for both of the same steels by simple immersion experiments.

The test coupons in the photograph YM spray fog test performed at NIT, Sylvania Ohio, (photos before and after are shown in Figure 3.13 B and C (experimental section) show that some parts of the specimens exposed to the YM water spray were totally corroded while some parts were still clear and shiny. From this appearance, the concentration cell effect is supposed to be in control for YM water spray tests [4]. Therefore, again, the partial immersion rates were in agreement with the rates of those spray tests.

In the YM spray fog test performed at NIT, Sylvania Ohio, we found that for the humid environment, corrosion rates for rock bolt and steel sets were much lower than in aqueous and fog environments discussed above. Weight loss measurements out of several identical coupon specimens of both steels are shown in Figure 7.12. However, I-beam showed noticeable resistance in this environment compared to the rock bolt. The ~ 35 μm/yr for rock bolt, 6 μm/yr for I-beam, with humidity tests in YM 1x waters for 20 days.

Figure 7.11. Weight loss of rock bolt and I-beam (steel set) in YM 1x spray environment.
Steel set CR=970 μm/yr, Rock bolt =814 μm/yr for this one week exposure at 35°C. (018AY.001 File: Graph of Salt spray and humidity.xls)

84
Figure 7.12. Weight loss of rock bolt and I-beam in YM humid environment. Steel set CR= 6μm/yr, Rock bolt 35 μm/yr for this 21 day exposure in YM 1x water at room temperature. (Comparing these results to the cyclic humidity tests ASTM G-60 test Steel set CR= 1265 μm/yr, Rock bolt 887 μm/yr for this 21 days.) (018AY.001 File: Graph of Salt spray and humidity.xls).

7.7 References for General Corrosion Results

VIII. ENVIRONMENTALLY INDUCED CRACKING RESULTS OF I-BEAM STEEL SETS

8.1 Summary of Stress Corrosion Cracking and Hydrogen Embrittlement

Stress corrosion cracking and hydrogen embrittlement tests performed on the steel sets showed interesting results. These tests were performed at very slow strain rates up to $10^{-7}/s$, and in addition these strain rates were varied to obtain the effect of strain rate on the reduction in cross sectional area. The apparatus used is shown in the experimental section with the chamber to house the electrolyte under various imposed metal-electrolyte interface potentials. Results showed dynamic strain aging embrittlement (DSAE) effects associated with Portevin-LeChatelier (PLC) effect and hydrogen induced cracking (HIC) at 85°C in simulated deaerated 100X YM waters. These failures were brittle and of sharp cracks inclined at $-45^\circ$ to the load axis. However, at room temperature (25°C) these SAE/PLC effects were not observed. In this case, relatively ductile failures were observed along secondary trans-granular cracks around the main cracks, with some anodic and cathodic over-potentials around $E_{corr}$. Thus the I-beams are susceptible to stress corrosion cracking (SCC) in the simulated repository environments.

The initiation of DSAE during the electro-mechanical tests by monitoring current and potential by potentiostatic methods showed that that Portevin LeChatelier (PLC) effect in I-beam starts at $\sim 55^\circ C$, and showed precise correlations with open circuit potential $E_{corr}$ and the corresponding current. Therefore, SSRT along the in-situ potential-current monitoring in aqueous environments becomes a powerful diagnostic research tool, especially for investigating DSAE/PLC phenomena of steel in aqueous environments.

8.2 Stress Corrosion Cracking and Hydrogen Embrittlement Studies on YM I-Beam Steel Sets

Slow strain rate testing (SSRT) results of LCS for failure susceptibility to environmentally assisted failures, such as stress corrosion cracking (SCC) and hydrogen embrittlement (HE) is presented in this section. We observed strain aging effects leading to Portevin-LeChatelier effect observed in I-beams that are low carbon steels at high water temperatures of 85°C. These tests were performed using 100x YM water electrolytes. The effect of temperature on scale formation, susceptible potentials determined by potentiodynamic polarization scans, stress-strain behavior, applied potential effects on “Time to Failure” (TTF), “Percent reduction in the cross section area” (%RA), and its dependency on strain rate are presented for the final evaluations of the environmental crack types. Then, we will discuss the temperature effects leading to serrations (Portevin-LeChatelier Effect) in the stress-strain plot. A correlation between serration amplitude and interface potential will be presented in details for the first time.

8.2.1 Precipitation of CaCO$_3$ During Heating YM 100x Waters on I-Beam Steel Sets

Simulated hundred times concentrated (100X) YM waters were made sure that they were clear prior to deaeration by purging with nitrogen gas. This clear and colorless appearance did not change within the half an hour nitrogen purging period at room temperature. There were slight changes observed on the appearance of the test solutions during the low temperature (25°C) slow strain rate tests (SSRT) within the test period of approximately two days. However, during the heating period of the solutions for the preparations of high temperature (85°C) experiments, the clearness started decreasing at around 50°C and stayed the same until reaching the test temperature 85°C was reached. Some white scales accumulated mostly over the wall of the test cell prior to starting of tests. This fog-like appearance of the solution occurred more frequently in high temperature experiments then in low temperature ones. These precipitates are the species of the solution, which became over saturated at increased temperatures. They are the similar precipitates appeared prior to the polarization tests, which have been discussed in the previous sections under potentiodynamic polarization results. The tensile test specimen placed in the middle of the SSRT glass cell was visible, which made visual examinations possible on the specimens for observing crack initiation and travel on the reduced gauge section.

The white precipitates that formed prior to testing, and deposited mostly on the cell walls were analyzed by a Phillips Bragg-Brentano X-ray diffractometer [1], and determined to be mostly aragonite (CaCO$_3$). The X-ray diffraction pattern of the initial precipitates is shown in Figure 8.1. Visual examination of the tensile test specimens showed differences in film formation on the rods tested at 25°C and 85°C, regardless of the applied potentials. These two different precipitates on the actual tensile test specimens broken by SSRT technique with a strain rate of $1.6 \times 10^{-5}/s$ at $E_{corr}$ were shown in Figure 8.2. The specimens tested at room temperature (~25°C) was covered with a “white and sooty” precipitate layer (Figure 8.2 Left). There was a clear transparent film formed on the specimen
surface during the 85°C tests (Figure 8.2 Right). Scanning electron microscopic examination and x-ray energy dispersive analysis white precipitates formed at the room temperature appears to be an oxide of iron with some chlorine. The transparent layer formed in the hot YM waters at 85°C showed that formation of magnesium silicates. The EDS analysis of the precipitate layers of these two specimens are shown in Figures 8.3 and 8.4. The strong Fe Kα peaks in Figure 7.3, indicate a thin porous layer on steel. The SEM micrograph given in Figure 8.5 confirms that these layers are formed by agglomeration of small salt islands in a porous, sponge-like manner. The strong peaks of Na, Mg, S, O, and Cl in Figure 8.3 indicate that the chlorides and sulfates of Na and Mg were contributing to most of the salt precipitates on the surface at room temperature (RT).

In contrast, high temperature films do not have that strong iron peak. Therefore, the scale formation is relatively thick or not permeable for EDS electrons. The strong presence of the Si peak at 85°C, shown in Figure 8.2 B, explains the different appearance of the high temperature films. Silicate compounds, of mostly transparent appearance, would likely be formed along with oxygen and Mg at these low solubility temperatures for metal silicates [2]. There is also the possibility of compound formation of Mg salts, since the relative intensity of Mg2+ and Cl− peaks are high. Then it may increase the pitting potentials due to reduced amount of Cl− anions.

Presence of the silicate film and the porous scale formations at both temperatures are important since they enhance the passivation of the metal (LCS) in anodically charged conditions. They may reduce the general corrosion rates, however they make the metal more susceptible to localized corrosions. Both types of the scales play important roles on environmentally induced cracking, especially on stress corrosion cracking via pitting and film rupture [3].

8.2.2 Susceptible Potentials to SCC by Polarization

Potentiodynamic polarization scanning of LCS in the de-aerated 100X YM waters revealed passive regions within a 200 mV anodic potential range for both temperatures, 25°C and 85°C. The potentiodynamic polarization curves for both of these temperatures are given in a semi-logarithmic plot in Figure 8.6, and show the susceptible potentials of I-beams to SCC, which are the transient sections between transpassive linear regions and passive regions at the lower and upper parts of these passive regions.

Passivation occurred approximately within a 200 mV potential range at both test temperatures, at 25 and 85°C. At 25°C, it starts around -0.6 mV and ends around -0.4 mV with a sharp pitting potential. The passive range stayed within almost the same potential interval at 85°C, however, it has shifted to more active values. The passive range is approximately in between -0.7 mV and -0.5 mV at 85°C. The shift of the cathodic branches between these two different temperatures is due to the corrosion rates. High temperatures lead to higher current densities referring to the higher corrosion rates.

We did not observe any passivation of the I-beam with aerated (oxygenated) 100X YM waters at 25°C as shown in Figure 8.7. The I-beam corroded uniformly in a fast manner in this environment. According to this result, it may be possible for the I-beam to experience corrosion fatigue cracking in this environment, but it does not satisfy the conditions to undergo SCC because there is no effective scale formation. In the hot (85°C) aerated waters, there is a narrow transpassive region as shown in Figure 8.7, which is again not enough for SCC susceptibility search for this particular environment [4].

Hydrogen embrittlement (HE) susceptibility on the other hand is completely independent from the film formation. Normally, in the aerated environments, the crack growth rate due to hydrogen embrittlement is decreased significantly, by the mechanism of displacement of hydrogen with oxygen at the crack tip[5]. Therefore, the susceptibility to HE in the deaerated environments would mean lesser susceptibility for the aerated environments. In another word, the deaerated environments are more suitable to design experiments for hydrogen induced cracking susceptibility.

Passivation occurred approximately within a 200 mV potential range at both test temperatures, 25°C and The passivation of LCS I-beam that occurred in a 200 mV range is relatively small compared to the passivities that are due to internal passive films. The current density during the passivation decreased by as much as a decade in the logarithmic scale at 25°C. Passivity was also present at 85°C with roughly 50 mV lower pitting potential, but the passivation current is relatively higher in this case, and high temperatures caused decreased pitting potentials, due to
Figure 8.1. X-ray spectra of the precipitates formed over the specimen and cell walls before conducting slow strain rate tests. (018AY.004 File: xray and edax data.doc).

Figure 8.2. I-beam specimens broken at 25 °C and 85 °C by SSRT at Ecorr. Surface appearance is different in each case.

Figure 8.3. (Left) Composition of precipitate layer on I-beam after electromechanical tensile tests using SSRT machine at 25°C showing small amounts of Mn-Mg-Si-Cl scale. (018AY.004 File: Xray and edax data.doc)

Figure 8.4 (Right) Composition of the precipitate layer on I-beam tensile specimen after the SSRT experiments A non-porous, dense scale formed at using 100x waters at at 85°C. It can be noted that Fe-Kα and Kβ are not observed due to a thick Mg-Si O layer formation on the surface. (018Ay.004 file: Xray and edax data.doc)
Figure 8.5 Scanning electron micrograph of a porous white scale formed on the I-beam after SSRT tensile test at 25°C showing non-adherent film formation.

Figure 8.6. Potentiodynamic polarization curves of I-beam in 100X YM water at 25°C and 85°C, showing passivities, (018JL.002 Files: 25°C: Joshpdib25Cym100xnl 85°C: Joshpdib85Cym100xnl).

the increased activity of chlorides present in the test solution. The cathodic branches appeared as approximately straight lines in both cases, which revealed the activation controlled nature of polarization of I-beam specimen in 100 X YM water environments. In another word, there was no concentration polarization effect observed on the cathodic branches of the curves for these deaerated environments. Despite the fact that there is passivity, which is based on the precipitation layer, the passive regions appeared as narrow at both temperatures. These small regions cannot be easily separated into those classical susceptible potential regions, like the one around $E_{pit}$ and one around $E_{prot}$. These two susceptible potential regions appeared already overlapped in the passive range of this I-beam of low carbon steel. Furthermore, the corrosion potentials will shift towards the noble or active values during the SSRT regardless of the applied potential. This effect will make the predetermined passive region to be diminished even more during the straining, therefore leaving out lesser effective passive region to experiment with for environmental failure susceptibility.
8.3 SSRT Electromechanical Results

The basic result of a slow strain SSRT experiment is a load-elongation, or stress-strain curve; this gives useful parameters such as time to failure, ultimate tensile strength (UTS), yield strength, fracture elongation, reduction of area, and fracture energy. In order to characterize the susceptibility of low carbon steel to both of the environmental failures such as stress corrosion cracking and hydrogen induced cracking, the SSRT parameters elongation, UTS, reduction of area, and time to failure have been used. The strain rate, which is used to determine temperature and specimen potential effects, is fixed to the most recognized value for carbon steel, 1.6x10⁻⁶/s. However, some higher and lower strain rates were also used for the evaluation of the cracking types at different temperatures.

Six different potentials were applied to the environmental specimens of the I-beam for testing susceptibility to environmental failures in 100X YM water. Besides $E_{corr}$, which is -700 mV, three cathodic potentials such as 50 mV, 200 mV, and 500 mV below $E_{corr}$, and two anodic potentials such as 50 mV and 100 mV above the $E_{corr}$ were applied. Initially, more than two data points (higher over potentials) were planned to be used in the anodic region with the SSRT. However, the experiment conducted with -550 mV resulted in excessive general corrosion. A photo of corroded specimen at -550 mV specimen potential is given in Figure 8.8. Normally, the number of anodic data points could have been increased from 2 to 3, or even 4 data points, since a large enough passive region has been revealed by potentiodynamic scans. However, the experiments repeatedly showed that there was a corrosion potential move in changing directions during the straining of this steel. Despite some experiments were initiated at a potential of -550 mV (150mV above $E_{corr}$), the specimens started to corrode rapidly, as the corrosion current increased to around 300 mV. Since the penetration rate was quite high in that case, the specimen diameter was decreasing rapidly making the data unusable for SCC or HE evaluation. This result, corrosion at 150 mV above $E_{corr}$, suggests that the pitting potential may also have been reduced by some mechanism, creating a decreased range of effective passive region. Therefore, it was not possible to use any other data beyond those two anodic potentials, -650mV and -600mV. Generally, a 50mV-interval among the chosen data points is good enough for the trend determinations for most of the electrochemical experiments, as applied in this work.

8.4 Stress-Strain behavior at Low Temperature (25°C)

Stress-strain curves for I-beams were carried out by SSRT at room temperatures that revealed continuous smooth plastic deformation regions with relatively sharp yield points at all specimen potentials and strain rates maintained constant during the experimental time periods from 20 minutes to 2 days. Similar curve features occurred with the
experiments conducted in air and inert glycerin environments. There were slight differences observed on the yield point (YP) of the stress strain curves carried out with various potentials and strain rates at room temperatures (RT), at 25°C. The load-elongation curve of the I-beam that carried out with no imposed potential in commonly accepted inert electrolyte glycerin is given in Figure 8.9, in order to introduce the common features of all curves obtained at RT. Figure 8.9 shows the load-elongation profile of the I-beam with its YP, UTS, and fracture points. The curve carried out with a strain rate of $1.6 \times 10^{-6}$/s also revealed a relatively narrow Lüders Band plateau, appearing as a serrated flow onset of plastic straining right after the YP. The rest of the experiments carried out at various potentials showed similar features including Lüders Bands, but expectedly with different SSRT parameters.

Figure 8.8. Specimen gauge appearance(right) after SSRT conducted at -550 mV surface potential. The specimen has been corroded during the test, therefore stayed out of evaluation because of it's reduced cross section by mechanisms (general corrosion) other than HE or SCC.

Figure 8.9. Load-elongation profile of LCS by SSRT in glycerin as an inert environment reference. (018AY.003 File: SSRT RT.xls).

The discontinuous plastic deformation showed Lüders bands occurring during SSRT tests of the I-beam. This phenomenon occurs mostly in steels containing interstitial elements such as carbon, nitrogen and hydrogen in their solid solutions. It is generally believed that these bands form because of pinning of dislocation motion by the diffusion of the solute atoms, however the exact mechanism of their formation is not completely understood [6]. This issue will be discussed in the section, "PLC Effects at High Temperature."

The parameters: time to failure, % elongation, reduction of area and UTS points determined by SSRT, for various specimen potentials in the de-aerated 100X waters at RT and also for the inert environments, showed significant differences among themselves. The stress-strain curves obtained for the various specimen potentials at RT is given in Figure 8.10. In order to make each curve separable enough for better view, the lower part of the linear region (Hooks Law region) was not included in the plot, thus the plastic deformation region was expanded. The experiments showed that YP was the lowest at the open circuit potential $E_{corr}$ (-700 mV) with a value around 330
MPa. At the potentials -750 mV (50 mV below E_{corr}) and -900 mV (200 mV below E_{corr}), the YP resulted close to 
that of E_{corr}. For the potentials -50 mV and -200 mV the UTS point resulted around 460 MPa, 30-40 MPa above that 
of E_{corr} (-700 mV) which showed the lowest UTS point of the experiments conducted at RT. The curves for the 
potentials -750mV and -900 mV were almost alike with respect to their YP and UTS points and also their trends, 
however the fracture points were slightly different from each other.

Figure 8.10. Stress as a function of % Elongation for LCS specimens at various potentials in de-aerated 100X YM 
waters at RT. The numbers represent the applied over potentials on the environmental test specimen in 
the units of mV. (018AY.003 File: SSRT RT.xls)

At the potential of -750 mV, 50 mV below E_{corr}, the SSRT resulted with smaller time to failure (TTF) and % 
elongation compared to the one at -900 mV, 200 mV below E_{corr}, despite the cathodically applied charge is higher at 
the potential of -900mV, and it might have increased the brittleness of the steel more. At the potential of -1200 mV, 
the parameters TTF and %elongation resulted in the smallest value among all curves, however the curve revealed a 
higher UTS point than the other two cathodically charged ones including the curve at the corrosion potential E_{corr}. In 
the anodically charged conditions, no significant difference occurred in the UTS points of -650mV and -600 mV (50 
mV and 100mV above E_{corr}) applied potentials. However, more anodically charged specimen (-600 mV, 100 mV 
above E_{corr}) failed relatively faster than the one charged at -650 mV (50 mV above E_{corr}). The test in glycerin 
environment, both of the anodic potentials, and the extreme cathodic potential -1200 mV all resulted in almost the same YP. The cathodic potential -1200 mV revealed the lowest TTF and % elongation as expected from the 
excessive high current densities of extreme cathodic charges, which results in more hydrogen evolution on LCS and 
at the crack tip causing embrittlement [7]. The specimens that revealed lower YP in a certain environment, also 
revealed lower UTS points, and wise versa. The slight differences in the YP among those curves can be attributed to 
the specimen gauge machining tolerance (1/1000 inch). The stress differences around 40-50 MPa might have come 
from the effect of the environment, i.e. the potential in this case.

Valuable information from the raw SSRT data given in Figure 8.10 can be extracted, on the susceptibility of LCS to 
the environmental cracking. The highest UTS point occurred with the well known inert environment glycerin, while 
lowest occurred with the applied potential E_{corr}. Since the curve at E_{corr} has the lowest YP and the lowest UTS points,
this potential may be a susceptible one, which enhances the environmental cracking. Besides, the TTF and % elongation are lower than that of the inert environment which confirms the slight ductility loss as environmental failures require.

Another interesting result is the quite close behavior of the curves for potentials -750 mV and -900 mV, two cathodically charged ones. There was 150 mV cathodic potential difference between them, however the one with -750 mV failed earlier than the one with -900 mV. If the hydrogen embrittlement is the only mechanism responsible from the failure, the observed case would never have occurred. The specimen of -900 mV would have been expected to fail earlier. Even though the specimen at -750 mV was charged cathodically, the potential value is still close to the E_{corr}, which still have anodic dissolutions around it. So, the combined effects of hydrogen embrittlement (HE) and stress corrosion cracking (SCC) would be the most possible scenario for this particular failure, at 50 mV below E_{corr}. Recently, observed similar behaviors of carbon steel was reported by R.M Schroeder et al. [8], concluding on the hydrogen embrittlement overlap with anodic dissolution. Also, R.H. Jones [9] observed the influence of hydrogen on the anodic dissolution in Al-Mg alloys. For instance, the experiment conducted with a specimen potential of -600 mV (100 mV above E_{corr}) also showed a significant decrease in TTF and % elongation, suggesting an SCC failure. However, there still can be a hydrogen influence on SCC, if the diffused hydrogen amount in the I-beam is high enough.

Despite of this, we can extract the findings above out of the raw data (stress-strain curves), mostly it is not possible to determine the environmental failure types by only the % elongation. It is necessary to combine the other parameters beside the TTF and % elongation results of SSRT, for correct assessments on the environmental failure types. The percent reduction of area (%RA), crack and surface appearance after the failure, fracture micrographs and current monitoring have vital importance on determining the susceptibility to a certain type of cracking.

8.5. Current Transients at Low Temperature (25°C)

Anodic and cathodic currents have been monitored to observe the changes on the passivation behavior of the surface films (precipitate layers), and also observe the crack proceedings (if possible) during the SSRT along the potentiostatically controlled various surface potentials. These current measurements under controlled surface potentials (vs Ag/AgCl half cell electrode) are given in Figure 8.11, as a function of time. In some cases, such as the applied potentials -700 mV (E_{corr}) and -750 mV, currents were more scattered than at other potentials due to the noise that generally appeared around E_{corr}. At the potential of -1500 mV, these fluctuations appeared with much higher and lower peaks especially during the plastic straining. This particular curve was well below the rest of the curves on the plot, so should be referred to the secondary current axis (on the right hand side). The rest of the curves were of relatively smooth appearance.

There was a common behavior in all the monitored currents that were carried out with various anodically and cathodically applied potentials over the specimens for a one to two day test period, which can be seen in Figure 8.11. The current values continued decaying through the values reached at the potential E_{corr} (exchange current density) within the test period. All of the anodic currents started decreasing as soon as the straining started, regardless of the over potentials, and they (belong to -600 mV and -650 mV potentials) decreased until reaching very small current values around that of E_{corr}. In a reverse manner, all of the cathodic currents started increasing right after applying load onto the specimens and they continued increasing until failure. Even though the trends of the currents did not change in time, their average slopes increased with increasing over potentials: More anodically applied potentials revealed more negative average slopes, while more cathodic ones revealed more positive average slopes. Visual examination on the specimens through the wall of the cell during the SSRT, and the observations after the tests showed that the precipitates over the specimens had been increasing with time. It was also observed that higher over-potentials resulted in more precipitates (thicker scales) over the specimens. For example, the test with -1500 mV resulted in an around 2-3 mm extremely thick precipitate layer, while the one with E_{corr} (-700 mV) was hardly visible to naked eye. The over-current (above and below the exchange current) drops in time, given in Figure 8.11, along the potentiostatically controlled surface potentials, closely agreed with the observations and examinations on the precipitate formations during and after the tests. Increased precipitate layer thickness created more passivity and caused over-current drop in time. These over-current drops were severe (the average slope was higher) when the scales were thicker in the presence of higher over-potentials. Consequently, the current results and observations both showed that the precipitate thickness formed in YM water during the tests increased with time and with over-potentials.
At a specimen potential of -1500 mV the over current drop was faster and its fluctuations occurred sharper. In some instances there were considerably high shifts, about 1-2 mA, which suggests the failures over the thick precipitate layer and re-healings with the continuing precipitation in the YM water environment. Since the brittle scale built-up occurred fast due to the higher over potentials, it became thick enough in a short time and was broken under the applied dynamic strains. Two of the current-time curves that belong to the potentials $E_{corr}$ (-700 mV) and 50 mV below $E_{corr}$ given in Figure 8.11 showed a noisy behavior, with small fluctuations during the tests which may come from the repetitive film (precipitate layer) breakage and re-filming processes. However, these fluctuations could also be noise, which normally occur around $E_{corr}$ with potentiostatically controlled cases with an environment of low conductivity, or could be a mix of noise with breakage and re-filming processes. Fractographic analysis of the specimens revealed more information about the experiments on LCS in these environments, which will be reported in the following sections with the comparisons of high and low temperature behavior of I-beam.

![Current profiles of LCS strained dynamically by SSRT method at 1.6x10^{-6}/s in de-aerated 100X YM waters with various specimen potentials. The curve of -1200 mV refers to the secondary ordinate, which is on the right hand side. Ag/AgCl electrode was used for all potential measurements.](018AY.003 File: CurrentRT.xls)

8.6. Portevin-LeChatelier Effect, PLC Effect at High Temperature (85°C)

The load vs elongation curves of the the 0.08%C I-beam at 85°C revealed serrated discontinuous plastic deformation regions at all specimen potentials with a slow strain rate of 1.6x10^{-6}/s. Figure 8.12 shows one of the serrated stress-
strain curves, carried out with the imposed potential $E_{corr}$ (-700 mV) to introduce the general behavior of high temperature (85°C) curves. These serrations occurred due to the strain-aging phenomenon in the plastic deformation region are called Portevin-LeChatelier (PLC) Effect, which are observed in most of the metals at certain temperature and strain rates.

The serrations observed in the plastic deformation of the I-beam at 85°C showed quite similar behavior to that of Lüder bands occurred at 25°C, onset of the plastic straining after the elastic region. Both, Lüder bands and Portevin-LeChatelier effect, showed approximately the same slope in the linear load increase period during serrations, which can be seen comparing the boxes A and B of Figure 8.13. One can conclude that the same physical event(s) may be
Luder Bands are responsible from both phenomena. However, it requires more research to determine the exact mechanisms at each case.

The average frequency of the serrations reduced with elongation during SSRT, ending up with the lowest value at the failure point. There is also a noticeable amplitude increase especially after the UTS point through the failure. For instance, at the Lüder plateau the upper and lower load difference is about 15 kg, but it is around 25-30 kg near the fracture point. One can analyze these serrations by Fourier analysis, or similar techniques to obtain further information on the serrated flow behaviors under dynamically strained conditions.

Since the strain aging effect with accompanying serrated discontinuous plastic flow did not occur at RT, according to our SSRT results obtained with the strain rate $1.6 \times 10^{-6}$/s, two questions arose about the behavior of serrations: (i) what was the exact temperature for strain aging to start at? and (ii) was there any relationship between the specimen surface potentials and those serrated plastic flow types?

In the present work an attempt was made to resolve the stated questions above. A newly planned and performed experiment with LCS revealed that the Portevin-LeChatelier (PLC) effect at strain rate $1.6 \times 10^{-6}$/s started around 55°C by showing serrations of very small, but noticeable enough magnitude. The results of changing the test temperatures in steps during the constant rate dynamic slow straining experiment are given in Figure 8.14 in detail. As illustrated in the figure, as soon as the temperatures started to drop from 85°C to 50°C, the serrated flow gradually diminished and became a smooth line of plastic flow at 50°C. The vertical lines separate the plastic flow regions serrated in different manners at different applied temperatures. When the temperature was raised to 60°C, the average amplitude of serrations were increased a little, and maintained within the same manner as long as the temperature did not change. The average amplitude increased even more at 65°C, and returned to the originally observed highest average serration amplitude at 85°C. The load drop observed around 50°C is the natural response of diminished serrated behavior i.e. the stopped strain aging effect. Since the UTS point was increased by the PLC effect, it had to go back to the values that belong to the non-serrated curves. Consequently, the increased temperatures by steps re-created more PLC effects with more loads toward the original UTS point of serrated curve at 85°C.

Simultaneously, during switching the temperatures in steps between 50°C and 85°C, so creating a various amplitudes of serrations, the interface potential $E_{corr}$ was recorded in order to detect the potential events that may occur on the surface of LCS in the test solution during the PLC effect. Test results showed that serrations were observed only at higher temperatures as illustrated in Figure 8.15. A shift of $E_{corr}$ in the amount of ~110 mV occurred between 50°C and 85°C test temperatures, which is quite different from the $E_{corr}$ fluctuation values around 10-15 mV due to temperature changes in LCS. Potentiodynamic polarization experiments carried out for LCS prior to the SSRT has already revealed that there was no significant $E_{corr}$ change in between a temperature range 25°C and 85°C (Figure 8.7). This result would also conclude that the shift in the $E_{corr}$ is only due to the events responsible for the PLC effect.

As clearly seen in Figure 8.15, during the first temperature decrease while the serrations were annihilated, the $E_{corr}$ value showed a sharp jump approximately from -0.70 mV to -0.60 mV. During the non-serrated plastic flow region, open circuit potential $E_{orr}$ did not show a noticeable change, other than some fluctuations that normally occurred within ~10 mV potential region with the SSRT tests all the time. Once the serrations of small amplitude were initiated at an applied temperature of 55°C, just 5°C above the previous one, there was approximately 70 mV potential increase observed. Higher amplitude serrations accompanied with higher open circuit potentials, until the original amplitude of serrations corresponding to the highest $E_{corr}$ value. The potential shift was the highest between the non-serrated discontinuous flow and the flow just started to srate weakly, i.e. during the creation of serrations. During the increased amplitudes of the serrations the potential shifts were relatively small and they gradually decreased at each step towards the highest serrations. At the serrations with the highest magnitudes, achieved at 85°C, the open circuit potential reached to the original value, and stayed the same until the failure of the specimen.

Consequently, the experiments conducted with temperature changes in the plastic deformation region showed that there was an interface potential ($E_{corr}$) increase during the PLC effect initiation in LCS. This result most likely applies to the rest of the metals since it is well known, that there is no electrolyte effect on the strain aging of metals. Interface potential monitoring can be used as a diagnostic tool to investigate the PLC behavior of metals and alloys. It may give valuable help for understanding the mechanisms of strain aging phenomenon, which has not been
completely understood yet. Besides, one can conduct similar experiments to determine the characteristic differences between Lüder bands and PLC effect. Present literature search showed that there were some techniques such as acoustic emission, laser extensometry, magnetic flux leakage signals, and tearing resistance tests (J-R) to correlate events to find more information about the sources of PLC effect[62,63,82]. However, there was no experimental

![Figure 8.14](serrations.xls)  
Figure 8.14. Stress-strain curve appearance with variation of test temperatures during SSRT of LCS at the strain rate of $1.6 \times 10^6$/s. A close-up view of the shown region is shown in Figure 8.15, revealing different serrated plastic deformation regions resulting from change in test temperatures during the tests. (018AY.004 File: serrations.xls).

![Figure 8.15](serra-imposed.xls)  
Figure 8.15. Correlated $E_{corr}$ change with the serration amplitudes of PLC effect during SSRT in YW water at the strain rate of $1.6 \times 10^6$/s. Just occurred or diminished PLC effect (by examination of the serration amplitude caused a large amount of potential change at the interface of LCS and the test solution. (018AY.004 File: serra-imposed.xls Note: for the temperature curve the file lists time starting at zero seconds, but for comparison to the load curve the initial time should be 30400 seconds).
study carried out thus far to correlate PLC effect with interface potential, or open circuit potential ($E_{corr}$) of metals. The experiment showed that the corrosion potential $E_{corr}$ changed with the serration amplitude at a precise frequency.

8.7 Stress-Strain Behavior at 85°C

All stress-strain curves at 85°C by SSRT revealed serrations of strain aging effect regardless of the applied over-potentials to the environmental tensile specimen, as seen in Figure 8.16. The curves with cathodic over-potentials revealed slightly lower yield points (YP) and ultimate tensile strength (UTS) values than the curves with anodic over-potentials, and the curve of mechanical test at 85°C. However, these differences in both YP and UTS should be attributed to the specimen differences because of the machining tolerances on the effective gauges. The mechanical tensile test of LCS at 85°C revealed some ductility (despite that it showed brittle failure compare to RT tests), which is important for the assessments of the brittle failures and their resources. For the mechanical test in Figure 8.16 the load difference between the UTS point and the failure point, the measure of ductility, showed that the mechanical test resulted in a relatively ductile manner despite the fact that the PLC effect was present. This result suggests that the PLC effect was not totally responsible for the brittle failures to occur with all cathodic over-potentials (-750 mV, -900 mV, -1200 mV) and one of the anodic over-potentials (-650 mV).

However, PLC effect also showed a significant contribution to the brittle failures, when the ductility of RT and 85°C experiments were compared. Normally, these two temperatures are not discrete enough from each other to play a significant role on the individual SCC or HE susceptibilities, therefore on the ductility as well. Consequently, the only significant difference observed between these two temperatures is the PLC effect, and it’s partial embrittlement contribution to I-beam.

![Figure 8.16. Serrated stress-strain behaviors of LCS hold at various potentials at 85 °C. Strain aging effect (Portevin-LeChatelier Effect) experienced by LCS at 85°C causes these serrated plastic flow behavior because of inclusions such as C, H, and N in the steel. (018AY.003 File: SSRT 85oC.xls)](image)
Applied over-potentials on I-beam specimens in the hot YM waters effected the SSRT parameters TTF and % elongation, or strain at failure, significantly, as occurred in the RT experiments. All three experiments with cathodic over-potentials (potentials below $E_{\text{corr}}$, -700 mV) resulted in brittle failures revealed a trend: Higher over-potentials resulted in lower % elongation and TTF, or lower strain at failure. Namely, for the over-potentials -750 mV, -900 mV and -1200 mV the % elongations were around 16.5, 16.0, and 14.5 respectively. This result clearly states that more cathodic over-potentials caused more cathodic reactions producing more hydrogen in the hot YM waters, and caused further embrittlement due to hydrogen. At the specimen potential -750 mV (50 mV above $E_{\text{corr}}$), one of the anodic over-potentials in the SCC susceptible region, the experiment also revealed a brittle failure with a sharp crack surface, suggesting an SCC failure in this slightly anodic film forming conditions. The % elongation and TTF of this particular potential occurred even smaller than that of -900 mV cathodic over-potential. The curve that belongs to $E_{\text{corr}}$ showed a brittle failure but with noticeably higher TTF and % elongation compared to that of all cathodic potentials. The experiment conducted at the potential of -600 mV (100mV above $E_{\text{corr}}$), revealed almost the same TTF and % elongation of the mechanical test at 85°C, suggesting the region was well beyond for SCC susceptibility. Since we have already observed a severe crack at 50 mV above $E_{\text{corr}}$, the potential 100 mV above would be out of the susceptible region, as the experiment confirmed. In order to observe severe cracks in the anodically charged conditions due to SCC, film rupture and healing processes should be synergistic, and obviously, it was not present in the case of the potential of -600 mV. Consequently, the film formation occurred because of the applied anodic potential, 100 mV above the $E_{\text{corr}}$. Either the film thickened rapidly and did not break to initiate corrosion on the surface, or film rupture and healing processes occurred rapidly and did not affect the behavior of LCS in the YM water at this -600 mV imposed surface potential.

8.8 Current Transients at 85°C

Current transients recorded under potentiodynamically controlled various specimen potentials during the high temperature (85 °C) SSRT is given in Figure 8.17.
The current transients for the applied anodic potentials -650 mV and -750 mV (50 mV above and below $E_{\text{corr}}$) revealed more fluctuations than the other curves, while the fluctuations were the least for the curves of -900 mV and -1200 mV. With the applied constant potential 650 mV, the initial anodic current first decreased and switched to the cathodic region. Then, in some part of plastic deformation region it switched to the anodic region and continued so until failure. This is the only potential which revealed anodic currents, suggesting that there was more anodic dissolutions than cathodic reductions in the specimen and on its surface. Since the potential of +50 mV above $E_{\text{corr}}$ (-650 mV) falls into one of the susceptible potential regions in polarization diagram, the resulting severe crack suggested that it was an SCC failure. However, secondary cracks generally observed around main cracks with SCC failures did not occur in this particular experiment on LCS. Secondary cracks predicting SCC did not occur with any one of the SSRT tests at 85°C regardless of the applied potentials. The current transient with -600 mV specimen potential revealed a non-expected profile for anodically applied potentials. It started decaying right after the beginning of straining and shifted towards the cathodic region, and stayed there until the failure. Along this current behavior, the test revealed the highest TTF and % elongation, which was very close to that of mechanical test at 85°C. The reason for the current to shift from anodic to cathodic regions is the overwhelming cathodic reactions due to the potential move during precipitate formation. As seen in low temperature results, the higher over-potentials leaded to rapid and thicker scale formations. In the case that they were not ruptured, their protective behavior increased as the current values indicated, while switched from anodic to cathodic regions. The current transient belongs to $E_{\text{corr}}$ (-700 mV) behaved similar to the potential of -600 mV, however, it showed a lesser shift to the cathodic currents, fluctuating around 1-5 microns. It should normally stay around the equilibrium current (0 mA), however, even at $E_{\text{corr}}$, the precipitate formation in YM water continued to occur and supplied a relative protection against dissolution reactions on LCS. Comparing the three curves in Figure 8.17 (-700 mV, 650 mV and 600 mV), one can conclude that increased cathodic currents supplied more protection to produce more % elongation and longer TTF under anodically applied potentials in this particular case.

Imposed cathodic surface potentials revealed cathodic current readings as expected. More precipitate scale formations at higher over-potentials caused reduced cathodic reaction rates especially at the surface potential of -1200 mV, which revealed approximately 50 mA current drop until the failure. The curve belongs to -900 mV was relatively smooth and stabilized. The curves of -1200 mV and -900 mV refer to the secondary current axes (adjacent to the main axis), and they are well below the other current transients as seen in the Figure 8.17. An other reason for them to appear in smother shape is the scale difference between the axes, otherwise they both have some fluctuations. The curve for the cathodic surface potential of -750 mV decreased in a rapid manner and stabilized around -20 μA and showed rather large fluctuations around that value until the failure.

Experiments carried out with cathodically applied surface potentials (-750 mV, -900 mV, and -1200 mV) revealed a trend in the SSRT parameters: More cathodically applied potentials revealed more cathodic current transients resulting in less TTF and % elongation. This behavior of LCS at cathodically applied potentials was already expected in an aqueous environment due to more hydrogen evolution by more cathodically charging, which leads to embrittlement of LCS I-beam by atomistic hydrogen diffusion.

8.9 Comparisons of the SSRT Results Under on the I-Beam At Different Temperatures

In this section we mainly compare the failure modes of two different environments parameters at 25°C and 85°C using 100x YM waters by measured ductility values from mechanical tests and fracture modes carried by scanning electron microscopy. All results from SSRT electromechanically tested specimens will be presented in Tables and plots for final assessments on the crack types of I-beam steel sets.

8.9.1. Failure Characteristics at 25°C and 85°C

The UTS points of the serrated stress strain curves at 85°C occurred at significantly higher values than those of the room temperature curves of smooth plastic deformation regions. The high and low temperature stress-strain curves, carried out under the same (-650 mV) surface potentials, are shown together in Figure 8.18, for comparison of the
SSRT parameters YP and UTS. While the YP’s at both temperatures occurred around the same values, approximately around 360 MPa, the UTS point with serrations at 85°C occurred at more than 150 MPa above that of the RT curve. This is not surprising because the UTS of alloys generally increase during the strain aging, around specific strain rates and temperatures of the alloy. Generally, work hardening rate becomes strain-rate dependent in the temperature range where dynamic strain aging occurs. The UTS point was increased at the rates of 1.6x10^{-6}/s for LCS, however it could have been much higher or lower with some other strain rates at the same temperature range [10].

All serrated stress-strain curves of the specimens carried out at 85°C showed much less elongation and RA than the ones done at RT. They failed shortly after reaching their UTS points, with relatively less necking in the effective gauge of the LCS specimens.

![Stress-strain curves at 85°C and 25°C](image)

Figure 8.18. Significant difference in UTS point and unchanged YP of stress-strain curves carried out at different temperatures (both of the curves belong to -650 mV surface potential). The picture on the right shows the characteristic differences in fracture surfaces at RT and at 85°C failures. (018AY.003 Files: 85°C: SSRT 85oC.xls 25°C: SSRT RT.xls)

Consequently, the failures always occurred in a brittle manner with sharp and shiny crack surfaces. Regardless of the applied surface potentials, all failed specimens showed the same crack surface angle, roughly around 45°, with respect to the tensile load direction, or the effective gauge cross section plane, as shown in Figure 45. None of the specimens at 85°C showed any secondary cracks around the main crack.

Observations and SEM micrographs showed that some longitudinal cracks occurred at 85°C in the effective gauge, extending parallel to the tensile load direction crossing the actual 45° angled main crack plane in the gauge. Some of the experiments resulted with two or more of these longitudinal cracks extending close to each other as shown in Figure 8.19. Even if there were a distance between them, as seen in Figure 8.19, on the left, the crack planes remained parallel to each other. One could explain why longitudinal cracks occurred despite the fact that there was no applied strain normal to those crack surfaces.

Since the Pearlite grains of LCS I-beam were aligned in a certain direction, by cold or hot rolling, these sites can be more susceptible for cracking due to their MnS inclusions. When more hydrogen evolution was taking place at these predetermined cathodic sites, in the Pearlitic grains, formed hydrogen gas after recombination of single hydrogen atoms would cause cracking by forming positive pressure in the voids formed after rapid dissolution of inclusions.

Unlike the single atoms, these large hydrogen molecules can not migrate through the structure of the steel [11]. Consequently, there was accumulation of hydrogen gas within the steel under cathodically charged conditions, which could generate enough pressure to blister or split the solid steel. The MnS nonmetallic inclusions shown in embedded in the Pearlite grains (previous section) as aligned in the same direction, made the cracking even easier because of their general soft and sooty existence in the grains. Moreover, they generally are the anodic sites that are open to rapid dissolution in steel while Pearlites and Cementites are the cathodic sites adjacent to them.
significant contribution may have been added by the PLC effect to make LCS more brittle to create such a result, because the existence of the longitudinal inner cracks are independent of applied potentials: They occurred in both cathodically and anodically charged conditions. The contribution of PLC to those inner cracks becomes significant because these cracks are not observed at RT where hydrogen embrittlement supposed to be more pronounced, and supposed to create similar cracks. However, if LCS became brittle due to the PLC effect, one still requires normal forces to create these splits such as hydrogen pressure in the metal. Consequently, the inner longitudinal cracks were resulted by the combined effects of HE and PLC according to all experimental results carried out at both temperatures.

Figure 8.19. The longitudinal cracks occurred in the gauge at 85°C during strain aging of LCS. All SSRT experiments at 85°C resulted in one or more longitudinal cracks regardless of applied potentials.

Experimental results carried out at 25°C showed more ductile failures than those of high temperatures as shown in Figure 8.19. Some of these experiments revealed secondary cracks (fissures), which are main tools for cracking assessment via examination of the effective gauge by eye only to characterize whether the failure is an SCC. Secondary cracks of LCS that occurred at RT (25°C) under \( E_{\text{corr}} (-700 \text{ mV}) \) and -900 mV imposed potentials are shown in Figure 8.20. At the surface potentials of \( E_{\text{corr}} (-700 \text{ mV}) \), 50 mV below \( E_{\text{corr}} (-750 \text{ mV}) \), and 200 mV below \( E_{\text{corr}} (-900 \text{ mV}) \), the secondary cracks nearby the main cracks were visible to the naked eye. No other visible secondary cracks were detected with the rest of the surface potentials, namely with -650 mV, -600 and -1200 mV, except for some crack-like marks which appeared too shallow to characterize the failure as SCC. Theoretically, secondary cracks of SCC are supposed to occur around the susceptible potential range introduced in background section, but not in the cathodic regions, like what occurred in LCS with the present SSRT tests. Secondary cracks at

Figure 8.20. Secondary cracks of LCS at room temperature(25°C), strained at the rate of \( 1.6 \times 10^{-7} \text{s} \) in 100X YM water under the imposed potentials A: \( E_{\text{corr}} (-700 \text{ mV}) \), and B: 200 mV below \( E_{\text{corr}} (-900 \text{ mV}) \). Both potentials are of reference Ag/AgCl electrode.
open circuit potential $E_{corr}$ are common because both anodic and cathodic reactions occur simultaneously at this equilibrium point, along the precipitate scale formations on the surface, which can cause dissolution of the fresh surface after film rupture, and cause the necessary synergistic cracking and re-filming processes for SCC. At the same time, the hydrogen that diffused in to LCS, created by the cathodic reactions, may create extra embrittlement to enhance this process. Normally, the similar mechanisms should not have occurred at the higher cathodic over-potentials especially at the potential of -900 mV. However, this case is not so uncommon. Some studies already reported the existence of these secondary cracks in carbon steels under cathodically imposed potentials. The experimental work of R.M. Schroeder [8] showed a carbon steel fracture mechanism of SCC associated with hydrogen action in aqueous Ca(OH)$_2$ environments, at the imposed potentials around -900 mV (vs.Ag/AgCl). R.H. Jones [9,12] reported SCC mechanisms of Al-Mg alloys with hydrogen influences and hydrogen uptakes.

Secondary cracks with -750 mV, 50 mV below $E_{corr}$ are more commonly reported but with lower susceptibilities to SCC. For instance, Z. Szklarska et al. [13] studied SCC of carbon steel X-52 in dilute aqueous solutions and reported that the cracking susceptibility was increased for potentials both more anodic and more cathodic than $E_{corr}$ in de-aerated solutions. The study above showed 20% intergranular fracture mode with secondary cracks at 50°C, under an imposed potential of -780 mV$_{SCE}$ ($E_{corr}$ is -740 mV$_{SCE}$) while it showed 50% intergranular fracture mode with an imposed -650 mV$_{SCE}$.

Observations during the several day-long tests showed that the precipitations had been continuous and deposited on LCS with the both anodically and cathodically imposed surface potentials at RT. Therefore, the precipitate layers probably stayed intact at any imposed potential, or always resealed after ruptures. One can check those current profiles in Figure 8.11, which are quite stable (other than the curve of -1200 mV which did not reveal secondary cracks) as they are decreasing gradually (when precipitate scale is thickening). In the case that the scale does not rupture, or heals rapidly after rupture, which is the most probable case of the present tests, it would be possible for the specimen to undergo secondary cracks under cathodically imposed potentials. The interface potential between metal and electrolyte decreases during film formations on any metal surface is a well known phenomenon. Increasing thickness of the surface films cause more potential drop of interface, and more insulator layers cause more potential drop as well [14]. Since the imposed potentials on LCS during the tests are those, that maintained constant at the interface of precipitate scale surface and the YM water, the potential of fresh LCS surface is always higher than the layer-solution interface potential with an intact scale. Then, in spite of the cathodically imposed potentials, there would be some dissolution processes occurring at the higher potential fresh steel surface, or at already initiated crack tip/surface. Since those sulfate or chloride salt precipitates are porous (Figure 7.3) the YM water test solution will be in contact with the LCS surface, or already developed crack surfaces to allow further dissolution reactions in there. Even if there was not enough permeation for the water, it would reach to the metal surface during short-term ruptures or thinning of the scale.

8.9.2. Fracture Characteristics

Optical photographs and metallographic analysis conducted by scanning electron microscope (Hitachi-S-4700) revealed various crack types and modes for the tests carried out in three different environments. Figure III shows the characteristics of the fractures of LCS in those environments such as glycerin (mechanical reference test), YM water at RT, and YM water at 85°C. The mechanical test revealed a ductile rupture of cup and cone type, as shown in Figure 8.21. The reduction of area (RofA) of mechanical test specimen occurred higher than in all other tests, revealing the highest ductility for the LCS in this inert environment. This particular test revealed the highest % Elongation and time to failure in all tests at both temperatures. SEM analysis of the fracture surface, given in Figure 8.22, shows a ductile-dimple fracture mode which is characteristic to non-brittle, cup and cone type ruptures, as the fracture appearance shows. The fracture mode took place in approximately 90% to 100% of the fracture surface area.

The test at low temperature (25°C) in 100X YM environment (Figure 8.21,B) with imposed potential $E_{corr}$ showed a semi-ductile failure with lesser necking (or RofA), along several fractures scattered in various planes. All environmental tests at RT revealed similar fracture modes, however in some cases (at -750 mV and -900 mV surface potentials) the fracture surfaces occurred sharper with one or two main crack facets. The SEM micrograph given in Figure 8.22 shows a trans-granular fracture mode that occurred in approximately 20% of the fracture surface area, while the rest was of ductile-dimple modes.
Mechanical Test (A) Test at 25 °C (B) Test at 85 °C (C)

Figure 8.21. SSRT Fracture characteristics of LCS strained at a constant rate of $1.6 \times 10^{-6}$/s in air and 100x deaerated YM water at 25°C and 85°C. Columns A, B, and C show mechanical test at RT, environmental test at 25°C, and environmental test at 85°C, with imposed $E_{\text{corr}}$ (-700 mV Ag/AgCl). The first row shows half of the fracture surface and the second shows the gauge length portion at the fracture location.

Inner parts of the fracture surface showed more ductile appearance with voids, dimples and sharp edged thin walls surrounding them (as shown in Figure 8.22,A), while the sides showed a more grainy fracture surface with semi-planar slip-like modes (Figure 8.22,B).

An attempt was made to characterize the nature of secondary cracks (Figure 8.23), by optical microscopy, which were located around the main cracks at RT. Optical micrographs of polished and etched side surfaces (where the secondary cracks were laying) showed the existence of both fractures types, such as intergranular and transgranular cracking that occurred in LCS. Figure 8.23 shows that these two types of cracks occurred at a time during SSRT of LCS. In the figure, some of intergranular and transgranular separations are shown by the characters IG and TG respectively. The arrows show the load direction normal to the secondary cracks (extended in the diagonal of the micrograph prior to grinding and polishing). The regions appearing dark are corroded, and already split during straining.

The test at the high temperature (85°C) with imposed potential $E_{\text{corr}}$ on LCS in de-aerated 100X YM water showed significantly different crack features than that of semi-ductile failure of room temperature tests, as shown in the Figure 8.25,C and the Figure 8.24. All environmental tests at 85°C showed brittle failures with sharp cracks angled as approximately 45° degree to the load direction. Also, all of the test specimens failed at 85°C revealed one or more longitudinal inner cracks with varying angles to the main crack surface. The fracture surface showed the same sharp features and the characteristic 45° angle fracture, although the TTF of the specimen was at a imposed potential -600 mV.
The SEM micrograph of the fracture surface given in Figure 8.24 shows the general fracture surface appearance of LCS specimen that failed at 85°C. The analysis revealed that the crack modes of the central part was of step-like discontinuous cleavage mixed with some quasi-cleavage (QC) modes, which again refer to trans-granular fracture modes[15]. Those two features that covered almost 50% of the fracture surface area are shown in Figure 8.24. While QC mode (Figure 8.24,A) occurred close to the edges, inner parts showed more step-like features (Figure 8.24,B) of trans-granular cracking behavior. The other 50% of the fracture surface area was covered by typical ductile-dimple modes. QC type crack initiation parts in the fracture surfaces showed ridge-like micro features, as shown in Figure 8.25. The same QC crack initiation region in Figure 8.24,A was magnified to show the ridges that occurred in the walls of QC ruptures. These SEM micrographs at magnifications of 7000X and 25000X are given in Figures 8.25,A and Figure 8.25,B respectively. Any similar type and size of these ridges were not found in the literature. D. Wagner [16] observed some ridges in C-Mn steel fracture surfaces with mechanical tests in the presence of dynamic strain.

Figure 8.22. SEM fractographs of fracture surfaces of LCS in air (mechanical test) and in100X deaerated YM waters at 25°C and 85°C. Sample strained at a constant rate of 1.6X10^-6/s with the open circuit potential (-700 mVAg/AgCl).
Figure 8.23. Optical micrograph of transgranular and intergranular cracks in LCS specimen that failed in a SSRT test performed in YM water at room temperature. IG and TG show some intergranularly and transgranularly separated grains respectively.

Figure 8.24. Quasi-cleavage (A) and discontinuous planar cleavage (B) cracking modes of LCS at 85°C.

Thermal aging effect. However, the ridges were around 10 micron long, and were mostly connected to each other revealing an appearance like ductile-dimple modes. The average ridge length occurred around 0.4 microns in the present investigations of LCS in hot YM waters. Ridges were found nowhere else other than the shown QC cracking regions shown in Figure 8.25. There are several possibilities: The ridge formations occurred first and allowed for easier slips or ruptures, or slips or ruptures might have created them. Also, a spontaneous creation of ridges during rupture is possible. In any of these cases, the ridges are signatures referring to embrittlement at the sites due to some mechanism. That must be true, since the QC rupture would otherwise not reveal these features. Since the ridges are
observed only on the wall of the QC cracks in high temperature experiments, in which the PLC effect was observed, there may be a connection between ridge formations and PLC effect. On the other hand, hydrogen evaluation in the metal may have caused those ridges too, creating micron size blisters prior to rupture. However, it requires further work to verify the relationship between the ridge formation on the QC crack walls and the embrittlement factors such as HE and PLC.

Figure 8.25. Inner wall details of QC modes in LCS failed by SSRT at 85°C. The ridges observed with PLC effect, and they showed an average length around 0.4 micron.

8.9.3. SSRT Parameters and Fracture Assessments

SSRT parameters time to failure (TTF), % Elongation, and reduction of area (RofA) determined for LCS under imposed anodic and cathodic potentials in deaerated 100x YM aqueous environments and in inert reference environments such as air and glycerin are given in Table 8.1. The fracture appearances on the effective gauge of the tensile test specimens examined by a stereo microscope at 75x magnification are also described briefly in Table 8.1. The TTF and % Elongation values given in the table are measured by the United software connected to the SSRT universal machine. Reduction of area (RofA) values are the calculated values out of measured average cross section areas before and after the tests, using a caliper of 0.001 mm accuracy. LCS specimens strained with various strain rates from $10^3$/s to $10^7$/s at both temperatures revealed information of vital importance for the assessments on SCC and HE susceptibilities. Determined SSRT parameters for LCS under the imposed open circuit potential -700 mV is given in Table 8.2. Several plots were produced out of Table 8.1 and Table 8.2, such as RofA vs potential, % Elongation vs potential and RofA vs. strain rate. The first two SSRT parameters, RofA and % Elongation revealed information on the ductility of LCS at various temperatures and potentials. Normally, increasing ductility of a metal would increase both of these parameters together. Therefore, ideally RofA versus % Elongation should be of a linear form. However, this is not always attainable with the environmental crackings, especially when many various factors involved with the failures.

Therefore both of these parameters should be examined together for ductility evaluations. In order to show ductility changes with imposed potentials on LCS, graphs for RofA vs potential and % Elongation vs. potential curves are given in Figure 8.26 and Figure 8.27, respectively. In both graphs (Figures 8.26, 8.27), the cathodically applied potentials revealed similar trends on the ductility of the steel for both temperatures: Both RofA and % Elongation were slightly increased with decreased cathodically imposed potentials through the open circuit potential $E_{corr}$, or decreased with more cathodically imposed potentials. This consistent behavior at both temperatures on these two parameters showed that the more the specimens were cathodically charged the more brittle failures occurred due to due to hydrogen embrittlement. The parameter % Elongation showed that the relative ductility is always higher at RT than at 85°C for any imposed potential. The same is true for the parameter RofA, however there is only one potential ($E_{corr}$) that showed the reverse result. Once we have to consider both parameters together to evaluate ductility, the overall combined results will completely agree with certain ductility difference between RT and 85°C.
under all imposed potentials. For instance, the reduction of area under the imposed potential of -700 mV at RT given in Figure 8.26, as representing the ductility in one way, appears slightly lower than that at 85°C. However, the % Elongation value at RT in Figure 8.27 at the same potential is much higher than that of 85°C, showing much more ductility difference between those temperatures, that compensates the reverse result of RofA at this particular potential.

Table 8.1. SSRT Parameters of LCS strained under various potentials and temperatures in deaerated 100x YM waters. A stereomicroscope has been used for observing the crack appearances. (018AY.003 Room temperature File: SSRT RT.xls; 85°C File: SSRT 85°C.xls)

<table>
<thead>
<tr>
<th>Imposed Potential (mV Ag/AgCl)</th>
<th>TTF (sec)</th>
<th>Elongation (%)</th>
<th>R of A (%)</th>
<th>Observations at 75x Mag.</th>
</tr>
</thead>
<tbody>
<tr>
<td>High Temperature (25°C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-600</td>
<td>97223</td>
<td>28.93</td>
<td>59.97</td>
<td>Ductile, necking, thicker scale</td>
</tr>
<tr>
<td>-650</td>
<td>106945</td>
<td>31.81</td>
<td>60.60</td>
<td>Ductile, necking</td>
</tr>
<tr>
<td>-700 (E_{corr})</td>
<td>105937</td>
<td>31.57</td>
<td>28.98</td>
<td>Ductile, necking and secondary cracks</td>
</tr>
<tr>
<td>-750</td>
<td>83776</td>
<td>24.94</td>
<td>31.90</td>
<td>Some necking, and secondary cracks</td>
</tr>
<tr>
<td>-900</td>
<td>84492</td>
<td>25.12</td>
<td>26.43</td>
<td>Brittle and severe secondary cracks</td>
</tr>
<tr>
<td>-1200</td>
<td>71576</td>
<td>21.31</td>
<td>22.52</td>
<td>Brittle, thicker scale formations</td>
</tr>
<tr>
<td>Glycerin</td>
<td>116607</td>
<td>34.75</td>
<td>63.98</td>
<td>Ductile, necking, shiny crack surface</td>
</tr>
<tr>
<td>Room temperature (25°C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-600</td>
<td>96958</td>
<td>28.87</td>
<td>27.71</td>
<td>Brittle 45° sharp crack, thicker scale</td>
</tr>
<tr>
<td>-650</td>
<td>74910</td>
<td>22.31</td>
<td>26.86</td>
<td>Brittle 45° sharp crack</td>
</tr>
<tr>
<td>-700 (E_{corr})</td>
<td>82476</td>
<td>24.65</td>
<td>33.54</td>
<td>Brittle 45° sharp crack</td>
</tr>
<tr>
<td>-750</td>
<td>78479</td>
<td>23.37</td>
<td>26.43</td>
<td>Brittle 45° sharp crack</td>
</tr>
<tr>
<td>-900</td>
<td>76578</td>
<td>22.81</td>
<td>24.27</td>
<td>Brittle 45° sharp crack</td>
</tr>
<tr>
<td>-1200</td>
<td>69141</td>
<td>20.56</td>
<td>17.60</td>
<td>Brittle 45° sharp crack, thicker scales</td>
</tr>
<tr>
<td>High Temperature (85°C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-600</td>
<td>97587</td>
<td>29.06</td>
<td>45.58</td>
<td>Semi-ductile, necking, shiny crack surface</td>
</tr>
</tbody>
</table>

The trends of ductility given with RofA (Figure 8.26) for RT and 85°C were the same, under cathodically imposed potentials until reaching -750 mV, 50 mV below E_{corr}. Both RofA values increased with increasing potentials. However, the trends for these two different temperatures occurred in a reverse manner with E_{corr} and with the rest of the imposed anodic potentials. In the anodic region, when the ductility of LCS at RT is increased, the ductility at 85°C is decreased under the same imposed potentials. Exactly the same behavior was observed with %Elongation values (another measure of ductility) as shown in Figure 8.27. This time the ductility at both temperatures was increased with decreasing cathodic over-potentials up to -700 mV, E_{corr}. Then in the anodic region, the ductility
Table 8.2. SSRT Parameters of LCS strained under various strain rates and temperatures in deaerated 100X YM waters under imposed potential $E_{corr}$(-700 mV$_{Ag/AgCl}$). (018AY.004 File: %RofA, Strain Rate, Potential, Elongation.xls; TTF column: 018AY.005 File: TTF.doc).

<table>
<thead>
<tr>
<th>Strain Rate (s$^{-1}$)</th>
<th>TTF (sec)</th>
<th>Elongation(%)</th>
<th>R of A (%)</th>
<th>Observations at 75x mag.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Room temperature (25°C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$10^{-7}$</td>
<td>608170</td>
<td>27.50</td>
<td>50.98</td>
<td>Ductile, necking, thicker scale</td>
</tr>
<tr>
<td>$10^{-6}$</td>
<td>105937</td>
<td>34.75</td>
<td>28.98</td>
<td>Ductile, necking</td>
</tr>
<tr>
<td>$10^{-5}$</td>
<td>11582</td>
<td>34.68</td>
<td>54.42</td>
<td>Ductile, necking and secondary cracks</td>
</tr>
<tr>
<td>$10^{-4}$</td>
<td>1265</td>
<td>37.75</td>
<td>63.08</td>
<td>Some necking, and secondary cracks</td>
</tr>
<tr>
<td>$10^{-3}$</td>
<td>218</td>
<td>39.56</td>
<td>63.38</td>
<td>Brittle and severe secondary cracks</td>
</tr>
<tr>
<td>High Temperature(85 °C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$10^{-7}$</td>
<td>520672</td>
<td>23.43</td>
<td>18.96</td>
<td>Brittle 45° sharp crack, thicker scale</td>
</tr>
<tr>
<td>$10^{-6}$</td>
<td>82476</td>
<td>28.50</td>
<td>23.40</td>
<td>Brittle 45° sharp crack</td>
</tr>
<tr>
<td>$10^{-5}$</td>
<td>7835</td>
<td>33.25</td>
<td>39.90</td>
<td>Brittle 45° sharp crack</td>
</tr>
<tr>
<td>$10^{-4}$</td>
<td>1102</td>
<td>28.53</td>
<td>56.08</td>
<td>Brittle 45° sharp crack</td>
</tr>
<tr>
<td>$10^{-3}$</td>
<td>220</td>
<td>34.24</td>
<td>57.72</td>
<td>Brittle 45° sharp crack</td>
</tr>
</tbody>
</table>

Figure 8.26. Measure of ductility by reduction of area values of LCS I-beam under various specimen potentials at room temperature and 85°C (018AY.004 File: %RofA, Strain Rate, Potential, Elongation.xls).
Figure 8.27. Measure of ductility by % Elongation of LCS under various potentials at room temperature and 85°C. (018AY.004 File: %RofA, Strain Rate, Potential, Elongation.xls)

Figure 8.28. Measure of ductility by RofA obtained with various slow strain rates from $10^{-3}/s$ to $10^{-7}/s$, at 25°C and 85°C for LCS under a imposed potential of -700 mV($E_{corr}$). (018AY.004 File: %RofA, Strain Rate, Potential, Elongation.xls).

trends for RT and 85°C became reversed. When the elongation was increased at RT under certain potential intervals in anodic region, it was decreased at 85°C. These results, confirmed by two of the SSRT parameters, revealed that the anodic potentials (including the $E_{corr}$) at these two different temperatures affected the ductility of LCS in opposite manner. Consequently, the results showed that the mechanisms for the fractures at these two different
temperatures should be different from each other. The RofA and % Elongation parameters given in Figures 8.26 and 8.27, for that reason, showed that SSRT at 85°C always resulted in relatively more brittle failures than that at RT, regardless of imposed potentials, and there may be different mechanisms responsible for RT and 85°C failures of LCS, especially under imposed E\text{corr} and anodic over-potentials. Despite this, it is not possible to determine the individual cracking mechanisms that played role in these failures, solely by ductility determination.

In order to determine the failure mechanisms it is always necessary to carry out experiments with various strain rates under the same specimen potential E\text{corr}, which has been carried out already with this present work. The RofA changes with various strain rates from 10^{-3}/s to 10^{-7}/s at both temperatures under the imposed potential -700 mV (E\text{corr}) and are shown in Figure 8.28. The change in RofA at 25°C in Figure 8.28 (upper curve) revealed a characteristic stress corrosion cracking behavior for LCS strained under the potential E\text{corr} in simulated concentrated 100x YM aqueous environments. The curve RofA vs. strain rate, revealed the exact classical stress corrosion cracking behavior for LCS strained under the open circuit potential E\text{corr}. The difference in behavior between 25°C and 85°C can be seen in Figure 8.28. The ductility at 85°C was always lower than that of 25°C for any strain rate. Most importantly, the lowest strain rate at this temperature revealed the lowest ductility (highest embrittlement) contrary to the results at 25°C. The shape of the curve given in Figure 8.28 for 85°C is known as hydrogen embrittlement shape in the literature [14,15,16], which is correct when hydrogen is the only embrittlement factor in an environment. Obviously, the curve RofA vs strain rate at 85°C shows the ductility loss, i.e. the embrittlement of LCS, but is not able to detect the source of embrittlement by any means. Therefore, the revealed embrittlement does not necessarily have to come from hydrogen. Because the experiments with those

![Figure 8.29](image)

Figure 8.29. Ductility differences of LCS revealed by mechanical tests at RT and 85°C in air with the strain rate 10^{-6}/s. The difference in rectangular surface areas as a measure of ductility shows the increased embrittlement in the steel due to strain aging, or PLC effect. (018AY.003 Files: 25°C; SSRT RT.xls 85°C; SSRT 85°C.xls)
various strain rates were conducted under open circuit potential ($E_{\text{corr}}$), the hydrogen evolution may not take place predominantly.

The stress strain curves in Figure 8.29 show the ductility differences in the tests performed at 25° and 85°C. The top curve at 85°C shows the PLC effect and the bottom curve at 25°C does not show any PLC effect in the I-beams. The surface areas of the hatched rectangular regions of both curves represent the ductilities at both temperatures, as a convenient tool. Stress-strain curves of 25°C and 85°C in Figure 8.29 revealed that the ductility of the specimen ran at 25°C was approximately twice that of the 85°C test. In other words, the serrated curve at 85°C revealed more brittle failure. The loss of ductility is proposed due to dynamic strain aging, or the PLC effect. The failure at 85°C is not completely brittle, as there some necking of the specimen (the stress difference between UTS point and failure point is not that small).

Consequently, the embrittlement determined by RofA vs. strain rate relationship given in Figure 8.28 (lower curve at 85°C) is neither due to hydrogen evolution, nor from the PLC effect. Therefore the overall results confirm that the I-beam (LCS) embrittled by combined effects of PLC and hydrogen evolution. These experimental results obtained at 85°C also agree with the earlier evaluations done by % Elongation and SEM micrographic analysis.

8.10 References for section VIII - Environmentally Induced Cracking of Steel Sets

IX. SUMMARY AND CONCLUSIONS

The corrosion rates of YM rock bolts (0.44%C) and I-beam steel sets (0.08%) have been determined by electrochemical linear polarization methods in simulated YM waters with different concentration, up to 100x. The beneficial effect of addition of ionic species such as bicarbonates and silicates found in the YM waters, hydrogen permeation showed possible ways of decreasing the corrosion rates in steels. In addition, in-situ electro-mechanical tests performed on the I-beams showed the propensity of stress corrosion cracking and hydrogen embrittlement.

Tables showing corrosion rates under various conditions, such as temperature and environment condition effects, are summarized in Tables 9.1 and 9.2. Important findings for the YM project are presented below:

**YM Rock Bolts Corrosion Rates**

The corrosion rates of rock bolts (0.44%C) determined by electrochemical methods ranged between -45 to 168 mm/year setting the lower CR limit in de-aerated simulated YM environments, ionic concentration of YM waters from 1x to 100x, between 25 to 85°C. Corrosion rates of rock bolts, in deaerated environments, increased noticeably with increasing temperatures for all simulated YM (1x, 10x, and 100x) waters; for example CR's are 45 to 160 mm/year for YM 1x waters. However, increasing YM water ionic concentration did not appreciably increase the CR of rock bolts; for example 45 to 51 mm/year by increasing YM 1x to 100x at 25°C or 160 to 168 mm/year at 85°C. (It should be noted that YM 10x and 100x simulated YM waters are nominal concentrations).

In aerated environments, the corrosion rates of rock bolts determined by various methods ranged between -124 to 1134 mm/year setting the upper CR limit in simulated YM environments, ionic concentration of YM waters from 1x to 100x, between 25 to 85°C. The corrosion rate of the rock bolts increased with increasing temperatures in relatively dilute 1x and 10x aerated YM waters. However, the corrosion behavior in 100x YM waters showed that the rates increased up to 45°C; subsequently there was a rapid drop of CR at 85°C; due to Ca/Mg carbonate scale formation. This may be termed as "extrinsic passivation" as precipitate layers formed act as protective films on rock bolt steel; this was confirmed by current decreases at 100x YM waters at 85°C. The Mg ions are present in the YM waters used in the tests but not in the steel. Thus, there is a peak of corrosion rate at 45°C. Other conventional tests on rock bolts, such as YM 1x water spray tests (without any salt) ASTM B-117 showed 729 mm/year, cyclic humidity tests ASTM G-60 showed 887 mm/year, immersion tests showed 45 mm/year for experiments performed at room temperature for fully immersed samples, and 200 mm/year at 75°C. Other immersion tests, such as partially dipped rock bolt samples showed a CR of 960 mm/year at 75°C. In addition the rock bolt sample placed just above the liquid level (1000% humid environment) showed a CR of 513 mm/year at 75°C.

Addition of silicate ions using bicarbonate ions reduced the passive current density of rock bolt steels significantly due to the preferential adsorption of silicate at the defects or pits on the passive film. This was deduced from polarization experiments and microcopy results. However, its effect was found to be less at low anodic polarization due to the complex formation of bicarbonate with Fe. The addition of HCO$_3^-$ in combination with SiO$_3^{2-}$ imparts good protection against hydrogen permeation in chloride solution as compared to that for any of these ions alone.

**YM I-Beams Corrosion Rates**

The corrosion rates of YM I-beams (0.08%C) determined by electrochemical methods ranged between -45 to 168 mm/year setting the lower CR limit in de-aerated simulated YM environments, ionic concentration of YM waters from 1x to 100x, between 25 to 85°C. Corrosion rates of I-beams, in deaerated environments, did not appreciably between room temperature and 65°C but there was a subsequent increase from 65 to 85°C. In the case 100x YM waters increased steadily up to 65°C followed by a slight decrease at 85°C.

In aerated environments, the corrosion rates of I-beams ranged between -216 to 1385 mm/year setting the upper CR limit in simulated YM environments, ionic concentration of YM waters from 1x to 100x, between 25 to 85°C. The corrosion rate of the I-beam showed a CR rate peaking at all YM waters (1x, 10x, and 100x) concentrations (as compared to rock bolts where there was CR peaking observed only with 100x waters). The peaking was encountered in two phases where there was a drop of CR at 10°C. One phase was observed only with 10x and 100x corrosion (in the case 100x the drop occurred at 10°C). The corrosion rate of the I-beam showed a drop in the range of all YM waters (1x, 10x and 100x) concentrations (in the case 100x the drop occurred at 10°C).

In the aerated environment the corrosion rate of I-beam steel was lower than that of rock bolts by a factor of 5 to 10 times.
Other conventional tests on I-beams, such as YM Ix water spray test (without any salt) ASTM B-117 showed 910 um/year, cyclic humidity tests ASTMG-60 showed 887 um/year.

Hydrogen Permeation Results
Permeation of hydrogen through rock bolts and I-beam plates showed that the critical hydrogen concentration ($C_k$) is 8.13 and 36.15 pptn, indicating that medium carbon rock bolt steel is more resistant towards HIC than low carbon I-beam steel. The presence of high C, Mn and S in this steel increased the density of trapping sites and improved the HIC resistance of this steel. The measured diffusivities were lower for the medium carbon rock bolt steel than for the low carbon I-beam steel due to the increased absorption of hydrogen at irreversible sites in medium carbon steel. The hydrogen uptake also found to decrease with the increase in YM electrolyte concentrations due to CaCO$_3$ precipitate formation on steel surface and that reduced the hydrogen uptake. The measured input hydrogen levels are below the critical concentration needed for nucleation of cracks in the absence of externally applied stress. The presence of high C, Mn and S content increased the density of trapping sites in rock bolts. As a result of this, diffusivity obtained was much lower and hydrogen content was found to be higher indicating that the hydrogen induced cracking tendency of this steel is more when compared to SSCS. The formation of CaCO$_3$ deposit reduced the hydrogen permeation and corrosion rate of carbon steel when the electrolyte concentration was increased. The compositions of the extrinsic film formed on the I-beam steel are different at room temperature as compared to 85°C. At higher temperatures, the solubility is lower for general metal silicates; therefore a protective SiO$_2$ type species formed on the steel. At lower temperatures, oxide and chlorides species formed on the steel due to lower solubility.

Environmental Assisted Corrosion (Stress Corrosion/Hydrogen Embrittlement) results
In-situ electro-mechanical slow strain rate test (SSRT) used in determining stress corrosion cracking and hydrogen induced cracking susceptibilities of YM I-beams gave very useful information. These SSRT tests performed at high and low temperature aqueous environments in deaerated YM waters showed that the thickness of the extrinsic film varied depending on the applied over-potential. Higher over-potentials caused thicker precipitate films in both anodically and cathodically charged conditions. The layer thickness increased substantially with time at room temperature. However, at higher temperatures ($T > 85°C$) the thickness did not increase with time indicating the different film formation behavior. The SSRT tests performed at 85°C and 25°C showed a protective SiO$_2$ type film was formed on the steel. These SSRT tests showed that the LCS I-beam did not experience stress corrosion cracking (SCC), but exhibited hydrogen induced cracking phenomena. Hydrogen embrittlement results showed that the LCS I-beam showed brittle failures due to hydrogen embrittlement at applied over-potentials. The I-beam showed some propensity to stress corrosion cracking (SCC) under applied over-potentials.
Table 9.1. Rock bolt corrosion rates and the amount of material thickness lost due to corrosion in 1, 100, 1000, and 10,000 years for rock bolts as determined by electrochemical methods. (Corrosion rates from Tables 4.3 and 4.4 as calculated from data in set 018AY.002 according to the polarization method discussed in chapter 2; Distance of material corroded away calculated by multiplying the corrosion rate by the stated time and converting units to inches or centimeters).

<table>
<thead>
<tr>
<th>Rock Bolt Type</th>
<th>Corrosion Rates mpy/mils/year</th>
<th>Inches or Centimeters of Material Corroded Away in 100 Years</th>
<th>Inches or Centimeters of Material Corroded Away in 1000 Years</th>
<th>Inches or Centimeters of Material Corroded Away in 10,000 Years</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogenated</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0°C</td>
<td>4.9</td>
<td>0.0048819</td>
<td>0.0535432</td>
<td>0.535432</td>
</tr>
<tr>
<td>5°C</td>
<td>12.6</td>
<td>0.124</td>
<td>1.24</td>
<td>12.4</td>
</tr>
<tr>
<td>10°C</td>
<td>24.8</td>
<td>0.248</td>
<td>2.48</td>
<td>24.8</td>
</tr>
<tr>
<td>15°C</td>
<td>45</td>
<td>0.45</td>
<td>4.5</td>
<td>45</td>
</tr>
<tr>
<td>20°C</td>
<td>5.4</td>
<td>0.054</td>
<td>0.54</td>
<td>0.54</td>
</tr>
<tr>
<td>25°C</td>
<td>16</td>
<td>0.16</td>
<td>1.6</td>
<td>16</td>
</tr>
<tr>
<td>30°C</td>
<td>30</td>
<td>0.3</td>
<td>3</td>
<td>30</td>
</tr>
<tr>
<td>35°C</td>
<td>42</td>
<td>0.42</td>
<td>4.2</td>
<td>42</td>
</tr>
<tr>
<td>40°C</td>
<td>9</td>
<td>0.09</td>
<td>0.9</td>
<td>0.9</td>
</tr>
<tr>
<td>45°C</td>
<td>18</td>
<td>0.18</td>
<td>1.8</td>
<td>18</td>
</tr>
<tr>
<td>50°C</td>
<td>20</td>
<td>0.2</td>
<td>2</td>
<td>20</td>
</tr>
<tr>
<td>55°C</td>
<td>15</td>
<td>0.15</td>
<td>1.5</td>
<td>15</td>
</tr>
<tr>
<td>60°C</td>
<td>10.3</td>
<td>0.103</td>
<td>1.03</td>
<td>10.3</td>
</tr>
<tr>
<td>65°C</td>
<td>7.9</td>
<td>0.079</td>
<td>0.79</td>
<td>0.79</td>
</tr>
<tr>
<td>70°C</td>
<td>7.6</td>
<td>0.076</td>
<td>0.76</td>
<td>0.76</td>
</tr>
<tr>
<td>75°C</td>
<td>1.7</td>
<td>0.017</td>
<td>0.17</td>
<td>0.17</td>
</tr>
<tr>
<td>80°C</td>
<td>2.7</td>
<td>0.027</td>
<td>0.27</td>
<td>0.27</td>
</tr>
<tr>
<td>85°C</td>
<td>4.7</td>
<td>0.047</td>
<td>0.47</td>
<td>0.47</td>
</tr>
<tr>
<td>90°C</td>
<td>6.4</td>
<td>0.064</td>
<td>0.64</td>
<td>0.64</td>
</tr>
<tr>
<td>95°C</td>
<td>6.7</td>
<td>0.067</td>
<td>0.67</td>
<td>0.67</td>
</tr>
</tbody>
</table>

Table 9.1. Rock bolt corrosion rates and the amount of material thickness lost due to corrosion in 1, 100, 1000, and 10,000 years for rock bolts as determined by electrochemical methods. (Corrosion rates from Tables 4.3 and 4.4 as calculated from data in set 018AY.002 according to the polarization method discussed in chapter 2; Distance of material corroded away calculated by multiplying the corrosion rate by the stated time and converting units to inches or centimeters).
Table 9.2. I-beam corrosion rates and the amount material thickness lost due to corrosion in 1, 100, 1000, and 10000 years for rock bolts as determined by electrochemical methods. (Corrosion Rates from Table 5.1 as calculated from data in set 018JL.002; Distance of material corroded away calculated by multiplying corrosion rate by the stated time and converting units to inches or centimeters)

<table>
<thead>
<tr>
<th>Temp °C</th>
<th>Corrosion Rates mpy</th>
<th>In/100 yrs</th>
<th>In/1000 yrs</th>
<th>In/10000 yrs</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>1.08</td>
<td>8.5</td>
<td>95.44</td>
<td>954.4</td>
</tr>
<tr>
<td>35</td>
<td>1.08</td>
<td>10.7</td>
<td>134.26</td>
<td>1342.6</td>
</tr>
<tr>
<td>45</td>
<td>1.08</td>
<td>12.9</td>
<td>162.12</td>
<td>1621.2</td>
</tr>
<tr>
<td>55</td>
<td>1.08</td>
<td>15.1</td>
<td>190.08</td>
<td>1900.8</td>
</tr>
<tr>
<td>65</td>
<td>1.08</td>
<td>17.3</td>
<td>218.04</td>
<td>2180.4</td>
</tr>
</tbody>
</table>

Inches or Centimeters of Material Corroded Away in

<table>
<thead>
<tr>
<th>Temp °C</th>
<th>In/100 yrs</th>
<th>In/1000 yrs</th>
<th>In/10000 yrs</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>8.5</td>
<td>95.44</td>
<td>954.4</td>
</tr>
<tr>
<td>35</td>
<td>10.7</td>
<td>134.26</td>
<td>1342.6</td>
</tr>
<tr>
<td>45</td>
<td>12.9</td>
<td>162.12</td>
<td>1621.2</td>
</tr>
<tr>
<td>55</td>
<td>15.1</td>
<td>190.08</td>
<td>1900.8</td>
</tr>
<tr>
<td>65</td>
<td>17.3</td>
<td>218.04</td>
<td>2180.4</td>
</tr>
</tbody>
</table>
Appendix A1

X-ray Photoelectron Spectroscopy (XPS) Data for Section IV (4.7)

XPS Spectra and Depth Profile Details of 0.5M HCO₃⁻, 0.1M SiO₂⁺ and 0.5M HCO₃⁻ + 0.1M SiO₂⁺ Additions to 3.5 M NaCl Solutions
Samples at active-passive transition potential in only bicarbonate media have shown enrichment of Carbon, Oxygen and Iron on the surface, while in combined bicarbonate and silicate media it has shown additional silica enrichment. Only Iron peaks (i.e. Carbon and Oxygen peaks were absent) were observed in XPS survey spectra for all the samples after Ar\textsuperscript{+} sputtering. Refer Figures A1.6-A1.10. This shows that base metal was reached after different sputtering cycles.

**Figure A1.2.** XPS Survey spectra of RBCS in HCO\textsubscript{3} solution at Active-Passive Transition (018V008).
Figure Al-3. XPS Survey spectra of RBCS in HCO$_3^-$ solution at 2nd Passive Potential (018VD.008 File: XPS survey scans.doc)

Figure Al-4. XPS Survey spectra of RBCS in HCO$_3^-$ + SiO$_3^2-$ solution at 2nd Passive Transition (018VD.008 File: XPS survey scans.doc)
Figure A1-5. XPS Survey spectra of RBCS in HCO$_3$ + SiO$_2$ solution at 2nd Passive Transition (018VD.008 File: XPS survey scans.doc)

Figure A1-6. XPS Survey spectra of RBCS in SiO$_2$ solution at Passive Potential (018VD.008 File: XPS survey scans.doc)
Figure A1-7. XPS Survey spectra of RBCS in HCO$_3^-$ solution at Active-Passive Potential after Ar$^+$ Sputtering (018VD.008 File: XPS survey scans.doc)

Figure A1-8. XPS Survey spectra of RBCS in HCO$_3^-$ solution at 2nd Passive Potential after Ar$^+$ Sputtering (018VD.008 File: XPS survey scans.doc)
Figure Al-9. XPS Survey spectra of RBCS in HCO$_3$ + SiO$_2$ solution at Active-Passive Potential after Ar$^+$ Sputtering (018VD.008 File: XPS survey scans.doc)

Figure Al-10. XPS Survey spectra of RBCS in HCO$_3$ + SiO$_2$ solution at 2nd Passive Potential after Ar$^+$ Sputtering (018VD.008 File: XPS survey scans.doc)
Figure A1-1: XPS survey spectra of RBCS in SiO$_2$ solution at Passive Potential after Ar$^+$ Sputtering.
Figure Al-12. O Is (A) and C Is (B) and Fe(2p) (C) Photoelectron spectra obtained from KBCS polarized at the pre-passive potential in 3.5% NaCl solution containing 0.5M HCO₃⁻.
Figure A1-13. XPS Spectrum of RBCS polarized at passive potential in 3.5% NaCl solution containing 0.01 M SiCV. A. O (Is) B. C (Is), C. Si (2p) D. Fe (2p) (018VD.005 File: Si-Passive Depth Profile and spectral.ppt)
Figure A1-14: XPS Spectrum of RBCS polarized at pre-passive potential in 3.5% NaCl solution containing 0.5M HCO$_3^-$ and 0.01M SiO$_2$.

A. Oxygen, O$_{1s}$

B. Carbon, C$_{1s}$

C. Silicon, Si$_{2p}$

D. Iron, Fe$_{2p}$
Figure 15. XPS Spectrum of RBCS polarized at the passive potential in 3.5% NaCl solution containing 0.5 M HCO$_3$- and 0.01 M SiO$_3$$^2$.

A. Oxygen, O$_{1s}$
B. Carbon, C$_{1s}$
C. Silicon, Si$_{2p}$
D. Iron, Fe$_{2p}$
Table 1. Binding energy values of Fe(2p), O Is and C Is components identified on RBCS in 3.5% NaCl solution containing 0.5M HCO₃⁻. (Non-Q for corroboration only, except for final row, which is an average value of the energy of the peaks found in 018VD.005).

<table>
<thead>
<tr>
<th>Data Source</th>
<th>Fe(2p3/2)</th>
<th>O(1s)</th>
<th>C(1s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ref 21</td>
<td>710.3 ± 0.2</td>
<td>531.8 ± 0.2</td>
<td>289.3 ± 0.2</td>
</tr>
<tr>
<td>Ref 20</td>
<td>710.2</td>
<td>531.5</td>
<td>289</td>
</tr>
<tr>
<td>Ref 18,19</td>
<td>710.9</td>
<td>530.9</td>
<td>290.3</td>
</tr>
<tr>
<td>Ref 17</td>
<td>711</td>
<td>532.6</td>
<td>289.5</td>
</tr>
<tr>
<td>O18VD.005 (average value)</td>
<td>710.3 ± 0.2</td>
<td>531.8 ± 0.2</td>
<td>289.3 ± 0.2</td>
</tr>
</tbody>
</table>
X-Ray Photoelectron Microscopy Details for the I-Beam Characterization

APPENDIX A 2
Figure A2-1: Optical micrographs of carbon steel samples exposed to 100x YM water (a) de-aerated 25°C, (b) de-aerated 45°C and (c) de-aerated 85°C.
Figure A2.2. XPS spectrum of Carbon steel recorded after potentiodynamic polarization test in 100X YM water at 25°C (a) Fe(2p), (b) O1s and (c) C1s. (C) Environmental XPS depth profile.
Figure A2-3: XPS spectrum of Carbon steel recorded after potentiodynamic polarization test in 100X YM water at 45°C. (a) Fe(2p), (b) O1s, and (c) Cl1s. (018VD.008 File: xps depth profile 2.doc)
Figure A2.1. XPS spectrum of Carbon steel recorded after potentiodynamic polarization test in 100X YM water at 85°C: (a) Fe(2p), (b) O(1s) and (c) Cl(1s) (018AD.008 File: XPS depth profile 2.doc).
Supplemental Information on Details of Polarization Curves for the I-Beam and Rock Bolt Specimens

Appendix A3
This Appendix shows detailed plots of the polarization curves as well as electromechanical stress strain curves. The recorded experimental data of potentiodynamic polarization scans and electrochemical impedance spectroscopy of rock bolt in 1x, 10x, and 100x YM aqueous environments, at the temperatures 25°C, 45°C, 65°C, and 85°C, and experimental Load-Time profiles of LCS I-beam, carried out in 100x simulated concentrated YM waters at various strain rates from \(-10^7/s\) to \(10^7/s\).

Please Note

In the four-curve electrochemical impedance spectroscopy (EIS) plots, Series 1, Series 5, Series 9, and Series 13 refer to 25°C, 45°C, 65°C, and 85°C, respectively. In the three-curve plots, Series 1, Series 5, and Series 9, refer to 1x, 10x, and 100x simulated YM waters, respectively.

In the slow strain rate experiments at a strain rate of \(2.4 \times 10^{-7}/s\), at both temperatures, the recordable number for the time axis (in seconds) cannot exceed a certain value with this particular software, therefore the original records are folded in the allowed time interval 250,000 s.
Figure A3-1. Polarization of rock bolt in 1x, 10x, and 100x deaerated YM waters at 45 °C. (018AY.002 Files: IX: Ixn45i.xls 10X: 10xn45i.xls 100X: 100xn45i.xls).

Figure A3-2. Polarization of rock bolt in 1x, 10x, and 100x deaerated YM waters at 65 °C. (018AY.002 Files: IX: Ixn65i.xls 10X: 10xn65i.xls 100X: 100xn65i.xls).
Concentration effect at 85°C

Figure A3-3. Polarization of rock bolt in 1x, 10x, and 100x deaerated YM waters at 100°C (018AY.002: 1x: 100x.txt)

Figure A3-4. Polarization of rock bolt in 1x, 10x, and 100x aerated YM waters at 25°C (018AY.002: 1x: 100x.txt)
Figure A3-5. Polarization of rock bolt in 1x, 10x, and 100x aerated YM waters at 45°C (018AY.002 Files: 1X: 10x45i.xls 10X: 10x45ii.xls 100X: 100x45i.xls)

Figure A3-6. Polarization of rock bolt in 1x, 10x, and 100x aerated YM waters at 65°C (018AY.002 Files: 1X: 10x65i.xls 10X: 10x65ii.xls 100X: 100x65i.xls)

Current Density (A/cm²) vs. Potential (V vs. Ag/AgCl)

Oxy.Conc.Eff.45°C

Oxy.Conc.Eff.65°C
Figure A3-7. Polarization of rock bolt in 10X, 100X, and 1000X de-aerated YM waters. (018AY.002 Files: 25: 10Xnrti.xls 65: 10Xn65i.xls 85: 10Xn85i.xls)

Figure A3-8. Polarization of rock bolt at 25°C, 45°C, 65°C, 85°C in de-aerated YM waters at 85°C. (018AY.002 Files: 25: 10Xnrti.xls 45: 10Xn45i.xls 65: 10Xn65i.xls 85: 10Xn85i.xls)
Figure A3-9. Polarization of rock bolt at 25°C, 45°C, 65°C, 85°C in 100x de-aerated YM waters. (018AY.002 Files: 25: 100xnrti.xls 45: 100xn45i.xls 65: 100xn65i.xls 85: 100xn85ii.xls).

Figure A3-10. Polarization of rock bolt at 25°C, 45°C, 65°C, 85°C in 1x aerated YM waters. (018AY.002 Files: 25: 1xorrti.xls 45: 1x45i.xls 65: 1x65ii.xls 85: 1x85ii.xls).
Figure A3-11. Polarization of rock bolt at 25°C, 45°C, 65°C, 85°C in 10x aerated YM waters (018AY.002 25: 10xorti.xls 45: 10xo45ii.xls 65: 10xo65i.xls 85: 10xo85i.xls).

Figure A3-12. Polarization of rock bolt at 25°C, 45°C, 65°C, 85°C in 100x aerated YM waters (018AY.002 25: 100xorti.xls 45: 100xo45i.xls 65: 100xo65i.xls 85: 100xo85i.xls).
Figure A3.16. EIS of rock bolt in 1X, 10X, and 100X de-aerated YM waters at 25 °C (018JL.003 Files: IX: JoshzrbrtymlxNl 10X: JoshzrbrtymlOxNl 100X: JoshzrbrtymlOOxN2).

Figure A3.15. EIS of rock bolt in 100x de-aerated YM waters (018JL.003 Files: 100X: JoshzrbrtymlOOxNl 45: JoshzrbrtymlOOxN2 65: JoshzrbrtymlOOxNI 85: JoshzrbrtymlOOxNI 100X).
Figure A3-17. EIS of rock bolt in 1x, 10x, and 100x de-aerated YM waters at 65 °C (018JL.003 IX:Joshzrb45Cyml00X):

Figure A3-18. EIS of rock bolt in 1x, 10x, and 100x de-aerated YM waters at 65 °C (018JL.003 IX:Joshzrb65Cyml00X):

Joshzrb45Cyml00X: Joshzrb65Cyml00X: Joshzrb45Cyml00X: Joshzrb65Cyml00X: Joshzrb45Cyml00X: Joshzrb65Cyml00X:

Joshzrb65Cyml00X: Joshzrb45Cyml00X: Joshzrb65Cyml00X: Joshzrb45Cyml00X: Joshzrb65Cyml00X: Joshzrb45Cyml00X:

Joshzrb45Cyml00X: Joshzrb65Cyml00X: Joshzrb45Cyml00X: Joshzrb65Cyml00X: Joshzrb45Cyml00X: Joshzrb65Cyml00X:

Joshzrb45Cyml00X: Joshzrb65Cyml00X: Joshzrb45Cyml00X: Joshzrb65Cyml00X: Joshzrb45Cyml00X: Joshzrb65Cyml00X:

Joshzrb45Cyml00X: Joshzrb65Cyml00X: Joshzrb45Cyml00X: Joshzrb65Cyml00X: Joshzrb45Cyml00X: Joshzrb65Cyml00X:

Joshzrb45Cyml00X: Joshzrb65Cyml00X: Joshzrb45Cyml00X: Joshzrb65Cyml00X: Joshzrb45Cyml00X: Joshzrb65Cyml00X:

Joshzrb45Cyml00X: Joshzrb65Cyml00X: Joshzrb45Cyml00X: Joshzrb65Cyml00X: Joshzrb45Cyml00X: Joshzrb65Cyml00X:

Joshzrb45Cyml00X: Joshzrb65Cyml00X: Joshzrb45Cyml00X: Joshzrb65Cyml00X: Joshzrb45Cyml00X: Joshzrb65Cyml00X:

Joshzrb45Cyml00X: Joshzrb65Cyml00X: Joshzrb45Cyml00X: Joshzrb65Cyml00X: Joshzrb45Cyml00X: Joshzrb65Cyml00X:

Joshzrb45Cyml00X: Joshzrb65Cyml00X: Joshzrb45Cyml00X: Joshzrb65Cyml00X: Joshzrb45Cyml00X: Joshzrb65Cyml00X:

Joshzrb45Cyml00X: Joshzrb65Cyml00X: Joshzrb45Cyml00X: Joshzrb65Cyml00X: Joshzrb45Cyml00X: Joshzrb65Cyml00X:

Joshzrb45Cyml00X: Joshzrb65Cyml00X: Joshzrb45Cyml00X: Joshzrb65Cyml00X: Joshzrb45Cyml00X: Joshzrb65Cyml00X:

Joshzrb45Cyml00X: Joshzrb65Cyml00X: Joshzrb45Cyml00X: Joshzrb65Cyml00X: Joshzrb45Cyml00X: Joshzrb65Cyml00X:
Figure A3-20. EIS of rock bolt in 1X, 10X, and 100X aerated YM waters at 25 °C (Files: IX: Joshzrb85Cymlxol 10X: Joshzrb85CymlOxol 100X: Joshzrb85CymlOOxol).

Figure A3-19. EIS of rock bolt in 1X, 10X, and 100X de-aerated YM waters at 25 °C (Files: IX: Joshzrb85CymlxNl 10X: Joshzrb85CymlOxNl 100X: Joshzrb85CymlOOxNl).
Figure A3-21. EIS of rock bolt in 1x, 10x, and 100x aerated YM waters at 45°C (File: IX: Joshzrb45Cymxol, 10X: Joshzrb45Cym10xol, 100X: Joshzrb45Cym100xol).

Figure A3-22. EIS of rock bolt in 1x, 10x, and 100x aerated YM waters at 65°C (File: IX: Joshzrb65Cymxol, 10X: Joshzrb65Cym10xol, 100X: Joshzrb65Cym100xol).
Figure A3-23. EIS of rock bolt at 25°C, 45°C, 65°C, 85°C in 1X aerated YM waters (018JL.003 Files: 25°C, 45°C, 65°C, 85°C).

Figure A3-24. EIS of rock bolt at 25°C, 45°C, 65°C, 85°C in 1X aerated YM waters (018JL.003 Files: 25°C, 45°C, 65°C, 85°C).
Figure A3-25. EIS of rock bolt at 25°C, 45°C, 65°C, 85°C in 10x aerated YM waters (018JL.003 Files: 25).

Figure A3-26. EIS of rock bolt at 25°C, 45°C, 65°C, 85°C in 100x aerated YM waters (018JL.003 Files: 25).
Figure A3-27. Load-Time Profile of LCS in 100x YM water at 85°C, strained at 1.6x 10^4/s (File: 205.xls).

Figure A3-28. Load-Time Profile of LCS in 100x YM water at 85°C, strained at 1.6x 10^4/s (File: 204.xls).
Figure A3-29. Load-Time Profile of LCS in 100x YM water at 85°C strained at 1.6x 10^-7/s. (Please note that there were too many data points and plotting routine had problem plotting it.) (018AY.004 File: 202R.xls).

Figure A3-30. Load-Time Profile of LCS in 100x YM water at 85°C strained at 1.6x 10^-7/s. (018AY.004 File: 203.xls).
Figure A3-31. Load-Time Profile of LCS in 100x YM water at RT, strained at 1.6x10^4 s⁻¹ (018AY.004 File: 193R.xls).

Figure A3-32. Load-Time Profile of LCS in 100x YM water at RT, strained at 1.6x10^5 s⁻¹ (018AY.004 File: 193R.xls).
Figure A3-34: Load-Time Profile of LCS in 100x YM water at RT, strained at 1.6 x 10^-7 s. (Please note that there were too many data points and plotting routine had problem plotting it.) (018AY.004 File: 184.doc).