CONTRIBUTORS TO WATERSIDE CORROSION OF SOIL-STEEL STRUCTURES

by

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Abstract

Soil-steel structures are designed and constructed worldwide for use in civil infrastructure and construction industries. As a result, extensive work has been devoted to understanding the corrosion of zinc and galvanized steel yielding the development of various corrosion models worldwide. Canada does not have a corrosion model required for use in design, but engineers and contractors often use that developed in the United States by the American Association of State Highway and Transportation Officials. This corrosion model defines the recommended range of pH, chloride concentration and soluble sulphate concentration as well as minimum resistivity for unsaturated soil applications. However, these design recommendations and associated corrosion model are often misused in aqueous environments. As a result, many structures have demonstrated significant evidence of premature corrosion raising concerns with the suitability of this corrosion model.

Field testing was conducted on both mechanically stabilized earth retaining walls as well as corrugated steel pipe. Steel samples were extracted for analyses with scanning electron microscope and energy dispersive x-ray spectroscopy while water samples were collected to determine the properties causing degradation. Linear polarization resistance was also completed on two mechanically stabilized earth walls to obtain in-situ corrosion rates.

To complement field work, laboratory experiments were conducted on galvanized steel samples in electrolytes simulating environments satisfying design criteria recommending by the American Association of State Highways and Transportation Officials as well as outside the scope of this model. Relative corrosion rates were calculated from results obtained from accelerated corrosion testing and sample surfaces were analyzed with the use of a scanning electron microscope.

Through laboratory experimentation and field testing it has been discovered that the hardness of water affects the formation of the outermost protective layer on zinc articles, the zinc patina. The following dissertation challenges the appropriateness of durability design criteria and associated corrosion model, defined by the American Association of State Highway and Transportation Officials, for use in aqueous environments while offering guidance on the development of more suitable guidelines for conditions other than unsaturated soil.
This dissertation is original, unpublished and independent work by the author, A.E. West.

Sections 2.1.2 Mechanically Stabilized Earth Walls and 3.1.2 Mechanically Stabilized Earth Walls were based on work completed in collaboration with Atlantic Industries Limited as well as the British Columbia Ministry of Transportation and Infrastructure. The work presented in this dissertation is original and has not been published elsewhere. However, different components of the same project were prepared in a report and submitted to the British Columbia Ministry of Transportation and Infrastructure. A.E. West was responsible for writing the manuscript for that submission.
## Table of Contents

Abstract ....................................................................................................................................................................................... ii
Preface......................................................................................................................................................................................... iii
Table of Contents........................................................................................................................................................................ iv
List of Tables........................................................................................................................................................................... vii
List of Figures.......................................................................................................................................................................... viii
List of Abbreviations .............................................................................................................................................................. x
Acknowledgements ............................................................................................................................................................... xi

1.0 Introduction ....................................................................................................................................................................... 1

1.1 Objective ......................................................................................................................................................................... 2

1.2 Scope ................................................................................................................................................................................. 2

1.3 Industry Background ................................................................................................................................................ 3

1.4 Literature Review ........................................................................................................................................................ 4

1.4.1 Steel Infrastructure ............................................................................................................................................ 4

1.4.1.1 Mechanically Stabilized Earth Retaining Walls ............................................................................... 6

1.4.1.1.1 Reinforcing Elements ....................................................................................................................... 7

1.4.1.1.2 Corrosion of MSE Walls ................................................................................................................... 8

1.4.1.2 Backfill Material ........................................................................................................................................ 10

1.4.1.2.1 Drainage ............................................................................................................................................... 11

1.4.1.3 Corrugated Steel Pipe ............................................................................................................................. 12

1.4.1.3.1 Corrugation Profiles ........................................................................................................................ 14

1.4.1.3.2 Corrosion of CSP ............................................................................................................................... 16

1.4.2 Surface Modifications ...................................................................................................................................... 17

1.4.2.1 Aluminized .................................................................................................................................................. 17

1.4.2.2 Polymer Coated ......................................................................................................................................... 18

1.4.2.3 Galvanized ................................................................................................................................................... 19

1.4.3 Corrosion .............................................................................................................................................................. 22

1.4.3.1 Galvanic Corrosion ................................................................................................................................... 24

1.4.3.2 Corrosion Allowance ............................................................................................................................... 25

1.4.3.2.1 Water ..................................................................................................................................................... 26

1.4.3.2.2 Soil .......................................................................................................................................................... 28

1.4.4 Existing Design Criteria and Corrosion Models ................................................................................... 28

1.4.4.1 Waterside Corrosion ............................................................................................................................... 29
# Table of Contents

3.2.1.4 Steel Samples ................................................................................................................................. 86
3.2.1.5 Discussion ........................................................................................................................................ 88
3.2.2 Hot-Dip Galvanized Steel Samples .................................................................................................. 90
   3.2.2.1 Electrolyte Properties ................................................................................................................. 90
   3.2.2.2 Electrochemical Testing ............................................................................................................. 93
   3.2.2.3 Corrosion Rate ......................................................................................................................... 99
   3.2.2.4 Steel Samples ........................................................................................................................... 101
   3.2.2.5 Discussion ............................................................................................................................... 109
4.0 Conclusions ......................................................................................................................................... 113
5.0 Recommendations & Future Considerations ...................................................................................... 116
Works Cited ............................................................................................................................................... 117
Appendix A: OCP from Mechanically Galvanized Samples ................................................................. 123
Appendix B: OCP from HDG Samples .................................................................................................. 126
Appendix C: SEM Images Captured at 600x of HDG Samples ............................................................. 130
Appendix D: SEM Images Captured at 600x of CSP ........................................................................... 134
# List of Tables

Table 1.1: Chemical Composition of Steel\(^{(11)}\) ................................................................................................................ 5  
Table 1.2: Mechanical Properties of Structural Steel\(^{(11)}\) .......................................................................................... 5  
Table 1.3: Mechanical Properties of Welded Wire Reinforcements\(^{(12)}\) ............................................................................. 5  
Table 1.4: Backfill Specifications for MSE Walls\(^{(34)}\) ........................................................................................................ 11  
Table 1.5: Corrugation Profiles for Structural Plate Corrugated Steel Pipe\(^{(39)}\) .................................................. 14  
Table 1.6: Corrosion of Galvanized Steel\(^{(50)}\) ................................................................................................................ 22  
Table 1.7: Waterside Corrosion Models\(^{(65,66,68)}\) ......................................................................................................... 29  
Table 1.8: Aqueous Parameters\(^{(65)}\) ................................................................................................................................. 30  
Table 1.9: Waterside Corrosion Models\(^{(65)}\) ..................................................................................................................... 30  
Table 1.10: Waterside Corrosion Allowances ............................................................................................................ 31  
Table 1.11: Soil-side Corrosion Models\(^{(66)}\) .................................................................................................................. 33  
Table 1.12: Electrochemical Soil Parameters\(^{(9,65,68)}\) ................................................................................................ 35  
Table 1.13: Metal Loss Rates\(^{(9,65,58)}\) ................................................................................................................................ 35  
Table 1.14: Soil-side Corrosion Allowances ............................................................................................................. 36  
Table 1.15: Abrasion Levels According to CSPI\(^{(65)}\) .......................................................................................... 36  
Table 1.16: Abrasion Levels According to CalTrans\(^{(69)}\) .......................................................................................... 37  
Table 2.1: Calculated Amounts of Substances for Testing .................................................................................... 53  
Table 2.2: Test Matrix .......................................................................................................................................................... 53  
Table 3.1: Field Culvert Water Properties ................................................................................................................... 61  
Table 3.2: EDS Results for Corrugated Steel Pipe .................................................................................................... 65  
Table 3.3: MSE Wall Water Properties ......................................................................................................................... 69  
Table 3.4: Corrosion Rates of MSE Wall Lateral Reinforcement ........................................................................ 73  
Table 3.5: Solution Properties .......................................................................................................................................... 76  
Table 3.6: Corrosion Rate of Mechanically Galvanized Steel Samples ............................................................. 85  
Table 3.7: Before and After Mechanically Galvanized Steel Samples .................................................................... 87  
Table 3.8: Impact of CaCO\(_3\) Additions ........................................................................................................................... 89  
Table 3.9: Solution Properties .......................................................................................................................................... 91  
Table 3.10: Corrosion Rates of Hot-Dip Galvanized Steel Samples .................................................................. 99  
Table 3.11: Before and After Hot-Dip Galvanized Steel Samples ............................................................................ 101  
Table 3.12: EDS Elemental Quantities ........................................................................................................................ 104  
Table 3.13: Impact of CaCO\(_3\) Additions ...................................................................................................................... 111
LIST OF FIGURES

Figure 1.1: Photo, taken May 2010, demonstrates the premature corrosion discovered on an AIL MSE wall. ..................................................................................................................................................................................... 3
Figure 1.2: Head Quarters of Atlantic Industries Limited Dorchester, NB. ..................................................................................................................................................................................... 4
Figure 1.3: Mechanically stabilized earth retaining wall(14). ..................................................................................................................................................................................... 6
Figure 1.4: MSE Wall construction(21). ..................................................................................................................................................................................... 7
Figure 1.5: a) CSP and b) SPCSP(14). ..................................................................................................................................................................................... 12
Figure 1.6: Dimensions of SPCSP(14). ..................................................................................................................................................................................... 13
Figure 1.7: Plate Dimension Template(39). ..................................................................................................................................................................................... 15
Figure 1.8: Comparison of Corrugation Profiles. 1) Ultra-Cor 2) Super-Cor 3) Bolt-A-Plate(9). ..................................................................................................................................................................................... 15
Figure 1.9: Fe-Zn alloy layers formed during HDG(50). ..................................................................................................................................................................................... 20
Figure 1.10: Corrosion Cell. ..................................................................................................................................................................................... 23
Figure 1.11: Galvanic series(64). ..................................................................................................................................................................................... 25
Figure 1.12: Schematic of corrosion allowance(46). ..................................................................................................................................................................................... 26
Figure 1.13: First Maintenance vs. Environment(50). ..................................................................................................................................................................................... 32
Figure 1.14: Comparison of soil-side corrosion allowances of galvanized structures. ..................................................................................................................................................................................... 34
Figure 1.15: Theoretical anodic potentiodynamic polarization curve(70). ..................................................................................................................................................................................... 38
Figure 1.16: Theoretical Tafel plot(70). ..................................................................................................................................................................................... 39
Figure 1.17: Typical linear polarization resistance curve(70). ..................................................................................................................................................................................... 41
Figure 2.18: a) Drilling out a 51 mm sample through a flowing water course and b) the replacement fender washer and toggle bolt. ..................................................................................................................................................................................... 46
Figure 2.19: Vertical columns for sampling locations on Wall A. ..................................................................................................................................................................................... 48
Figure 2.20: Vertical column of wall cut away from remainder of wall during deconstruction for the collection of steel samples. ..................................................................................................................................................................................... 48
Figure 2.21: Wire diameter measurement locations. ..................................................................................................................................................................................... 49
Figure 2.22: Section of wire cleaned for diameter measurement. ..................................................................................................................................................................................... 49
Figure 2.23: LPR probes inserted into wall face. ..................................................................................................................................................................................... 51
Figure 2.24: Hach Waterproof Handheld H170G multimeter. ..................................................................................................................................................................................... 54
Figure 2.25: Accelerated corrosion laboratory setup. ..................................................................................................................................................................................... 57
Figure 3.26: a) Demonstration of waterline distinction and b) degradation observed. ..................................................................................................................................................................................... 63
Figure 3.27: a) Microorganism or organic contaminant observed on the surface of CSP2; and b) CSP1 at 150x magnification on the edge of a perforation caused by environmental degradation. ..................................................................................................................................................................................... 65
Figure 3.28: SEM image captured at 150x magnification of CSP2. Image was taken on the edge of a crater that penetrates deep into the depth of the sample. .................................................................66
Figure 3.29: SEM image captured at 150x magnification of SPCSP .................................................................67
Figure 3.30: Open circuit potentials from MSE Walls B and C in British Columbia .........................................................70
Figure 3.31: Plot of linear polarization resistance testing on MSE Walls B and C....................................................71
Figure 3.32: Wire diameter data ....................................................................................................................................74
Figure 3.33: OCP plot for (0,0,z) solutions ......................................................................................................................78
Figure 3.34: Potentiodynamic plot for (0,y,0) solutions ..................................................................................................79
Figure 3.35: Potentiodynamic plots for (0,0,z) solutions ..............................................................................................79
Figure 3.36: Potentiodynamic plots for (x,0,0) solutions ..............................................................................................80
Figure 3.37: Potentiodynamic plots for (0,y,z) solutions ..............................................................................................81
Figure 3.38: Potentiodynamic plots for (x,y,0) solutions ..............................................................................................81
Figure 3.39: Potentiodynamic plots for (0,0,z) solutions ..............................................................................................82
Figure 3.40: Potentiodynamic plots for (x,y,z) solutions ..............................................................................................83
Figure 3.41: Reproducibility plot ...................................................................................................................................93
Figure 3.42: Potentiodynamic plots of (0,y,0) solutions ..............................................................................................94
Figure 3.43: Potentiodynamic plots for (0,0,x) solutions ..............................................................................................94
Figure 3.44: Potentiodynamic plots for (x,0,0) solutions ..............................................................................................95
Figure 3.45: Potentiodynamic plots for (0,y,z) solutions ..............................................................................................96
Figure 3.46: Potentiodynamic plots for (x,y,0) solutions ..............................................................................................97
Figure 3.47: Potentiodynamic plots for (x,0,z) solutions ..............................................................................................98
Figure 3.48: Potentiodynamic plots for (x,y,z) solutions ..............................................................................................98
Figure 3.49: Sample EDS plot of HDG surface ................................................................................................................103
Figure 3.50: a) HDG sample to demonstrate the surface morphology prior to exposure of an electrolyte; All remaining images are HDG sample surfaces, at 150x magnification, following electrochemical testing in b)solution (0,250,0); c) solution (0,0,700); and d) solution (90,0,0)...106
Figure 3.51: All images are HDG sample surfaces, at 150x magnification, following electrochemical testing in a) solution (0,50,100); b) solution (120,350,0); c) solution (120,0,100); and d) and solution (120,350,700)........................................................................................................107
Figure 4.52: Corrosion rate and resistivity ..................................................................................................................114
LIST OF ABBREVIATIONS

AASHTO – American Association of State Highway and Transportation Officials
Ag/AgCl – silver/silver chloride
AIL – Atlantic Industries Limited
ASTM – American Society for Testing and Materials
BAP – Bolt-A-Plate®
CIP – cast-in-place
CS – carbon steel
CSP – corrugated steel pipe
CSPI – Corrugated Steel Pipe Institution
Cu/CuSO₄ – copper/copper sulphate
DOT – Department of Transportation
DSL – design service life
EDS – energy dispersive x-ray spectroscopy
HDG – Hot-Dip Galvanizing
LPR – linear polarization resistance
MIC – microbially influenced corrosion
MSE – mechanically stabilized earth
NHE – normal hydrogen electrode
OCP – open circuit potential
PDP – potentiodynamic polarization
ppm – parts per million
SC – Super·Cor®
SCE – saturated calomel electrode
SEM – scanning electron microscopy
SPCSP – structural plate corrugated steel pipe
SRB – sulphate reducing bacteria
TDS – total dissolved solids
UC – Ultra·Cor®
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1.0 INTRODUCTION

Traditionally the concrete industry has dominated civil infrastructure as the material is strong (compressive strength of 17 MPa to 34 MPa\(^1\)), durable and able to take on many forms. However, concrete infrastructure is expensive. As a result to the infrastructure industry searching for a more economical solution, steel manufacturers have responded. Steel structures are quicker to erect, do not require specially skilled labourers or equipment and easier to transport to remote locations resulting in savings in the range of 20% to 60% over concrete structures\(^2\). Steel is also more flexible to accommodate the natural expansion and contraction of the earth as well as localized settling or seismic activity. While concrete has great strength in compression, steel is better suited for designs in which strength is required when the structure is in tension. But steel has its disadvantages as well. The primary concern with steel is its susceptibility to corrosion\(^3\). As society becomes more and more comfortable with steel's inherent capabilities it continues to push its limits. This has resulted in wonderful technological advances and the development of high strength low alloy steels, duplex steels and various modifications of existing steels but the issue of corrosion still remains\(^4,5\). While there are certain alloys that are highly resistant they are extremely costly, making steel unfeasible in many applications. A cost effective solution that is commonly exercised to protect steel against corrosion in mildly aggressive environments is galvanizing steel by coating it with a bonded zinc layer.

The following dissertation discusses the corrosion of galvanized steel at great length. The focus of the report is waterside corrosion of galvanized soil-steel structures, specifically mechanically stabilized earth (MSE) retaining walls, corrugated steel pipe (CSP) and structural plate corrugated steel pipe (SPCSP). Discussion and experimentation are concerned with water environments and contributing factors which cause corrosion of galvanized steel. The results provide valuable information to the steel and civil infrastructure industries pertaining to the environmental conditions suitable for galvanized steel structures and when an alternative solution is required to maintain the viability of MSE walls and CSP/SPCSP. The durability design criteria currently used in North America was developed in Florida, United States by the American Association of State Highway and Transportation Officials (AASHTO). The design criteria outline the environmental parameters for unsaturated, free-draining backfill material used for soil-steel structures. However, as there are no durability design criteria for aqueous environments, this AASHTO corrosion model has been inappropriately adopted for these applications as well.
1.0 Introduction

As not intended for use in aqueous environments, AASHTO's design criteria and associated corrosion model do not consider water properties. While in North America there are no design requirements for galvanized steel in contact with water, the United Kingdom has defined three categories based on the aggressiveness of surrounding conditions. However, the only parameters specified are chlorides and soluble sulphates; water hardness is not considered. Water hardness is measured in parts per million (ppm) of calcium carbonate (CaCO₃) and is required for the formation of the zinc patina, or protective scale (zinc carbonate; ZnCO₃), on the outermost surface of galvanized steel. While there are no recommendations on the hardness of water, failures have occurred in structures that satisfy all requirements of the design criteria but have corrosion rates that greatly exceed those predicted by the associated corrosion model. This discrepancy is addressed in the following dissertation.

1.1 Objective

The objective of the following report is to conduct and interpret both field and laboratory testing to determine the correlation of water constituents to corrosion rates of galvanized steel. Regarding waterside corrosion, particular focus was paid to water hardness, chlorides and sulphates. Relationships were developed that challenge the appropriateness of design criteria, defined by AASHTO for unsaturated soil, that are commonly assumed for aqueous environments.

1.2 Scope

This work addresses corrosion and performance of galvanized steel under the studied conditions. The study will not discuss corrosion of other metallic products or coatings. While it is known that abrasion and erosion assist in preventing the required protective scale resisting corrosion to form, consideration of those two factors are outside the scope of this study. The most common source of abrasion for soil-steel structures is flowing waters containing bedload or debris. As MSE walls are not commonly constructed to contain such environments and SPCSP are often designed as bottomless structures, abrasion and mechanical degradation is limited to rough handling during transportation and installation.

Temperature is another known contributing factor affecting corrosion rates. Research has stated that a 10°C increase in temperature will approximately double corrosion rates, all other variables remaining constant(6). Canadian streams, rivers and groundwater have an average temperature of 5.3°C, fluctuating by ± 2.0°C(7). Temperature is also concern for applications in which climates
fluctuate from below freezing to above freezing resulting in contraction and expansion. As the coefficient of thermal expansion (CTE) for steel and zinc, approximately 12.5 μm/m-°C and 31.2 μm/m-°C\(^8\), respectively, are relatively similar there is little concern of freeze-thaw cycles creating a stress raiser. Additionally, testing was carried out at room temperature (20°C). Therefore, corrosion rates measured and discussed throughout this dissertation are liberal. For these reason, the effects of temperature are not being considered.

1.3 INDUSTRY BACKGROUND

In the fall of 2009 AIL became aware of premature corrosion occurring on the face of one of their supplied retaining walls. The wall was constructed in 2000/2001 with a 75 year design service life (DSL) including a 100 year corrosion model. After less than 10 years the structure had enough visible corrosion to raise concern for the future integrity of the wall. See Figure 1.1. This was AIL’s first recorded issue with corrosion. During the construction of this MSE retaining wall both design criteria and corrosion model, developed by the AASHTO, were followed. The models were said to be conservative in the most adverse conditions\(^9\). In approximately 10% of the wall’s DSL there was a clear indication that the model was less than conservative in this particular case. With the assistance of a retained third party corrosion expert, a forensic analysis to determine the root cause of corrosion was conducted and recommendations made for remedial action. In the interest of addressing the science, AIL sponsored the research for this thesis in response.

Figure 1.1: Photo, taken May 2010, demonstrates the premature corrosion discovered on an AIL MSE wall.
The company, headquartered in Dorchester, NB (Figure 1.2), is a world leader in developing innovative engineered solutions in corrugated metal structures, retaining wall systems, corrugated pipe and modular steel bridges for the transportation, public works, mining, forestry and development sectors. By design, AIL’s turn-key infrastructure solutions are easy to ship and install with favourable equipment and labour requirements, making them ideal even for remote locations\(^{(10)}\).

![Image of Atlantic Industries Limited Headquarters](image)

**Figure 1.2: Head Quarters of Atlantic Industries Limited Dorchester, NB.**

### 1.4 Literature Review

The following subsections provide detailed explanations of all aspects further referenced and covered throughout this dissertation. Sources range from published theses, industry publications, textbooks, technical journals and websites as well as standards/accepted practices.

#### 1.4.1 Steel Infrastructure

Infrastructure constructed of steel is becoming more common as an economical alternative to concrete in many applications. Steel offers many advantages over concrete, with the two primary being efficiency of installation and weight\(^{(3)}\) – which ultimately relates back to cost savings\(^{(2)}\). Structural steel used by AIL meets the chemical compositions outlined in Table 1.1. The mechanical properties are given in Table 1.2 for structural plate and Table 1.3 for welded wire reinforcements.
1.0 Introduction

Table 1.1: Chemical Composition of Steel\(^{(1)}\)

<table>
<thead>
<tr>
<th>Element</th>
<th>Corrugated steel pipe and spiral rib pipe</th>
<th>Structural plate corrugated steel pipe</th>
<th>Deep corrugated structural plate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>0.15</td>
<td>0.10</td>
<td>0.25</td>
</tr>
<tr>
<td>Manganese</td>
<td>0.60</td>
<td>0.50</td>
<td>0.90*</td>
</tr>
<tr>
<td>Phosphorous</td>
<td>0.08</td>
<td>0.08</td>
<td>0.08</td>
</tr>
<tr>
<td>Sulphur</td>
<td>0.05</td>
<td>0.05</td>
<td>0.04</td>
</tr>
</tbody>
</table>

*The 0.90% limit of manganese for deep corrugated structural pipe does not apply to material covered in ASTM A 1011/A 1011M and ASTM A1018/A 1018M, which has a limit of 1.50%.

Table 1.2: Mechanical Properties of Structural Steel\(^{(1)}\)

<table>
<thead>
<tr>
<th>Product</th>
<th>Minimum yield strength, MPa</th>
<th>Minimum tensile strength, MPa</th>
<th>Minimum elongation in 50 mm, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structural plate</td>
<td>195</td>
<td>290</td>
<td>30</td>
</tr>
<tr>
<td>Deep corrugated structural plate</td>
<td>275</td>
<td>380</td>
<td>25</td>
</tr>
</tbody>
</table>

Notes:
\(1\) These mechanical properties are for the virgin material before corrugating and galvanizing. See Annex A for design base steel properties.
\(2\) The designer should consult the fabricator for finished product properties.

Table 1.3: Mechanical Properties of Welded Wire Reinforcements\(^{(2)}\)

<table>
<thead>
<tr>
<th>Yield Strength</th>
<th>Tensile Strength</th>
<th>Reduction in Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>ksi [MPa]</td>
<td>ksi [MPa]</td>
<td>%</td>
</tr>
<tr>
<td>56 [385]</td>
<td>70 [485]</td>
<td>30</td>
</tr>
</tbody>
</table>

The following subsections discuss in detail both welded wire reinforcements and corrugated steel products, the two most common structures designed and manufactured by AIL.
1.0 Introduction

1.4.1.1 Mechanically Stabilized Earth Retaining Walls

MSE retaining walls are constructed of a reinforcing element and soil (Figure 1.3). They are used in rural, urban and industrial applications with a variety of uses. Reinforced walls differ from reinforced slopes in their applications and degree of angle. A reinforced slope is less than 70° while a reinforced wall has a batter of greater than 70°\(^{(13)}\).

![Mechanically stabilized earth retaining wall](image)

**Figure 1.3: Mechanically stabilized earth retaining wall\(^{(14)}\).**

MSE structures rely on backfill and its interaction with the reinforcing elements. When constructing a soil reinforced retaining wall the primary goal is to support the outward earth pressure while maintaining the full bearing capacity in the foundation. There are several different types of soil available, but currently only select granular backfill material is suitable for the success of a MSE structure. The friction angle, compressibility, shear strength and electrochemical properties must all be considered prior to selecting a material and beginning construction\(^{(15)}\). Engineered backfill material is further discussed in 1.4.1.2 Backfill Material.

Nearly 850,000 m\(^2\) (Over 9 million ft\(^2\)) of MSE walls are built for transportation applications each year with the tallest to date in 2007 being 40 m at the Seattle-Tacoma International Airport\(^{(16)}\). MSE walls are becoming more popular than cast-in-place (CIP) walls due to their simplicity, efficiency applicability and economic benefits with estimated annual savings of $180 million\(^{(17)}\). MSE walls are far more flexible than rigid structures tolerating significant total and differential settlements\(^{(18)}\).
The service life of a MSE wall is defined as the period of time in which the tensile stress of the soil reinforcement is equal to or less than that allowable of the reinforcement material. Corrosion is the largest contributing factor to limiting service lives. The service life of ‘permanent’ structures is required to be greater than 70 years\(^{17}\).

MSE retaining walls are generally constructed in 61 cm lifts. Once grading is complete, a layer of L-shaped mats is placed down, with 61 cm contributing to the front facing and the remaining length, behind the 90° bend, making up the lateral reinforcement. The length of the lateral reinforcement is at least 70% of the wall height, with a minimum length of 244 cm\(^{18}\). Following the placement of the welded wire mats, soil is tightly compacted to a minimum of 95%\(^{18,19,20}\), until it is level with the top of the facing element (61 cm). At this point the next layer of mats is laid and the process repeated. For wire faced walls, geotextile is used to encapsulate the engineered backfill envelope and isolate it from the frontal region where free draining material creates a drain as well as improves aesthetics. See Figure 1.4 for further clarification on the main components of a MSE retaining wall.

![MSE Wall construction](image)

**Figure 1.4: MSE Wall construction\(^{21}\).**

1.4.1.1 **Reinforcing Elements**

There are two different classes of reinforcing elements each with their own advantages and disadvantages suitable for different applications, wall heights, etc. The first class is inextensible reinforcements and the second extensible reinforcements.
1.0 Introduction

Extensible reinforcement elements have tensile strain that is equal to or greater than the horizontal extension required to create an active-plastic state within the soil. Fully extensible reinforcing elements have such a low modulus of elasticity that little to no tensile forces are introduced into the soil at the strain required for the active-plastic state (i.e. geosynthetics, polyester resins). Extensible reinforcements are more suited to reinforced slopes or temporary walls as they stretch to have the strain of the reinforcement equal that of the soil resulting in significant lateral movement of both the granular material and the facing\(^{(22,23)}\).

Inextensible reinforcement elements have tensile strain that is significantly less than the horizontal extension required to create an active-plastic state within the soil. Fully inextensible reinforcing elements reach equilibrium at approximately zero horizontal extension due to their stiffness (i.e. steel, fiberglass). Inextensible reinforcements are preferred for structures that are permanent or in situations where deformation is crucial to the integrity of the structure, such as bridge abutments\(^{(22,23)}\).

It is important to note that both inextensible and extensible reinforcements are not designed to handle compressive forces, but are only to be serviced in tension\(^{(24)}\).

1.4.1.1.2 Corrosion of MSE Walls

MSE retaining walls, as shown above in Figure 1.4, are constructed with a frontal free-draining region and a region of engineered backfill compacted to a minimum of 95\%\(^{(18,19,20)}\). The free draining region is less compacted due to close proximity of the wall face as well as the characteristics of the fill material. Due to the variances in the two regions, the area with the most metal loss is generally located within 61 cm of the wall face\(^{(25)}\). Surface runoff tends to accumulate and percolate through the free-draining material and groundwater takes the path of least resistance at the interface of the two backfill regions. In addition, the level of compaction dictates the oxygen availability. A variance in this property between the free-draining, loosely compacted material, and the engineered, highly compacted backfill material, can set up a corrosion cell again at the interface between the two regions.

The corrosivity of backfill and moisture content can be large contributors to accelerated corrosion rates. As soil saturation is dependent not only on the initial installation, but the climatic conditions
and surroundings, proper drainage is to be installed to ensure water is not collecting near the wall face or settling in the backfill of a retaining wall. Other considerations are\(^\text{26}\):

- Build-up of chlorides and sulphates as a result of road salts or surface runoff;
- Wet/dry cyclic exposure at the wall face;
- Winter months interfering with drainage; and
- Oxygen differentials between the front and back of an MSE wall.

Corrosion only occurs in an environment where moisture is present (further discussed in Section 1.4.3 Corrosion). When considering MSE walls, moisture comes in the form of atmospheric humidity and precipitation, groundwater in the backfill, percolating surface runoff from road surfaces, accumulated snow, etc. Corrosion of MSE walls is caused by one of two factors, or a combination of both:

- Unsuitable conditions for the material selected (or vice versa; i.e. inappropriate reinforcement material for conditions)
- Conditions changing over time

Corrosion failure of MSE walls is prevented or predicted in one of three ways\(^\text{27}\):

- Addition of sacrificial anode/thickness/galvanizing of reinforcing elements;
- Satisfying electrochemical requirements for backfill material; and
- Proper drainage/installation of a geomembrane preventing the drainage of deicing salts through MSE walls.

Controlling the engineered backfill material, discussed later, is the recommended solution to the first potential cause of corrosion. Backfill meeting certain approved electrochemical limits is brought to site and an envelope of this approved material creates a barrier between the reinforcing elements and the surrounding natural soil. The second potential cause of corrosion is more difficult to predict and prevent. Conditions can change over time, the result of infiltrating contaminants. In North America, one of the most common contaminants on highways and roadways is road deicing salts\(^\text{28}\). To prevent the infiltration of deicing salts, and other runoff from road surfaces, a drainage
system can be designed to direct the contaminants from contact with the reinforcements and a geomembrane installed between the wall and superstructure (i.e. road or asphalt).

Corrosion of a retaining wall is not always visible from the roadside, but can occur behind the wall face. Monitoring of the reinforcing elements and backfill material should be carried out periodically to ensure the integrity of the structure is maintained\textsuperscript{(27)}. When using coupons for corrosion monitoring, they should be placed at the top of the wall face where there is more runoff and available oxygen. This allows for collection in areas with increased corrosion rates\textsuperscript{(29)}. In environments where it is probable snow will accumulate near the base of the wall, additional coupons should be placed here to account for the increased wetting durations.

Alternative solutions to corrosion prevention of MSE walls are to:

- Change the reinforcement to a material more corrosion resistant or apply a barrier coating
- Impress a live current through the metallic reinforcing elements\textsuperscript{(30)}

There are several other types of reinforcing elements suitable for retaining walls beyond just black or galvanized steel, as previously mentioned in Section 1.4.1.1 Reinforcing Elements. Some of which are: plastic, polymer coated steel, aluminum, aluminized steel, fiberglass, etc. Steel is often the more desired material for permanent structures due to its strength and relatively low cost, particularly on larger and higher walls\textsuperscript{(22,23)}. Cathodic protection is a secondary solution. In cathodic protection systems an impressed current is driven through the metallic reinforcing elements to drive the corrosion potential more negative, removing the structure from the active corrosion region. The primary disadvantages of such a system are the regular required maintenance, added cost, risk of accelerated corrosion in locations of electrical discontinuities and risk of accelerated corrosion on nearby metallic elements caused by stray currents\textsuperscript{(31)}. However, used in conjunction with a coated structure (zinc, polymer or aluminum), the locations of any breaks or gouges in the coating that may occur during shipping or installation remain protected\textsuperscript{(9,32,33)}.

1.4.1.2 Backfill Material

The strict engineered parameters that are required to be met by all select granular backfill material for use in MSE structure are outlined in Table 1.4. The parameters are both mechanical and electrochemical in nature\textsuperscript{(34)}.
1.4.1.2.1 Drainage

The design life of MSE walls is often 75 to 100 years. All subsurface drainage is to be channeled away from the back and face of the wall by a proper draining pipe system\(^{(35)}\). While the select granular backfill material is free draining, drainage must be carefully directed away from the wall and disallowed to filter through the interior of the wall. This is done with perforated drain pipes, filter cloth and outlet pipes\(^{(36)}\). Otherwise moisture will travel the path of least resistance either at the front face of the wall where material is not as tightly compacted or the rear of the wall at the interface between the imported engineered backfill and natural soil\(^{(35)}\).
1.0 Introduction

1.4.1.3 Corrugated Steel Pipe

Corrugated steel pipe (CSP) and structural plate corrugated steel pipe (SPCSP) are both used for culverts, bridges and drainage applications. The difference between the two is their capability. CSP is pipe constructed of helically rolled corrugated steel. As the corrugated steel is rolled, a lock seam is created to form pipe. CSP is used for smaller applications where the cover, span and load are relatively less significant. SPCSP is constructed by curved corrugated steel plates. Standard structures are constructed by placing and bolting plates together in shingle formation. SPCSP is often used in transportation and mining applications where the cover and span are far greater and the load more significant than CSP. See Figure 1.5 for a visual on the different sizes and strength of CSP versus SPCSP. It should also be noted that SPCSP can be manufactured into various shapes such as ellipse, pear, arch, box and of course round. As CSP is rolled, the pipes always have a closed conduit (invert) while SPCSP are often bottomless (open conduit; no invert) to suit a vast magnitude of applications.

![Figure 1.5: a) CSP and b) SPCSP](image)

Structures are sized according to their span, rise and length with the terms corresponding to Figure 1.6.
1.0 Introduction

Individual plates are measured according to length, perpendicular to the corrugations, and width, parallel to the corrugations. When given a radius of curvature the individual plates are formed such that the outer 120 mm widths are kept straight for joining of the longitudinal seams. The nominal radius is taken at the middle of a corrugation while the curving radius is taken at the inner extremities(37).

By nature, soil-steel structures are extremely weak in flexure (100 kN-m/m to 200 kN-m/m(39)). As a result structures are often braced with ties or struts during construction. This counteracts horizontal pressures during construction as the backfill is compacted in lifts. Free standing, a steel pipe would deform laterally with vertical loads. However, the compacted backfill envelope provides the necessary support for the structure to sustain its own weight; the backfill transforms the loading from vertical to radial. The weakness in flexure is an asset to design as it allows plastic hinges to naturally form at strategic locations in the haunches, crown and shoulders of a soil-steel structure. Because of the formation of the plastic hinges and weak flexural strength, bending moments are negligible in design in most common cases and structures are designed for thrust only(37).

There are three different arching effects possible: no-arching, positive arching and negative arching. No-arching can only occur when the stiffness of the structural steel in the pipe is exactly that of the soil column above and no load transfer occurs between one column of soil to the adjacent. This condition is impossible in practice(37). Positive arching occurs when the middle soil column above the pipe deflects and transfers load to the adjacent columns of soil, relieving the pipe of some load it would have otherwise sustained in a no-arching scenario. Negative arching is the opposite in which
load transfer occurs as the side columns deflect more than the center, requiring the pipe to sustain more load than in the case of no-arching\(^{37}\).

Thrust is non-uniform around the circumference of a soil-steel structure and is dependent on shape. The thrust is greatest on the vertical axis of a vertical ellipse as the arch is stiffer than the soil column above. This results in negative arching. Conversely, a horizontal ellipse has the greatest thrust near the spring line, or sides of the structure. The soil above the center of the horizontal ellipse is therefore stiffer and the result is positive arching\(^{37}\).

1.4.1.3.1 Corrugation Profiles

Atlantic Industries Limited (AIL) manufactures three corrugation profiles of its standard structural plates. The three corrugation profiles are called Bolt-A-Plate\(^{®}\) (BAP), Super-Cor\(^{®}\) (SC) and Ultra-Cor\(^{®}\) (UC). See Table 1.5 and Figure 1.7 for more details on the differences between the three products:

\[
\text{Table 1.5: Corrugation Profiles for Structural Plate Corrugated Steel Pipe\(^{39}\)}
\]

<table>
<thead>
<tr>
<th>Corrugation Plate</th>
<th>Depth</th>
<th>Pitch</th>
<th>Length</th>
<th>Circumferential Bolt Spacing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bolt-A-Plate</td>
<td>51 mm (2 in)</td>
<td>152 mm (6 in)</td>
<td>1219 mm (48 in)</td>
<td>&quot;N&quot; where N = 244 mm (9.6 in)</td>
</tr>
<tr>
<td>Super-Cor</td>
<td>140 mm (5.5 in)</td>
<td>381 mm (15 in)</td>
<td>762 mm (30 in)</td>
<td>&quot;S&quot; where S = 406 mm (16 in)</td>
</tr>
<tr>
<td>Ultra-Cor</td>
<td>237 mm (9.5 in)</td>
<td>500 mm (20 in)</td>
<td>1000 mm (40 in)</td>
<td>&quot;U&quot; where U = 500 mm (20 in)</td>
</tr>
</tbody>
</table>

To clarify, a plate is dimensioned using the following template:
BAP structures are small in comparison to those of SC and UC with a shallow corrugation. They have less load-bearing capacity and are manufactured from thinner gauged steel. Typical BAP structures are culverts on residential roadways and animal crossings. SC structures have deep corrugations and are stronger in every respect. The span, rise and cover can be greater with typical structures being bridges, tunnels, underpasses and overpasses for residential traffic, trains and mine sites. Finally, UC structures have a great deal of strength and are capable of withstanding even greater span, rise, cover and live loads than SC. The main industry for UC is mine site solutions but they are also appropriate for heavy traffic highways and converting two under/overpasses into one due to their increased capabilities. To better visualize the three profiles in relation to one another see Figure 1.8.
1.4.1.3.2 Corrosion of CSP

The potential sources of corrosion for CSP/SPCSP are much the same as that of MSE walls and can be controlled in the same manners. However, there are two additional sources of potential degradation that should be discussed and are more commonly associated with structures located in a watercourse with an invert (bottom):

- Microbial attack
- Abrasion

Microbial attack, or MIC, is defined as material degradation initiated and/or accelerated by microorganism activity; MIC results from bacterial growth on the surface of a metal forming a biofilm\(^{40}\). For MIC to proceed, four components must be present: the host metals, nutrients, water and oxygen. Oxygen is necessary for microbial growth but is often depleted in soil buried structures making MIC more prevalent in waterside corrosion than soil-side corrosion. However, there are some bacteria that can grow in low oxygen environments. Sulphate reducing bacteria (SRB) is one of these bacteria, but requires plenty of organic nutrients to survive. SRB affect the corrosion behavior of buried steel structures more than any other bacteria due to the anaerobic (oxygen deficient) conditions such as those found in bogs, marches and clay\(^{41}\). While sulphates can be present in water and soil, soluble sulphates are present in water and groundwater offering corrosion issues in anaerobic or stagnant conditions. SRB favour temperatures between 25°C and 35°C for growth\(^{41}\).

Two other common bacteria associated with MIC are iron-related bacteria and low nutrient bacteria. Once one type of bacteria has formed deposits on a metallic surface, it can become a host site for other types of bacteria. Depending on the type of bacteria formed, MIC is most common in temperatures ranging from 4°C to 49°C and stagnant waters\(^{41,42}\). As the passive layers that form on steel are less dense than other metals, they are easily infiltrated by bacteria; MIC is detected on steel substrates more often than any other metallic alloy\(^{42}\).

Abrasion is a concern with structures that are on a watercourse and contain an invert (closed conduit). The flow and level of the water, the size and type of bedload and the incline of the structure all play a factor in the severity of abrasion\(^{43}\). While abrasion is not directly related to corrosion, the result is still degradation in the form of metal loss. A galvanized structure in an
abrasive environment is not able to form or maintain the protective scale necessary to protect the structure; on top of the wear directly due to mechanical means, the corrosion rate is increased as new metal is constantly exposed\(^{(43)}\). This is termed erosion corrosion\(^{(41)}\). To prevent wearing as a result of water flow, structures in abrasive conditions can be lined with polymer, concrete or an asphalt pavement. As previously mentioned, in many cases an alternative structure that does not contain an invert, such as an arch, is often considered.

### 1.4.2 Surface Modifications

As steel corrodes readily in many natural environments it is rarely used for modern infrastructure without some sort of surface modification or coating to provide defense against environmental degradation. A common method is to apply a coating, either organic or inorganic, to provide barrier and, in some cases, galvanic protection. The three most prevalent coatings are zinc, aluminum and polymer. Both zinc and aluminum coatings can be applied abiding by galvanizing procedures where the substrate is first cleaned and abrasive blasted, then dipped into a molten metal bath of a specified composition. While both aluminum and zinc can be applied to a steel substrate using galvanizing procedures, the term “galvanize” and all its derivatives imply zinc specifically. Polymer coatings can be applied as a paint, spray, laminate or powder that is thermally bonded to the substrate. Coatings are selected based on\(^{(44)}\):

- Type of service: submersion, intermittent splash and spill, gaseous or vapour;
- Temperature variants; and
- Chemical or mechanical degradation mechanisms.

All coatings have advantages as well as disadvantages and their performance varies according to substrate, surface preparation and the environment in which the structure is exposed.

#### 1.4.2.1 Aluminized

Aluminum coatings are known for their ballistic resistance and strength. However, they can also be very prone to pitting corrosion in some applications\(^{(45)}\). Aluminum coatings are most effective due to their ability to form a protective alumina layer, or scale. Chemical vapour deposition (CVD) aluminide coatings offer excellent resistance to degradation in atmospheres containing water vapour, but not those which contain low oxygen or sulphur\(^{(46)}\). However, as the aluminide coating and iron/steel substrates have significant differences in their thermal expansion properties, caution
1.0 Introduction

is required as well as careful control and evaluation of phase evolution in environments that experience great temperature variances\(^{(46)}\).

1.4.2.2 Polymer Coated

The following information is a brief summary of the highlights, limitations and overall differences of polymer coatings versus metallic coatings.

As polymers often have low melting temperatures, polymer coatings are not often appropriate for high temperature applications nor can welding be conducted following coating but must be completed prior to, unless a suitable repair method has been developed for the localized and surrounding weld affected region.

Neutral coatings can be organic or inorganic and often are ceramic or polymer. Neutral coatings are known for the chemical and abrasion resistance beneficial in more aggressive environments. These coatings are most commonly applied as a paint or thermal-spray\(^{(47,48)}\).

Polymer coatings are often tested for their performance. However, to date, correlation from the test results to service life has not been investigated in depth\(^{(47)}\). All performance testing is done on a comparison basis with known baseline articles. Testing a polymer coating on a steel substrate and relating its performance to galvanized steel tested in the same manner will give a relative performance scale; the polymer coating will perform better or worse than galvanized steel in certain conditions. With some field experience/performance to substantiate, the qualitative comparison can be related to service life\(^{(47)}\). Some of the advantages of thermal-spray plastics are\(^{(48)}\):

- Form tough, firmly adherent coatings;
- Applied at relatively low ambient temperatures (even below freezing);
- Repaired easily by re-melting or adding material;
- Good resistance to impact and abrasion and do not become brittle at low temperatures;
- Good chemical resistance; and
- Good ultra violet degradation resistance.
1.0 Introduction

However, coatings that are not chemically bonded (unlike when galvanized with zinc or aluminum) can fail and expose the underlying substrate in two manners:

- Delamination (de-adheres)
- Fracture (cracks)

Coating thickness, elastic modulus, coefficient of thermal expansion, moisture, stress levels and surface preparation are all factors that play into the success or failure of an applied coating\(^{(49)}\).

Coating systems can fail as a result of improper surface preparation, mix ratio, incomplete coverage or wrong product selection. Two of the most common causes of delamination are blistering/disbondment and exposure to salt environments. Failures can be minimized if a proper quality assurance/quality control program is put into place to ensure coatings are selected, prepared and applied in a suitable manner, minimal damage is caused by installation and performance is measured and monitored from the beginning of the process until the end\(^{(44)}\).

1.4.2.3 Galvanized

Galvanizing steel is a very common method of protecting an article against corrosion. It works by providing a barrier to the corrosive environment, as well as anodically protecting the article by the rules of galvanic corrosion. Zinc is more reactive than iron and so will corrode preferentially to the article, even if small areas (under 6.5 mm in diameter\(^{(50)}\)) of the underlying iron are exposed. However, the rate of corrosion for zinc is less than that of steel, providing long term protection\(^{(51)}\).

Prior to hot-dip galvanizing (HDG) the surface of the steel must be properly prepared. If the surface is not perfectly clean, the zinc will not adhere and will result in a patchy coating, ineffective for corrosion protection. The three main steps of surface preparation are\(^{(50)}\):

- Caustic cleaning – a hot alkali solution is used to remove dirt, grease and oil;
- Pickling – hot sulphuric acid, or ambient hydrochloric acid, is used to remove scale and rust. Scale and rust can also be cleaned by abrasive blasting, which can be used to remove weld spatter, epoxies, paint, etc. as well; and
- Fluxing – zinc ammonium chloride is used to remove any surface oxides present and to prevent further oxides from forming on the steel surface.
Following surface preparation, the steel is dipped in a bath of molten zinc. The bath must contain a minimum of 98 weight percent (wt%) zinc. As the melting temperature of zinc is approximately 420°C, the temperature of the bath is maintained between 450°C to 465°C to ensure proper melting of all alloying elements as well as the reactions to form the required intermetallics\(^{51,52,53,54}\). The articles are left submerged to allow time for the zinc layer to form and dwell time is dependent on the desired coating thickness. Common dwell times are 12 – 16 minutes for structural plate\(^{55}\). Following removal, the excess zinc is removed by draining or centrifuging and the articles cooled to room temperature. Often times the galvanized surface is re-passivated with sodium dichromate to eliminate the formation of zinc hydroxide (ZnOH\(_2\)).

There are three Zn-Fe layers that form during the HDG process, along with the base Fe and outer Zn (Figure 1.9)\(^{56}\).

![Figure 1.9: Fe-Zn alloy layers formed during HDG\(^{56}\).](image)

The outermost layer (\(\eta\)) is ductile, improving the impact resistance of the base metal and is the first to form upon submersion. For the remaining layers, Zn-Fe intermetallics form as zinc diffuses into the steel surface and iron diffuses into the galvanized coating. The gamma (\(\gamma\)) layer has the greatest hardness but is only 1 – 2 \(\mu m\)\(^{56}\) in thickness. The delta (\(\delta\)) layer is the second intermetallic. It has slightly less hardness than the \(\gamma\)-phase, but still significantly harder than the base steel. The \(\delta\)-phase is in the range of 30 – 40 \(\mu m\)\(^{56}\) thick so is therefore the primary protector against abrasion\(^{51,52,54,57,58,59,60}\). The third and final intermetallic is the zeta (\(\zeta\)) layer which ranges in thickness from 7 to 25 \(\mu m\)\(^{56}\). Finally the outermost layer, \(\eta\), which is 100% zinc, is the most ductile
and thickness of this layer ranges between 8 and 15 μm\(^{[56]}\). While the softness of this layer does little for abrasion protection, the \(\eta\)-phase demonstrates excellent impact resistance and formability and is also necessary for the formation of the zinc patina\(^{[51,52,54,57,58,59,60]}\). The zinc patina is a dense and well adhered zinc carbonate (ZnCO\(_3\)) that forms over time in service. The zinc patina can take anywhere from 6 months to 2 years to properly form\(^{[61]}\). The process for formation requires first a zinc oxide (ZnO) and then zinc hydroxide (Zn(OH)\(_2\)) prior to the final zinc carbonate. This is most conducive in cyclic wet-dry atmospheres or hard water environments.

The most important characteristic of hot-dip coatings is the formation of a metallurgical bond as a result of the reaction between steel and molten zinc. Following the molten zinc bath, the HDG article can be heat treated to maximize the Zn-Fe reactions and reduce the amount of pure zinc creating a harder coating with little ductility, the HDG article can be air cooled to obtain a mixture of Zn-Fe alloy layers and a pure Zn outer layer or the article can be water quenched to minimize the Zn-Fe alloy layers and maximize the thickness of the pure Zn layer to create a more ductile coating. While the mechanical properties change according to the HDG post treatment followed, the corrosion resistance is dependent only on total coating weight/thickness which is independent of the post treatments\(^{[60]}\).

The following table, Table 1.6, outlines the expected corrosion resistance in a variety of soil burial conditions.
1.0 Introduction

Table 1.6: Corrosion of Galvanized Steel\(^{(50)}\)

<table>
<thead>
<tr>
<th>Soil Type</th>
<th>Total Weight Loss (oz/ft(^2))</th>
<th>After Burial Period</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.1 yrs</td>
<td>4.0 yrs</td>
</tr>
<tr>
<td>Inorganic Oxidizing Acid Soils</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cecil clay loam</td>
<td>0.3</td>
<td>1.4</td>
</tr>
<tr>
<td>Hagerstown loam</td>
<td>0.3</td>
<td>1.2</td>
</tr>
<tr>
<td>Susquehanna clay</td>
<td>1.0</td>
<td>2.3</td>
</tr>
<tr>
<td>Inorganic Oxidizing Alkaline Soils</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chino silt loam</td>
<td>1.1</td>
<td>2.3</td>
</tr>
<tr>
<td>Mohave fine gravelly loam</td>
<td>1.6</td>
<td>3.3</td>
</tr>
<tr>
<td>Inorganic Reducing Acid Soils</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sharkey clay</td>
<td>0.6</td>
<td>1.5</td>
</tr>
<tr>
<td>Acadia clay</td>
<td>3.3</td>
<td>--</td>
</tr>
<tr>
<td>Inorganic Reducing Alkaline Soils</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Docas clay</td>
<td>3.2</td>
<td>1.6</td>
</tr>
<tr>
<td>Merced silt loam</td>
<td>2.1</td>
<td>4.5</td>
</tr>
<tr>
<td>Lake Charles clay</td>
<td>3.7</td>
<td>3.9</td>
</tr>
<tr>
<td>Organic Reducing Acid Soils</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carlisle muck</td>
<td>1.2</td>
<td>3.4</td>
</tr>
<tr>
<td>Tidal marsh</td>
<td>1.2</td>
<td>2.1</td>
</tr>
<tr>
<td>Muck</td>
<td>4.3</td>
<td>5.4</td>
</tr>
<tr>
<td>Rifle peat</td>
<td>4.3</td>
<td>7.2</td>
</tr>
<tr>
<td>Cinders</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cinders</td>
<td>6.7</td>
<td>5.4</td>
</tr>
</tbody>
</table>

(a) This is weight of coating on one side of the pipe. 1 oz sq ft (305 g/m\(^2\)) is equivalent to approximately 1.72 mil (43.7 um) thickness of coating.

As the zinc of galvanizing protects the steel electrochemically due to zinc's increased reactivity compared to iron, HDG is a superior alternative to paint for corrosion protection in many environments. This is due to the galvanic nature of defense where damaged areas of up to 6.5 mm diameter are still protected by the surrounding zinc\(^{(50)}\).

1.4.3 CORROSION

Corrosion is often confused with erosion\(^{(62)}\), but the two are, in fact, very different. Erosion is degradation caused by mechanical means, such as abrasion or wearing of a material due to chaffing whereas corrosion is defined as the deterioration of a material as a result of an electrochemical
reaction with its environment\(^{41}\). A corrosion cell must have an anode, a cathode and electrolyte for the reaction to occur. See the schematic in Figure 1.10.

![Corrosion Cell Diagram](image)

Figure 1.10: Corrosion Cell.

The above figure demonstrates a typical corrosion cell of which the electrolyte is water and the anode and cathode are different regions on the same iron surface. The following reactions are examples of those that take place during corrosion:

**Anodic (Oxidation) Reaction** – This is the breakdown of elemental (pure) iron, from the anode, into its ion and free electrons:

\[
Fe \rightarrow Fe^{2+,3+} + 2e^-, 3e^-
\]

(Equation 1)

**Cathodic (Reduction) Reaction** – This is the decomposition of the electrolyte, water, into the hydrogen and hydroxyl ion:

\[
H_2O \rightarrow H^+ + OH^-
\]

(Equation 2)

The following equation describes the formation of the hydrogen bubbles that appear on the cathode:

\[
2H^+ + 2e^- \rightarrow H_2
\]

(Equation 3)

**Overall (Red-Ox) Reaction** – Adding the three previous equations together yields the following:
1.0 Introduction

\[
Fe + 2H_2O \rightarrow Fe(OH)_2 + H_2 + \{e^- + H^+\}
\]

In layman terms, pure iron reacts with water to form hydrogen bubbles at the cathodic (reduction) site while the pure iron is dissolved into solution (ions). The formation of rust (iron oxide/hydroxide) often appears on the surface of iron and steel; the iron ions react with the rogue oxygen and hydrogen ions (from \(H_2O\)) to form FeO, Fe\(_2\)O\(_3\) and Fe(OH)\(_2\), more commonly known as rust.

The difference between the anode and cathode can be as slight as a variance in internal electrical properties, a variance of oxygen concentration at the surfaces or as vast as a galvanic couple created between two different metals\(^{(41)}\). In such cases, the anode is the more reactive metal while the cathode is the more noble metal. This is further explained in the following section, 1.4.3.1 Galvanic Corrosion.

1.4.3.1 Galvanic Corrosion

Galvanic corrosion is the corrosion of dissimilar metals. The more noble metal acts as the cathode and the more reactive metal the anode. While the corrosion of a given metal in a given environment is at a certain rate, when coupled with a dissimilar metal the corrosion rate of the cathode decreases, while the corrosion rate of the anode increases\(^{(41)}\). This is further exaggerated according to the area ratio — if there is proportionately a small area of anode and a large area of cathode, the corrosion rate of the anode is further accelerated\(^{(41)}\).

The following, Figure 1.11, presents the Galvanic Series. The more reactive a metal, the higher it appears in the series and the more noble a metal, the lower it appears in the series. Zinc and low alloy steel have been outlined in the series to demonstrate the theory behind galvanizing. Zinc is higher on the series and therefore more reactive. As a result zinc will corrode preferentially to steel; the corrosion rate of zinc is increased while the corrosion rate of any exposed steel is significantly decreased thus the zinc provides sacrificial protection. It is important to note that while a more reactive metal will corrode preferentially to a more noble metal, therefore protecting it in a sacrificial manner, the rate of corrosion is the determining factor on how long the protection lasts; while magnesium is even more reactive than zinc, it is not generally used to sacrificially protect steel due to its reaction rate with chlorides and sulphates resulting in an uneconomical solution or appreciable service life advantage\(^{(63)}\).
1.4.3.2 Corrosion Allowance

The corrosion allowance of a structure is the sacrificial steel addition to ensure that any degradation does not negatively affect the integrity of the structure. The additional thickness is directly dependent on the aggressiveness of the environment a structure will be exposed to as well as the DSL. At the end of the DSL a structure must be able to maintain its strength. A corrosion allowance is calculated and then added to a structure so that degradation will not affect the thickness required to meet the structural requirements.

Buried steel structures are exposed to atmosphere, soil and/or water. A corrosion allowance is to be calculated for each side of the structure and added together to obtain the total sacrificial thickness required (see Figure 1.12). For example, a buried culvert with an invert is exposed to all three environments: on the outside of the culvert there is soil and on the inside there is water in the invert and atmosphere in the crown. Corrosion allowances for both water and soil are to be added
together to obtain the total sacrificial thickness for the invert. Corrosion allowances for both atmosphere and soil are to be added together to obtain the total sacrificial thickness for the crown. However, atmospheric exposure is considered to have a minimal effect on the performance of soil-steel structures with the exception of structures subject to heavily concentrated industrial gases, extreme heat sources or coastal areas with salinity\(^{(65)}\).

![Figure 1.12: Schematic of corrosion allowance\(^{(66)}\).](image)

### 1.4.3.2 Water

Determining the waterside corrosion of galvanized steel is the most complicated of the three environments. This is due to oxygen availability and flow velocity which can vary throughout the year and be difficult to determine. Articles that are fully submerged are exposed to a deaerated (oxygen deficient) environment while articles that are only seasonally submerged are exposed to atmosphere when not underwater, often times reducing the corrosion rate. However, structures that are within the “splash zone” are exposed to conditions that are frequently wet but also in an aerated (excess oxygen) environment, a worst-case scenario. The water properties to be considered in the development of waterside corrosion models are as follows\(^{(65)}\):

- **pH** is the measure of acidity. A low pH (pH < 7) indicates an acidic environment where a high pH (pH > 7) indicates an alkaline or basic environment. A pH of 7 indicates a neutral environment. Steel is most negatively affected by low pH. However, zinc and aluminum are both susceptible to corrosion in alkaline environments as well;
• Resistivity is the reciprocal of conductivity. Resistivity is the measure of water’s inability to carry a current and is a function of the soluble salts and total dissolved solids (TDS). Typically the lower the resistivity, the more corrosive the environment;

• Chlorides (Cl⁻) are a highly soluble salt (solubility of CaCl₂ is 74.5 g/100 g water⁶⁷) that is often found in the natural environment as well as in acid rain, deicing salts, etc. Chlorides are the largest contributing factor to low resistivity;

• Sulphates (SO₄²⁻) contribute to lower pH levels in water (acid rain). Sulphates are generally considered to be less harmful than chloride ions regarding metallic corrosion (solubility of CaSO₄ is 0.255 g/100 g water⁶⁷). However, sulphates can be converted to highly corrosive sulphides by anaerobic SRB; and

• Flow velocity has a direct influence on the bedload and thus the abrasion rating. Abrasion can degrade the plate finish and lead to a loss of plate thickness on the upstream corrugation crests due to impacts by aggregate or debris suspended in the flow. The oxygen availability, frequency of wetness and type of bedload all contribute to the aggressiveness of flowing water.

The velocity of any flowing water carrying bedload also affects the corrosion rate significantly by incorporating erosion/abrasion into the equation. The degree of flow and bedload characteristics affect the formation of protective scale on the metallic structure as well as increases degradation by mechanical means. Abrasion levels are defined based on the characteristics of carried bedload and anticipated maximum flow velocity. Abrasion velocities should be evaluated on the basis of frequency and duration. Consideration should be given to a frequent storm, such as a two year event, or mean annual discharge. Choosing a less conservative (i.e. less frequent) flow condition for a design basis may extend the calculated service life but will also increase the risk of erosion failure in the bottom of the structure. Selection of the correct abrasion level is less critical for structures without a metal invert⁶⁵.

An additional property that has not been considered in corrosion models is water hardness:

• Hardness is indicated by the amount of calcium carbonate (CaCO₃) dissolved in the water (solubility of 7.0 × 10⁻⁴ g/100g water⁶⁷). The level of water hardness determines the buffering capacity or ability of the water to neutralize acidity from rainwater and other sources. Low hardness waters have a low concentration of CaCO₃ and are termed soft water. CaCO₃ is necessary for the formation of the protective scale on zinc. Therefore, despite high
resistivity, soft water may indicate a corrosion potential for galvanized steel. Hard water is rich in CaCO₃ which neutralizes acidity and forms a protective scale on galvanized steel.

The formation of the protective outer layer on a galvanized structure requires first a zinc oxide to form, followed by a zinc hydroxide and finally the zinc carbonate that is the zinc patina, as described in Section 1.4.2.3 Galvanized. Generally, a wet-dry cycle is required to have all three reactions to occur in sequence. However, all necessary reactions can also be achieved in hard water environments. The division between hard and soft water is in the vicinity of 60 ppm and 100 ppm CaCO₃(66).

1.4.3.2.2 Soil

The environmental parameters for soil-side corrosion are similar to those for water, but simplified. Buried structures do not undergo abrasion due to flowing bedload and the available oxygen is considered deficient. Soil in contact with MSE walls or CSP can be either saturated or unsaturated soil. Saturated soil approaches corrosion rates of waterside corrosion while unsaturated soil is defined below. There are five primary factors affecting the corrosion rate. The first four are similar to those for waterside corrosion. However, the addition of organic content is described(65):

- pH;
- Resistivity;
- Chlorides (Cl⁻) in soil are similar to those found in water. However, engineered backfill material acts as a storage locale for chlorides allowing filtration and then accumulation when they are collected by means of runoff or deicing salts;
- Sulphates (SO₄²⁻) occur naturally and are also commonly found in polluted air and are deposited on soil; and
- Organic material in the backfill can initiate the formation of anaerobic pockets of soil which could be contaminated with SRB, thereby initiating MIC in the form of severe pitting. Total organic content should be limited to 1% by weight of the total soil fraction for structural purposes as well(9,19,20).

1.4.4 Existing Design Criteria and Corrosion Models

In North America the most commonly used design criteria and accompany corrosion model for specifying environmental limitations pertaining to durability was developed by AASHTO. AASHTO
was designed to state the parameters for structure interaction with a surrounding unsaturated soil environment. However, there are no design criteria or associated corrosion models to specify the environmental requirements for galvanized steel structures in saturated soil or immersed in water. As a result these unsaturated soil parameters defined by AASHTO and outlined in Table 1.4 have been adopted to encompass all environments, regardless of whether or not this is appropriate or follows the intent of the original model.

### 1.4.4.1 Waterside Corrosion

Table 1.7 outlines the environment limitations and waterside corrosion models for galvanized steel taken from two sources that do make recommendations for such conditions – the United Kingdom and New Mexico’s Department of Transportation (DOT):

---

**Table 1.7: Waterside Corrosion Models**

<table>
<thead>
<tr>
<th>Source</th>
<th>pH Range</th>
<th>Resistivity (Ω-cm)</th>
<th>Cl⁻ (ppm)</th>
<th>SO₄²⁻ (ppm)</th>
<th>Corrosion Loss/Service Life</th>
</tr>
</thead>
</table>
| UK Non-Aggressive | 6.0 - 9.0| N/A                | ≤ 50      | ≤ 240       | Zn: 4 μm/yr  
Fe-C: M=22.5t⁰.⁶⁷ μm |
| UK Aggressive     | 5.0 - 6.0| N/A                | 50 - 250  | 240 - 600   | Zn: 14 μm/yr  
Fe-C: M=40.0t⁰.₈₀ μm |
| UK Very Aggressive| < 5.0 or > 9.0| N/A              | ≥ 250     | ≥ 600       | Not Recommended |
| New Mexico DOT    | 6.0 - 8.5| > 1000             | < 250     | < 250       | 50 years |

*Where: t = (design service life – life of zinc coating in yrs)*

As it is assumed that resistivity is a function of chlorides and sulphates, resistivity is not defined in the UK models.

Incorporating hardness into the United Kingdom waterside corrosion models and interpolating assumptions based on the soil models, the following table has recently been proposed by the
Corrugated Steel Pipe Institute (CSPI) in the Durability Guideline. Table 1.8 outlines the design considerations for corrugated steel plate structures exposed to water. As plate products and wire retaining walls are manufactured from similar materials, it is assumed that these recommendations can be transferred to MSE walls as well. The electrochemical properties for water are presented in Table 1.8 as well as the corrosion model, Table 1.9, and applicable corrosion allowances in Table 1.10. The required water hardness, or parts per million (ppm) calcium carbonate (CaCO₃), is assumed 80 ppm as it lies directly in the middle of the 60 to 100 ppm range stated by several sources. However, there has been no published works on the validity of this assumption or field surveys completed to confirm its accuracy.

\[ M = 22.5(t - 16)^{0.67} \mu m \]

\[ M = 40.0(t - 4.5)^{0.80} \mu m \]

Where: \( t = \) design service life in yrs

\[ \text{Non Aggressive: } 2000 - 8000 \text{ (Ω-cm)} \]

\[ \text{Aggressive: } 2000 - 8000 \text{ (Ω-cm)} \]

\[ 6 \leq \text{pH} < 9 \]

\[ \leq 50 \]

\[ \leq 240 \]

\[ > 80 \]

\[ 5 \leq \text{pH} < 6 \]

\[ 50 < \text{Cl}^- \leq 250 \]

\[ 240 < \text{SO}_4^{2-} \leq 600 \]

\[ > 80 \]
1.0 Introduction

Table 1.10: Waterside Corrosion Allowances

<table>
<thead>
<tr>
<th>DSL (years)</th>
<th>Corrosion Allowance (μm)</th>
<th>UK Non-Aggressive</th>
<th>UK Aggressive</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>98</td>
<td>448</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>239</td>
<td>848</td>
<td></td>
</tr>
<tr>
<td>75</td>
<td>346</td>
<td>1204</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>438</td>
<td>1535</td>
<td></td>
</tr>
</tbody>
</table>

While this corrosion model can be accepted for the short term, further studies, such as this one, are required to solidify quantifiable results rather than settling for the baseline estimate of 80 ppm CaCO₃ derived from water quality assumptions.

1.4.4.2 Soil Side Corrosion

Extensive research has gone into determining the corrosion rate of galvanized steel in various soils. An example of such work is demonstrated in Figure 1.13, a chart constructed that predicts the time to first maintenance (years) versus the thickness of the coating and environments in which the structure lies. This chart has been published by the American Galvanizers Association. The five environments in order of decreasing zinc life expectancy are: rural, suburban, temperate marine, tropical marine and industrial.
1.0 Introduction

The National Bureau of Standards conducted a study of metal loss of steel and galvanized steel from buried structures that had been in service for greater than 50 years. It is believed that corrosion rate decreases with time according to an exponential rate of metal loss:

\[ x = k t^n \]

(Equation 5)

The exponential equation is based on the protective qualities of zinc. However, some models follow a linear rate of metal loss incorporating a delayed initiation to account for the depletion of the outer zinc coating. Table 1.11 and Figure 1.14 demonstrate many soil corrosion models from various studies. While most models are for galvanized steel, Models 9, 10, 11 and 12 consider black steel only. To be appropriate for comparison with the remaining models, an offset to account for the benefits of galvanizing would be required. As they are incomparable as they are, these particular models were excluded from Figure 1.14 as well as other models that do not meet the electrochemical parameters for select backfill material.
1.0 Introduction

Table 1.11: Soil-side Corrosion Models

<table>
<thead>
<tr>
<th>Model</th>
<th>Corrosion Allowance</th>
<th>Ref</th>
<th>Additional Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$M = 40.0(t-16)^{0.80}$</td>
<td>7</td>
<td>UK Aggressive; 64 μm galvanizing</td>
</tr>
<tr>
<td>2</td>
<td>$M = 22.5(t-4.5)^{0.67}$</td>
<td>7</td>
<td>UK Non-Aggressive; 64 μm galvanizing</td>
</tr>
<tr>
<td>3</td>
<td>$M = 12(t-10.5)$</td>
<td>6</td>
<td>AASHTO; 64 μm galvanizing</td>
</tr>
<tr>
<td>4</td>
<td>$M = 71(t-6)$</td>
<td>3</td>
<td>CalTrans &quot;Corrosive&quot; ($\rho &lt; 1,000 , \Omega\cdot\text{cm}$); 86 μm galvanizing</td>
</tr>
<tr>
<td>5</td>
<td>$M = 33(t-10)$</td>
<td>3</td>
<td>CalTrans &quot;Acidic&quot; ($\rho &gt; 1,000 , \Omega\cdot\text{cm}$); 86 μm galvanizing</td>
</tr>
<tr>
<td>6</td>
<td>$M = 28(t-10)$</td>
<td>3</td>
<td>CalTrans &quot;Neutral &amp; Acidic&quot; ($\rho &gt; 1,000 , \Omega\cdot\text{cm}$, pH &gt; 7); 86 μm galvanizing</td>
</tr>
<tr>
<td>7</td>
<td>$M = 13(t-30)$</td>
<td>3</td>
<td>CalTrans &quot;Select Granular&quot; (clean, free draining gravels with &lt; 5% fines &amp; $\rho &gt; 1,000 , \Omega\cdot\text{cm}$); 86 μm galvanizing</td>
</tr>
<tr>
<td>8</td>
<td>$M = 28(t-10)$</td>
<td>3</td>
<td>Nominal sacrificial steel requirement for marginal quality fill; 86 μm galvanizing</td>
</tr>
<tr>
<td>9</td>
<td>$M = 80.0t^{0.80}$</td>
<td>3</td>
<td>Nominal sacrificial steel requirement for plain carbon steel in good quality fill</td>
</tr>
<tr>
<td>10</td>
<td>$M = 13t$</td>
<td>3</td>
<td>Nominal sacrificial steel requirement for plain carbon steel in high quality fill</td>
</tr>
<tr>
<td>11</td>
<td>$M = 80t^{0.80}$</td>
<td>1</td>
<td>Maximum loss for plain carbon steel based on NBS work</td>
</tr>
<tr>
<td>12</td>
<td>$M = 40t^{0.80}$</td>
<td>1</td>
<td>Average loss for plain carbon steel based on NBS work</td>
</tr>
<tr>
<td>13</td>
<td>$M = 50t^{0.65}$</td>
<td>1</td>
<td>Maximum loss for galvanized steel based on NBS work</td>
</tr>
<tr>
<td>14</td>
<td>$M = 25t^{0.65}$</td>
<td>1</td>
<td>Average loss for galvanized steel based on NBS work</td>
</tr>
<tr>
<td>15</td>
<td>$M = 50t^{0.60}$</td>
<td>1</td>
<td>Maximum loss from Electrochemical Test Cell Data at 50% and 100% Saturation (Darbin et al, 1988)</td>
</tr>
<tr>
<td>16</td>
<td>$M = 5.5t^{0.60}$</td>
<td>1</td>
<td>Minimum loss from Electrochemical Test Cell Data at 50% and 100% Saturation (Darbin et al, 1988)</td>
</tr>
<tr>
<td>17</td>
<td>$M = 25t^{0.65}$</td>
<td>1</td>
<td>Maximum loss from Electrochemical Test Cell Data at 25% Saturation (Darbin et al, 1988)</td>
</tr>
<tr>
<td>18</td>
<td>$M = 2.8t^{0.65}$</td>
<td>1</td>
<td>Minimum loss from Electrochemical Test Cell Data at 25% Saturation (Darbin et al, 1988)</td>
</tr>
</tbody>
</table>

Where: $M$ = corrosion allowance of steel per side in μm and $t$ = design service life in years
The AASHTO model (3) is the most common corrosion model used in Canada and the United States. The United Kingdom models define electrochemical parameters for the soil in three categories: Non-Aggressive, Aggressive and Very Aggressive. Galvanized steel is not recommended in Very Aggressive environments and the limitations for Aggressive are less conservative than those of AASHTO. Looking back at Figure 1.14, the AASHTO (3) and UK Non-Aggressive (2) models sandwich many of the other models, particularly for DSLs greater than 75 years. The recently published Durability Guideline released by the CSPI, suggests use of both the UK Non-Aggressive and AASHTO corrosion models. Those models are presented below for comparison of the electrochemical parameters (Table 1.12) and metal loss rates (Table 1.13) for use when determining the corrosion allowance (Table 1.14).
### 1.0 Introduction

#### Table 1.12: Electrochemical Soil Parameters\(^{(9,65,68)}\)

<table>
<thead>
<tr>
<th>Backfill Material Parameters</th>
<th>AASHTO Test</th>
<th>ASTM Test</th>
<th>Galvanized Limits UK</th>
<th>AASHTO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistivity</td>
<td>T288-91 G 57</td>
<td>T288-91 G 57</td>
<td>&gt; 3000 Ω-cm</td>
<td>&gt; 3000 Ω-cm</td>
</tr>
<tr>
<td>pH</td>
<td>T289-91 G 51</td>
<td>T289-91 G 51</td>
<td>6 - 9</td>
<td>5 - 10</td>
</tr>
<tr>
<td>Chlorides</td>
<td>T291-91 D 512</td>
<td>T291-91 D 512</td>
<td>&lt; 50 ppm</td>
<td>&lt; 100 ppm</td>
</tr>
<tr>
<td>Sulphates</td>
<td>T290-91 D 516</td>
<td>T290-91 D 516</td>
<td>&lt; 240 ppm</td>
<td>&lt; 200 ppm</td>
</tr>
<tr>
<td>Organics</td>
<td>T267-86 N/A</td>
<td>T267-86 N/A</td>
<td>&lt; 1%</td>
<td>&lt; 1%</td>
</tr>
</tbody>
</table>

#### Table 1.13: Metal Loss Rates\(^{(9,65,58)}\)

<table>
<thead>
<tr>
<th>Material</th>
<th>Time Period</th>
<th>AASHTO Standard Loss Rate/yr/side (µm)</th>
<th>UK Non Aggressive Loss Rate/yr/side (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc Layer</td>
<td>≤ 2 years</td>
<td>15</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>&gt; 2 years</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Carbon Steel</td>
<td>After Zn depletion</td>
<td>12</td>
<td>M = 22.5(t - 16)(^{0.67}) µm</td>
</tr>
</tbody>
</table>

Where: \(t = \) design service life in yrs
1.0 Introduction

Table 1.14: Soil-side Corrosion Allowances

<table>
<thead>
<tr>
<th>DSL (years)</th>
<th>Corrosion Allowance (μm) UK Non-Aggressive</th>
<th>AASHTO</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>98</td>
<td>174</td>
</tr>
<tr>
<td>50</td>
<td>239</td>
<td>474</td>
</tr>
<tr>
<td>75</td>
<td>346</td>
<td>774</td>
</tr>
<tr>
<td>100</td>
<td>438</td>
<td>1074</td>
</tr>
</tbody>
</table>

*Note: Based on a galvanizing thickness of 64 μm*

1.4.4.3 Abrasion

Pure zinc is soft and will wear rapidly under abrasive conditions. As a result of the zinc chemically bonding with steel substrate there is Fe-Zn alloy layer which is actually harder than the steel substrate. However, galvanized steel is not recommended in Abrasion Level 3 and 4 as presented in Table 1.15(65). Table 1.16(69) states abrasion levels as defined by the California Department of Transportation (CalTrans), which differ slightly from those in Table 1.15. According to this scale, steel is not recommended in Abrasion Level 6. For levels 3, 4 and 5 steel is fine to use, but additional gauge thickness and/or a protective liner is recommended for sacrificial loss and to ensure the strength of the structure is not compromised.

Table 1.15: Abrasion Levels According to CSPI(65)

<table>
<thead>
<tr>
<th>Abrasion Level</th>
<th>Bedload Description</th>
<th>Anticipated Maximum Flow Velocity (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><strong>Non Abrasive</strong> - very low velocities and no bedload (ie. storm sewers, stormwater detention systems, arches)</td>
<td>N/A</td>
</tr>
<tr>
<td>2</td>
<td><strong>Low Abrasive</strong> - minor bedloads of sand and gravel</td>
<td>1.5</td>
</tr>
<tr>
<td>3</td>
<td><strong>Moderate Abrasive</strong> - moderate bedloads of sand and gravel</td>
<td>4.5</td>
</tr>
<tr>
<td>4</td>
<td><strong>Severely Abrasive</strong> - heavy bedloads of sand, gravel and rock</td>
<td>&gt; 4.5</td>
</tr>
</tbody>
</table>
Table 1.16: Abrasion Levels According to CalTrans\(^{(69)}\)

<table>
<thead>
<tr>
<th>Abrasion Level</th>
<th>Bedload Description</th>
<th>Anticipated Maximum Flow Velocity (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Virtually no bedload</td>
<td>(v &lt; 1.5)</td>
</tr>
<tr>
<td>2</td>
<td>Bedloads of sand, silts or clay, regardless of volume</td>
<td>(0.9 \leq v \leq 2.4)</td>
</tr>
<tr>
<td>3</td>
<td>Moderate bedload volumes of sands and gravels with maximum grain sizes up to 38 mm</td>
<td>(1.5 &lt; v \leq 2.4)</td>
</tr>
<tr>
<td>4</td>
<td>Small to moderate bedload volumes of sands, gravels and/or small cobbles/rocks with maximum stone sizes up to 152 mm</td>
<td>(2.4 &lt; v \leq 3.7)</td>
</tr>
<tr>
<td>5</td>
<td>Moderate bedload volumes of sands, gravels and/or small cobbles/rocks with maximum stones sizes up to 152 mm</td>
<td>(3.7 &lt; v \leq 4.6)</td>
</tr>
<tr>
<td>6</td>
<td>Heavy bedload volumes of sands, gravels and rocks with stone sizes 152 mm or larger</td>
<td>(3.7 &lt; v \leq 6.1)</td>
</tr>
</tbody>
</table>

### 1.4.5 Analysis Techniques

Several different techniques were utilized to obtain raw data, convert this data into industry terms and analyze results. Initial tests to obtain raw data were conducted both in the field and in the laboratory with all further evaluations of results conducted in the laboratory using specialized theories and technology. The primary analysis techniques were used to generate Tafel plots from the raw data obtained in both potentiodynamic polarization (PDP) and linear polarization resistance (LPR) testing as well as analyzing steel samples with a scanning electron microscope (SEM) and energy dispersive x-ray spectroscopy (EDS).

#### 1.4.5.1 Potentiodynamic Polarization

PDP tests can be done in either the anodic or cathodic direction, either starting just below or just above the resting potential, respectively. To determine information on the active region and susceptibility to pitting, anodic PDP tests are preferred. The scan for an anodic PDP test begins just below the resting potential, or open circuit potential (OCP) at which the sum of the anodic and cathodic reaction rates on the electrode surface is zero. The scan then continues, at a rate of approximately 0.1667 mV/sec, in the positive direction. PDP scans are plotted on an Evans diagram.
of $E$ vs. $\log(i)$ where $E$ is the potential with respect to the reference electrode and $i$ is the current density in A/cm$^2$. Current density is plotted in a log scale of absolute values as signage is insignificant, demonstrated in Figure 1.15.

![Figure 1.15: Theoretical anodic potentiodynamic polarization curve(70).](image)

The scan begins in the cathodic region (point 1 in Figure 1.15) and as the potential is increased the current density increases to approach zero (A). The point at which the scan changes directions (A) to have current density decrease with increasing potential is the transfer to the anodic, active region (B). In the active region metal oxidation is the dominant reaction taking place(70). Passivation potential is reached at point C when the scan again reverses and current density again increases with increasing potential (D) until the passive region (E) is achieved. This continues until the breakaway potential (F) is reached and the transpassive region (G), in which current density rapidly decreases with increasing potential, dominates. The transpassive region is unpredictable can often indicate susceptibility to pitting. The scan concludes at point 2.
1.0 Introduction

1.4.5.2 Tafel Plots
Analyzing the entirety of a PDP plot can offer a vast amount of information on a material-environment relationship including the susceptibility to pitting and breakaway potential. The passivation potential and the corrosion rate of a given material in a given electrolyte by focusing on what is known as the Tafel region, encircled above in Figure 1.15. A Tafel plot involves both the cathodic curve immediately preceding the active regime as well as the anodic curve within the active regime. Figure 1.16 offers a schematic of a typical Tafel plot, ignoring the remainder of the PDP scan.

The potential is again plotted versus the current density in a log scale of absolute values, taking into account the surface area exposed. The linear sections of both the anodic and cathodic curves, as demonstrated in blue dashed lines above, are extrapolated to find their intersection. The slopes of these two lines are Tafel constants, $\beta_a$ for the anodic branch and $\beta_c$ for the cathodic branch. The intersection point is highly important as its coordinates, indicated by the red dashed lines in Figure 1.16 are $(i_{corr}, E_{corr})$, where $i_{corr}$ is the corrosion current density and $E_{corr}$ the corrosion potential. As it can be unclear where exactly $i_{corr}$ is due to the log scale of the x-axis, further analysis is required. However, for quick reference, it can be stated that a smaller corrosion current density (e.g. $1 \times 10^{-9}$)
has a lower corrosion rate than a larger corrosion current density (e.g. $1 \times 10^{-5}$); when looking at a series of Tafel plots, the farthest left curve will have the slowest corrosion rate while curves to the right will have more rapid corrosion rates.

### 1.4.5.3 Butler-Volmer Equation

The Butler-Volmer equation is an equation used to determine the rate of an electrochemical reaction by describing the current density at an electrode in terms of the over potential. In its raw form, the Butler-Volmer equation is\(^{(71)}\):

\[
I = A \cdot i_0 \cdot \left\{ \exp \left[ \frac{\alpha_a nF(E - E_{eq})}{RT} \right] - \exp \left[ \frac{\alpha_c nF(E - E_{eq})}{RT} \right] \right\}
\]

(Equation 6)

Where:

- $I$ = electrode current (A)
- $A$ = electrode active surface area (cm\(^2\))
- $i_0$ = exchange current density (A/cm\(^2\); $i_{corr}$)
- $\alpha$ = charge transfer coefficient; anodic and cathodic
- $n$ = number of electrons involved in transfer (valence)
- $F$ = Faraday constant (96 485 J)
- $E$ = electrode potential (V)
- $E_{eq}$ = equilibrium potential (V; $E_{corr}$)
- $R$ = universal gas constant (8.314 J/mol·K)
- $T$ = absolute temperature (K)

The slopes of the Tafel plots are the Tafel constants, which are otherwise expressed as the following\(^{(71)}\):

\[
\beta = \frac{RT}{\alpha nF}
\]

(Equation 7)

Replacing current with current density to account for the surface area exposed during experimentation and using the Tafel constants simplifies the above Butler-Volmer equation to:
1.0 Introduction

\( i = i_0 \cdot \left\{ \exp \left( \frac{OP}{\beta_a} \right) - \exp \left( \frac{OP}{\beta_c} \right) \right\} \)

Where:

\( OP = \text{over potential } (E - E_{eq}) \)

Once the exchange current, \( i_0 \), otherwise known as corrosion current density, \( i_{corr} \) has been determined, further calculations can be completed to convert that value into a more common corrosion rate in terms of metal loss per year.

1.4.5.4 Linear Polarization Resistance

Unlike PDP, LPR is an electrochemical technique to measure corrosion rate in a non-destructive manner\(^{(70)}\). The magnitude of potential is small, only typically ranging ± 25 mV about the OCP and the scan rate decreased. Due to the close proximity of the OCP, a plot of potential versus current density is linear. See Figure 1.17 for a typical LPR curve.

![Figure 1.17: Typical linear polarization resistance curve\(^{(70)}\).](image)

The curve crosses through the y-axis, where current density is zero, at the corrosion potential, \( E_{corr} \). Following Ohm's Law, \( V = IR \), where \( V \) = potential, \( I \) = current and \( R \) = resistance, the slope of the LPR curve is determined about the \( E_{corr} \) to find the polarization resistance, \( R_p \). Once \( R_p \) has been
determined the Stern-Geary equation is used to calculate the corrosion current density, $i_{corr}$. The Stern-Geary equation is as given:\(^{(70)}\):

$$R_p = \frac{\beta_a \beta_c}{2.3 \cdot i_{corr}(\beta_a + \beta_c)}$$

(Equation 9)

As the technique is a non-destructive and rapid approach, LPR is the preferred electrochemical method for field testing. However, LPR gathers instantaneous results reflective of the surrounding environment only during the moments of collection. Because of this, it is common for LPR experiments to occur seasonally in order to obtain a broader range of conditions and improve accuracy of the interpreted results.

1.4.5.5 Scanning Electron Microscopy

SEM is a surface analysis technology to observe a sample at high magnification. SEM is capable of viewing samples on a three-dimensional basis as well as with significant resolution to allow for clearly visible details at high magnification.

SEM is often used for analyzing fracture surfaces as the depth of field allows for observation on rough surfaces that are visible to the microscope, depending on the operating conditions. The scanning electron microscope used was a Hitachi S-3000N Scanning Electron Microscope and works by shooting a beam of high energy electrons at the surface of a specimen under vacuum. The energy is dissipated as the beam makes contact with the specimen. The electron beam is scanned over the surface and the intensity of the signal recorded creates a 2D image\(^{(72)}\). Secondary electron (SE) and back scatter electron (BSE) are the two forms of signals received. SEs, the signals used to obtain images for this dissertation, are activated electrons that are diffracted from the specimen surface and detected on a detector adjacent to the electron beam and sample. These electrons are low energy and sensitive to topography producing a high resolution image. BSEs are the primary electrons that are scattered back to a detector that is located above the sample (in line with the original electron beam). These electrons are high energy from the depth of the sample. BSE is sensitive to atomic number and produces a lower resolution image\(^{(72)}\).

The controllable operating conditions are: working distance, beam energy, magnification, aperture, tilt angle and detection mode which dictate the signal mode, resolution and depth of field.
While SEM is ideal for viewing samples at high magnification and resolution to obtain visual information regarding the crystal structure, phases and mechanical properties relating to fracture surface, specimens are required to be conductive and so are often sputtered with gold. However, this can be a disadvantage to the analysis technique as it increases the equipment required, cost and alters the surface under evaluation. The samples used for this dissertation were not sputtered with gold so as to not affect the surface morphology or chemical analysis conducted by EDS.

1.4.5.6 Energy Dispersive X-Ray Spectroscopy

EDS (or EDX) determines the chemical composition in a material. The relative quantities of each element are determined by the intensity of the spectrum. This is a very useful technology to determine phase boundaries by utilizing the line scan technique. EDS is often used in conjunction with x-ray diffraction (XRD) to get the full picture of chemical composition as well as crystal phases. However, XRD requires smooth, flat surfaces and so that technology was not used in the construction of this dissertation.

EDS works by shooting the same electron beam as in SEM analysis at a specimen's surface. The beam emits electrons from the valence shells of the specimen. The vacancies left from the emitted electrons are filled with electrons from a higher energy shell. The energy required to do so results in x-ray which are characteristic of the elements in the specimen. A lithium-doped silicon semiconductor converts the x-ray energy to an electrical signal (current). The relative abundance of an emitted x-ray is converted to intensity and a spectrum is then portrayed that relates the intensity of a given x-ray to its energy expressed in kiloelectron volts (keV; 1 keV = 1.602 x 10^{-16} J) and correlated to an element\(^{73}\). The EDS for this dissertation was conducted on the same Hitachi S-3000N Scanning Electron Microscope with a beam voltage of 20 kV and working distance of 15.0 mm. X-rays are typically generated from the surface to a depth of approximately 2 µm\(^{74}\).

Samples for EDS are required to be 2D, similar to those for optical microscopy, but conductive, as is the case with SEM. EDS is capable of scanning the entire visible surface at a given magnification and is also capable of area, line and spot analysis to focus in on a particular phase. In addition to the spectrum, mapping can be conducted to demonstrate visually where each element is present and to what degree. This is beneficial when combining with XRD to determine the chemical composition of a particular phase. EDS is also not suitable for the detection of light elements, such as carbon, beryllium, etc. and the resolution of elemental mapping is relatively poor due to the efficiency of the
semi-conductor. As only the gross morphology and a general idea of the corrosion products formed on the surfaces were of interest, mapping and localized analyses were not completed.
2.0 Methodology

For a complete study, laboratory testing of galvanized steel samples was conducted complementary to field testing of pre-existing galvanized soil-steel structures. The following subsections outline the testing that was undertaken as well as justification for the parameters selected.

2.1 Field Testing

Galvanized steel structures have been used in service since the 1930s with mixed performance. While applications have ranged from grade separations to bridges covering flowing watercourses, small conduits were more common during early installations.

Field testing was conducted on two different types of soil-steel structures. The first type was SPCSP. Testing was completed by obtaining steel and water samples of soil-steel structures servicing flowing watercourses. Sites were selected from various locations across New Brunswick. In New Brunswick, issues with galvanized culverts have become so common that galvanized structures are currently limited to grade separations and arches (contain no invert). The second type of soil-steel structure examined was MSE retaining walls. Samples of steel and groundwater were extracted from walls demonstrating premature corrosion on the outer facings. These samples were obtained in British Columbia during the deconstruction of retaining walls that had been in service for approximately 12 years.

2.1.1 Structural Plate Corrugated Steel Pipe

Once on site, two samples were taken – one of the water flowing through the steel structure and one of the steel itself. The water samples were collected in 250 mL Kartell water sample bottles from approximately the middle of the flow through the invert. For steel samples, a DeWalt 18 V XRT cordless drill was used with a 15 cm extension, MIBRO bi-metal High Strength Steel 31.75 mm hole saw and 4.75 mm pilot drill were required for the extraction. Samples were removed from as deep into the invert as possible. However, there were some uncontrollable factors that prevented the invert from being accessible:

- Depth of water too deep for the drill and extension;
- Excessive bedload covered the invert;
- Invert corroded away; and
- Flow of water too strong to be safe wading in the water with a drill.
The hole left in the steel structure was then filled in with a galvanized fender washer and spring toggle bolt. The fender washers measured 38 mm outer diameter with the inside diameter 9.5 mm accompanied with the toggle bolts, 6.5 mm in diameter and 76 mm in length (Figure 2.18).

Figure 2.18: a) Drilling out a 51 mm sample through a flowing water course and b) the replacement fender washer and toggle bolt.

The water samples were tested with both handheld electronics and titration strips; pH and temperature were measured using a non-glass pH probe while conductivity, total dissolved solids and salinity were measured using a Scientific Instruments electrode. Both probes were connected to a Hach Waterproof Handheld H170G multimeter. Prior to obtaining readings the probes and multimeter were calibrated for pH and conductivity utilizing pre-prepared, known solutions. The following titration strips were used for the remaining parameters measured:

- Hach Titrators for Chloride: Low Range 30 – 600 ppm Cl-
- EM Quant® 10019-2 Sulfate Test
- Hach Water Quality Test Strips for Total Hardness
- Hach Water Quality Test Strips for pH

Three of obtained steel samples were also analyzed with a SEM and EDS. SEM images were captured to obtain a general idea of the surface morphology while EDS assisted with identifying the extent of degradation and elemental composition. The microscope used to conduct both analyses
was a Hitachi S-3000N Scanning Electron Microscope with a beam voltage of 20 kV. Prior to using
the microscope, the backs of the samples were leveled by sanding with a 120 grit grinding wheel.
Double-sided carbon tape was then used to ensure metal-to-metal contact with the sample tray.
SEM images were captured at both 150x magnification and 600x magnification. Beam current #1
was used for SEM imaging and beam current #2 for EDS analyses. A working distance of 15.0 mm
and duration of 100 seconds were used for EDS analyses to retain both the generated spectrums
and qualitative analyses. The software coupled with the microscope was Quartz Xone – X-Ray
Microanalysis System.

2.1.2 MECHANICALLY STABILIZED EARTH WALLS

Eight MSE retaining walls were erected in 2000/2001 in southeastern British Columbia. Of the
eight walls installed, one showed significant amounts of premature corrosion after only 10 years of
service. An investigation was started by the British Columbia Ministry of Transportation and
Infrastructure (BCMtoI) involving both the University of British Columbia’s (UBC) Materials
Engineering Department and AIL. After an additional two years of service the opportunity arose for
three of the eight walls to be deconstructed in a project to further widen the road with the
installation of a new retaining wall. Groundwater and steel samples as well as LPR readings were
collected during this deconstruction.

Three walls were deconstructed and done so in such a manner that lateral reinforcement wires
could be extracted from each 61 cm lift of the MSE retaining walls from the top capping mat to the
base mat. Samples were collected from two vertical columns of Wall A allowing for samples from
every depth and height as the layers were exposed by excavator. Each mat was 122 cm wide and
244 cm long with an additional 61 cm facing following a 90° bend. The diameter of every section of
wire was measured on the two full vertical columns of Wall A. Wire diameter measurements were
taken using a Performance Tool 0-6” (150 mm) Digital Caliper after first cleaning the wire with
steel wool to remove any dirt and excess carbonate buildup. See Figure 2.19 through Figure 2.22 for
further clarification.
2.0 Methodology

Figure 2.19: Vertical columns for sampling locations on Wall A.

Figure 2.20: Vertical column of wall cut away from remainder of wall during deconstruction for the collection of steel samples.
Water samples were collected in 250 mL Kartell water sample bottles from the creeks flowing both upstream and downstream of the affected retaining walls. The water samples were tested for pH,
temperature, conductivity, TDS and salinity. pH and temperature were measured using a non-glass pH probe while conductivity, total dissolved solids and salinity were measured using a Scientific Instruments electrode. Both probes were connected to a Hach Waterproof Handheld H170G multimeter. Prior to obtaining readings the probes and multimeter were calibrated for pH and conductivity utilizing pre-prepared, known solutions. The following titration strips were used for the remaining parameters measured:

- Hach Titrators for Chloride: Low Range 30 – 600 ppm Cl⁻
- EM Quant® 10019-2 Sulfate Test
- Hach Water Quality Test Strips for Total Hardness
- Hach Water Quality Test Strips for pH

LPR readings were collected from Walls B and C. These readings were taken on a Pine Instruments WaveNow USB portable potentiostat, and accompanying AfterMath software, utilizing the rods that had been inserted into the walls in May, 2010 with the original investigation. At that time three probes were inserted into each wall face, approximately halfway across horizontally, spaced 30.5 cm apart and 152 cm down from the top of the wall. The rods were 122 cm in length, with the front 61 cm incased in plastic shrink wrap to isolate them allowing only the back 61 cm (from 61 cm to 122 cm in wall depth) of rod to interact with the engineered backfill material. Of the three rods in each wall, one was galvanized steel to simulate the original condition of the welded wire reinforcement, one was black steel to simulate the welded wire reinforcement following zinc depletion and the final rod was titanium mixed metal oxide to act as an inert anode. See Figure 2.23. A copper/copper sulphate (Cu/CuSO₄) half cell reference electrode was used with 0.314 V vs. NHE\(^{75}\).
The portable potentiostat was programmed as follows:

- Starting Potential: -0.25 V vs. OCP
- Ending Potential: 0.25 V vs. OCP
- Scan Rate: 0.1 mV/s
- Current Range: Auto

After conducting the LPR, a linear plot of potential versus current was yielded. The raw data was converted from current to current density, taking into account the 61 cm of exposed rod embedded in the engineering backfill material. After using the Stern-Geary equation to determine the corrosion current density, corrosion rate, in microns per year (μm/yr), was calculated.

2.2 LABORATORY EXPERIMENTATION

To substantiate field testing, laboratory testing was conducted as well. Two sets of laboratory experiments were completed, consisting of accelerated corrosion testing. OCP and PDP were conducted on all samples. The samples in the first set, used to obtain baseline knowledge of the appropriate range of values for zinc, were mechanically galvanized while the second set of samples were taken directly from AIL inventory of structural steel plate. These samples replicated materials used during the design and construction of soil-steel structures and were hot-dip galvanized.
2.2.1 MECHANICALLY GALVANIZED STEEL SAMPLES

Mechanically galvanized steel samples were used to obtain baseline knowledge of zinc corrosion. The samples were commercial carbon steel (CS) sheet Type B as designated in the American Society for Testing and Materials (ASTM) A1011/A1011M – 12b: Standard Specification for Steel, Sheet and Strip, Hot-Rolled, Carbon, Structural, High-Strength Low-Alloy, High-Strength Low-Alloy with Improved Formability, and Ultra-High Strength. The galvanized steel sheet used was fabricated to comply with ASTM A653/A653M – 11: Standard Specification for Steel Sheet, Zinc-Coated (Galvanized) or Zinc-Iron Alloy-Coated (Galvannealed) by the Hot-Dip Process. Samples measured 15.84 ± 0.01 mm in diameter and 0.38 ± 0.02 mm in thickness, including the zinc layer of 24 ± 4 μm, per side of sample. Prior to testing, samples were weighed on a Scientech ZSA 120 analytical balance with precision to 0.1 mg. The galvanized and overall thicknesses were measured using a PosiTector 6000 coating thickness gauge and a PosiTector UTG ultrasonic thickness gauge, respectively. Three measurements were made for each parameter on every sample and the average of these measurements calculated. Following testing and drying of the samples, the same three parameters were measured again. It is common practice for samples being subjected to accelerated corrosion testing to be polished to a mirror finish. However, as these samples were coated with a thin zinc layer, no polishing was completed for fear of removing the galvanizing.

The amount of each substance used to create the different electrolytes was determined in parts per million (ppm) according to the ranges given by known corrosion models (presented in Table 1.8). Each electrolyte was 1 L in volume and the quantities were converted appropriately according to the total molecular mass of the constituent and the desired quantity. For example, the amount of calcium chloride, CaCl₂, needed to simulate 50 ppm chloride (Cl⁻) was calculated as follows:

\[
Molar \ Mass \ of \ CaCl_2 = 40.08 \frac{g}{mol} + 2 \left(35.45 \frac{g}{mol} \right) = 110.98 \frac{g}{mol}
\]

\[
\frac{Cl_2}{CaCl_2} = \left(\frac{2(35.45)}{110.98}\right) \cdot 100 = 63.89\% 
\]

\[
50 \text{ ppm} = 50 \frac{mg}{L}
\]

\[
50 \div 0.6389 = 78.26 \text{ mg CaCl}_2 \text{ in 1 L of distilled water}
\]
The same process was followed for calculating the appropriate amounts of the other constituents to create the remaining solutions (Table 2.1). The electrolyte solutions were prepared according to the test matrix provided in Table 2.2:

### Table 2.1: Calculated Amounts of Substances for Testing

<table>
<thead>
<tr>
<th></th>
<th>CaCO₃</th>
<th>CaCl₂</th>
<th>CaSO₄·2H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 ppm</td>
<td>50 ppm = 50.0 mg</td>
<td>50 ppm = 78.3 mg</td>
<td>100 ppm = 179.2 mg</td>
</tr>
<tr>
<td>60 ppm</td>
<td>100.1 mg</td>
<td>150 ppm = 324.8 mg</td>
<td>300 ppm = 537.7 mg</td>
</tr>
<tr>
<td>90 ppm</td>
<td>150.1 mg</td>
<td>250 ppm = 391.3 mg</td>
<td>500 ppm = 896.2 mg</td>
</tr>
<tr>
<td>120 ppm</td>
<td>200.1 mg</td>
<td>350 ppm = 547.8 mg</td>
<td>700 ppm = 1254.6 mg</td>
</tr>
<tr>
<td>350 ppm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>700 ppm</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Table 2.2: Test Matrix

<table>
<thead>
<tr>
<th></th>
<th>CaCO₃</th>
<th>CaCl₂</th>
<th>CaSO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCO₃</td>
<td>(x,0,0)</td>
<td>(x,y,0)</td>
<td>(x,0,z)</td>
</tr>
<tr>
<td>CaCl₂</td>
<td>(x,y,0)</td>
<td>(0,y,0)</td>
<td>(0,y,z)</td>
</tr>
<tr>
<td>CaSO₄</td>
<td>(x,0,z)</td>
<td>(0,y,z)</td>
<td>(0,0,z)</td>
</tr>
<tr>
<td>ALL</td>
<td>(x,y,z)</td>
<td>(x,y,z)</td>
<td>(x,y,z)</td>
</tr>
</tbody>
</table>

All substances were weighed in a Scientech ZSA 120 analytical balance with precision 0.1 mg, after zeroing out the contributions of the disposable Petri dish. Solutions were mixed in a 1,000 mL Erlenmeyer flask. When adding the measured substances to the flask, the dishes were rinsed with distilled water and poured into the flask to ensure all remnants were removed and accounted for. The solution within the Erlenmeyer flask was stirred to ensure any solids were dissolved prior to beginning experimentation. Once dissolved, a small portion of the solution was poured into a 250 mL beaker and put aside for further analysis. The remaining solution was used as the electrolyte for
accelerated electrochemical experimentation. Solutions were tested using both probes, accompanying an electronic multimeter, as well as titration strips. pH and temperature were measured using a non-glass pH probe and connected to a Hach Waterproof Handheld H170G multimeter as shown in Figure 2.24. The titration strips used were:

- Hach Titrators for Chloride: Low Range 30 – 600 ppm Cl-
- EM Quant® 10019-2 Sulfate Test
- Hach Water Quality Test Strips for Total Hardness
- Hach Water Quality Test Strips for pH

Before and after every experiment all equipment was rinsed thoroughly with distilled water to avoid contamination. The electrolyte was transferred to a standard Princeton Applied Research G0096 corrosion flask (bulb cell). The bulb cell was placed on a Thermo Scientific Cimarec mechanical stirrer, set to level 6, to avoid anything within the solution from settling at the bottom of the flask. Three probes were inserted into the bulb cell: a reference electrode, a counter electrode,
and a working electrode. The reference electrode for the mechanically galvanized samples was a silver/silver chloride (Ag/AgCl) electrode with reference potential of 0.198 V vs. normal hydrogen electrode (NHE)\(^{75}\). The reference electrode was housed in Luggin capillary to obtain close proximity with the working electrode, within 1 mm, via the salt bridge. The counter electrode for all experiments was a rod of pure graphite. The working electrode was a prepared galvanized steel sample, as previously described, with 1 cm\(^2\) surface area exposed to testing. All electrodes were connected via alligator clips to a Princeton Applied Research VersaSTAT 4 potentiostat accompanied with the VersaStudio software package.

Testing began with determining the OCP. Potential values were recorded every second for one full hour to allow stabilization, totaling 3,600 readings. The final reading at the end of the hour was assumed the OCP by the VersaStudio software. Immediately following, PDP was conducted. The controllable variables were set as follows:

- Starting Potential: -0.25 V vs. OCP
- Ending Potential: 1.00 V vs. OCP
- Step Height: 1 mV
- Step Time: 6 s
- Scan Rate: 0.1667 mV/s
- Current Range: Auto; minimum range: 10 nA, maximum range: 10 A

Following the completion of a test cycle, samples were removed, rinsed with distilled water and allowed to dry. The electrolyte solution was disposed of and all equipment rinsed thoroughly with distilled water.

When the samples were dry, their masses were again obtained from a Denver Instrument P-114 analytical balance with precision to 0.1 mg. Overall sample thickness and the coating thickness were also measured using a PosiTector 6000 coating thickness gauge and a PosiTector UTG ultrasonic thickness gauge, respectively. Again, three measurements were made on each sample for each parameter and the average calculated.
2.2.2 Hot-Dip Galvanized Steel Samples

The samples used for testing were small discs of HDG steel punched from actual plate measuring 15.78 ± 0.05 mm in diameter and 1.58 ± 0.05 mm in thickness, including the galvanizing layer of 64 ± 8 μm, per side of sample. Prior to being submitted to testing, samples were weighed on a Denver Instrument P-114 analytical balance with precision to 0.1 mg. Again, the galvanized and overall thicknesses were measured using a PosiTector 6000 coating thickness gauge and a PosiTector UTG ultrasonic thickness gauge, respectively. Three measurements were made for each parameter and the average calculated. Measurements were made on every sample before and after being submitted to accelerated corrosion testing. As explained in Section 2.2.1 Mechanically Galvanized Steel Samples, the galvanized samples were not polished for fear of removing or altering the thin zinc layer.

All substances used to make the electrolytes were weighed in a Denver Instrument P-114 analytical balance with precision to 0.1 mg, after zeroing out the contributions of the disposable Petri dish. Solutions were mixed in a 1,000 mL PYREX® graduated beaker. Once ensuring all substances were dissolved into solution, a small portion of the solution was poured into a glass for analysis while the remaining solution was used as the electrolyte within the corrosion cell. As with the mechanically galvanized samples, pH and temperature were measured with non-glass pH probe connected to a Hach Waterproof Handheld H170G multimeter. Titration strips were used to measure chloride content, sulphates, total hardness in the form of CaCO₃ and pH as previously outlined. In addition, conductivity, TDS and salinity were measured using a Scientific Instruments electrode connected to the same Hach Waterproof Handheld H170G multimeter as used for pH and temperature.

A standard Princeton Applied Research G0096 corrosion flask (bulb cell) was used for experimentation. Again, three probes were inserted into the bulb cell: a reference electrode, a counter electrode and a working electrode. While the counter electrode remained the same, pure graphite, the reference electrode used was a saturated calomel electrode (SCE) containing a reference potential of 0.241 V vs. NHE (0.043 V vs. Ag/AgCl)(75) and the working electrode was a 1 cm² HDG samples from AIL inventory as opposed to the mechanically galvanized samples used prior. All electrodes were connected via alligator clips to an Ivium CompactStat potentiostat accompanied with IviumSoft software package. The entire setup is shown in Figure 2.25.
The OCP was obtained after one hour of collecting readings. Following that, a 15 second stabilization period was allowed prior to conducting PDP. The controllable variables were set as follows:

- Starting Potential: -0.25 V vs. OCP
- Ending Potential: 1.00 V vs. OCP
- Step Height: 0.2 mV
- Scan Rate: 0.2 mV/s
- Current Range: Auto; minimum range: 10 nA, maximum range: 10 A

Following the completion of a test cycle, samples were removed, rinsed with distilled water and allowed to dry. The electrolyte solution was disposed of and all equipment rinsed thoroughly with distilled water.

When the samples were dry, measurements were again taken to obtain overall thickness and coating thickness with PosiTector UTG ultrasonic thickness gauge and PosiTector 6000 coating thickness gauge, respectively. In addition, each sample’s mass was obtained using a Denver Instrument P-114 analytical balance with precision to 0.1 mg. Three measurements were made for each parameter on every sample and the average calculated.
Unlike the mechanically galvanized samples, the HDG samples were analyzed with a SEM which conducted EDS as well. SEM images were captured to gather information on the gross morphology of the samples while EDS assisted with detecting the chemical composition of the corroded surfaces. Samples preparation was minimal, only involving attaching the samples to the sample tray. This was done with double-sided carbon tape to ensure metal-to-metal contact. The microscope used to conduct both analyses was a Hitachi S-3000N Scanning Electron Microscope with a beam voltage of 20 kV. Beam current #1 was used for SEM imaging and beam current #2 for EDS analyses. EDS analyses were conducted at a working distance of 15.0 mm for duration of 100 seconds. The software coupled with the microscope was Quartz Xone – X-Ray Microanalysis System. The EDS spectrums and qualitative analyses were retained.
3.0 RESULTS & DISCUSSION

The following subsections present raw data, evaluate and convert that data into common industry terms. Discussion of the relationship between all aspects of testing and analyses is also completed. This chapter has been subdivided into two categories: Field Conditions and Laboratory Experimentation, further broken down as deemed necessary.

3.1 FIELD TESTING

Structural steel samples were taken directly from the inverts of existing culverts servicing watercourses across New Brunswick. The samples collected represent a variety of field conditions. Some of the sites selected contained structures that were in acceptable condition while others demonstrated structures with the inverts completely degraded due to aggressive environments. The intent of conducting field testing was to gain a better understanding of service conditions to correlate with structure performance and durability and substantiate laboratory testing.

In addition, samples were collected from the lateral reinforcements of three MSE retaining walls in British Columbia as well as ground water samples from nearby watercourses. LPR results were collected from the surrounding backfill material and the HDG steel samples were visually inspected as well as measured to determine any metal loss since installation.

3.1.1 CORRUGATED STEEL PIPE

Galvanized steel is often the material of choice for buried metal structures in New Brunswick. Corrugated steel culverts have been successful in many applications. However, HDG steel culverts have been found to be unsuccessful in certain aqueous conditions and so are limited to bottomless structures. The successes and failures of galvanized steel were used to recommend environmental soil parameters in Table 1.12. Yet, even since the development and guidance of these models, there have been instances where corrugated galvanized steel culverts have continued to demonstrate premature degradation. The most significant degradation has been observed to generate in the invert and splash zone of culverts servicing flowing watercourses. Ten culverts/conduits, originally containing an invert, were selected from across New Brunswick. Water and steel samples were collected from the structures’ inverts, when available and accessible, to develop a correlation between water properties and culvert performance.
3.1.1.1 Electrolyte Properties

The conduits selected came from across New Brunswick. While some structures were in suitable condition, many were experiencing extensive corrosion around the splash line and/or invert. Water samples were collected and tested with titration strips as well as probes and the accompanying Hach Waterproof Handheld H170G multimeter for pH, chlorides, sulphates, total hardness, temperature, conductivity, total dissolved solids and salinity. The results are presented in Table 3.1.
3.0 Results & Discussion

Table 3.1: Field Culvert Water Properties

<table>
<thead>
<tr>
<th>Structure</th>
<th>Notes</th>
<th>Strips</th>
<th>Probes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>pH (ppm)</td>
<td>Cl⁻ (ppm)</td>
</tr>
<tr>
<td>CSP₁</td>
<td>Invert rusted through in several locations. Crown of structure also has surface rust. Sleeve of structure installed 10 - 12 years ago.</td>
<td>~ 7</td>
<td>~ 484</td>
</tr>
<tr>
<td>CSP</td>
<td>Invert rusted.</td>
<td>~ 9</td>
<td>~ 30</td>
</tr>
<tr>
<td>CSP</td>
<td>Invert rusted.</td>
<td>6 - 7</td>
<td>&lt; 30</td>
</tr>
<tr>
<td>CSP₂</td>
<td>Invert rusted through. Medium sized bedrock visible.</td>
<td>~ 7</td>
<td>&lt; 30</td>
</tr>
<tr>
<td>CSP</td>
<td>Too deep/too much flow for good footing to remove sample. Invert not visible.</td>
<td>~ 7</td>
<td>~ 0</td>
</tr>
</tbody>
</table>
### 3.0 Results & Discussion

<table>
<thead>
<tr>
<th>Structure</th>
<th>Notes</th>
<th>pH (ppm)</th>
<th>Cl⁻ (ppm)</th>
<th>SO₄²⁻ (ppm)</th>
<th>CaCO₃ (ppm)</th>
<th>Temp (°C)</th>
<th>pH</th>
<th>Cond (μS/cm)</th>
<th>TDS (ppm)</th>
<th>Sal (ppt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPCSP</td>
<td>Too deep/too much flow for good footing to remove sample. Invert not visible, but lower sides dark with rust and scale.</td>
<td>~ 6</td>
<td>~ 0</td>
<td>&lt; 200</td>
<td>~ 25</td>
<td>21.2</td>
<td>6.7</td>
<td>16</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>CSP</td>
<td>Invert rusted through. Bottom replaced with large bedrock.</td>
<td>6 - 7</td>
<td>~ 0</td>
<td>&lt; 200</td>
<td>25 - 50</td>
<td>21.3</td>
<td>7.4</td>
<td>20</td>
<td>10</td>
<td>0.008</td>
</tr>
<tr>
<td>SPCSP</td>
<td>Invert rusted through.</td>
<td>5 - 6</td>
<td>~ 0</td>
<td>&lt; 200</td>
<td>0 - 25</td>
<td>20.5</td>
<td>6.1</td>
<td>23</td>
<td>11</td>
<td>0.009</td>
</tr>
<tr>
<td>Riveted CSP</td>
<td>Invert has surface rust and scale.</td>
<td>~ 7</td>
<td>~ 0</td>
<td>&lt; 200</td>
<td>25 - 50</td>
<td>21.1</td>
<td>8.2</td>
<td>26</td>
<td>14</td>
<td>0.012</td>
</tr>
<tr>
<td>CSP</td>
<td>Was asphalt coated, but only remnants of coating left.</td>
<td>7 - 8</td>
<td>~ 0</td>
<td>&lt; 200</td>
<td>~ 25</td>
<td>21.4</td>
<td>8.1</td>
<td>23</td>
<td>12</td>
<td>0.009</td>
</tr>
</tbody>
</table>
Samples were collected in the summer months when deicing salts are not applied. However, the properties of the flowing watercourses ranged from low salt, soft water to ocean water. All structures had been in service for 10 to 20 years. Information was not available on exact installation dates. Following AASHTO’s durability design criteria commonly used in aqueous environments when intended only for use in unsaturated soil, the galvanized layer is estimated to withstand 10.5 years of service, based on a galvanizing layer 64 μm thick, prior to complete depletion and attack directly on the underlying steel substrate. While information was not available on the original thicknesses of the structures, four of the ten structures listed in Table 3.1 no longer contained an invert able to bear any load or contribute to the structural integrity of the culvert due to significant degradation. An example of such a structure is pictured in Figure 3.26 a) demonstrating the distinction between material exposed only to soil and atmosphere and material that is sometimes submersed or within the splash zone. B) shows significant metal loss, to the extent of large perforations, just below the waterline.

![Figure 3.26: a) Demonstration of waterline distinction and b) degradation observed.](image-url)

As mentioned in Section 1.4.3.2.1 Water, conductivity is the reciprocal of resistivity. The lowest conductivity, and conversely the highest resistivity, in the above table is 16 μS/cm or approximately 63,000 Ω-cm, respectively. The highest conductivity was approximately 1,000 μS/cm. This is equivalent to the lowest resistivity in the table of an approximate value of 1,000 Ω-cm. The AASHTO recommended minimum resistivity for galvanized steel is 3,000 Ω-cm (300 μS/cm). Modifying the United Kingdom model, CSPI recommends resistivity remain between 2,000 Ω-cm (500 μS/cm) and 8,000 Ω-cm (100 μS/cm) as resistivities less than 2,000 Ω-cm are indicative of high soluble salts and resistivities greater than 8,000Ω-cm are again indicative of aggressive conditions. Converting
3.0 Results & Discussion

the conductivities from the above table to resistivities all line items except the top one satisfy AASHTO while the only line item satisfying CSPI’s modification of the UK’s criterion is the second CSP structure listed.

3.1.1.2 Steel Samples

Three collected samples were also analyzed with SEM and EDS. The EDS results are presented in Table 3.2. The top row is of a HDG sample and provides a comparison of relativity for HDG steel without exposure to service conditions. As can be seen in the table, the dominating element is zinc. This is due to the fully intact galvanized layer. There is also some oxygen from the zinc patina as well as alloying elements from the HDG coating. The remainder of the table entries, from two CSP structures and one SPCSP structure currently in service, indicate there is no zinc remaining; the zinc has been completely depleted by environmental degradation while elements from underlying steel substrate (Fe) are listed. As these samples were exposed to natural watercourses rather than simulated laboratory conditions, there are many unknown contaminants, microorganisms and plant matter in contact with the culverts. To validate this assumption, an image was captured of a microorganism on CSP2 and is shown in Figure 3.27 a). The dominating elements to account for the corrosion products are zinc, oxygen, and in the case of fully depleted zinc, iron. Due to erroneous results, as EDS is not suited to detect light elements, the table was normalized following the removal of carbon.

SEM images of the three bolded entries in Table 3.1, CSP1, CSP2 and SPCSP, have been provided in Figure 3.27 b) through Figure 3.29. Images were captured at 150x magnification to observe the gross morphology. A second image of each sample is provided in Appendix D at 600x magnification.
3.0 Results & Discussion

Table 3.2: EDS Results for Corrugated Steel Pipe

<table>
<thead>
<tr>
<th>Structure</th>
<th>N (wt%)</th>
<th>O (wt%)</th>
<th>Mg (wt%)</th>
<th>Al (wt%)</th>
<th>Si (wt%)</th>
<th>Cl (wt%)</th>
<th>K (wt%)</th>
<th>Fe (wt%)</th>
<th>Zn (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDG</td>
<td>-</td>
<td>9.28 (0.63)</td>
<td>-</td>
<td>&lt; 1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>89.41 (1.96)</td>
<td></td>
</tr>
<tr>
<td>CSP₁</td>
<td>-</td>
<td>40.68 (2.03)</td>
<td>1.10 (0.89)</td>
<td>&lt; 1</td>
<td>1.42 (1.66)</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
<td>55.46 (10.23)</td>
<td>-</td>
</tr>
<tr>
<td>CSP₂</td>
<td>-</td>
<td>37.23 (5.52)</td>
<td>-</td>
<td>-</td>
<td>&lt; 1</td>
<td>1.99 (1.56)</td>
<td>-</td>
<td>60.54 (4.13)</td>
<td>-</td>
</tr>
<tr>
<td>SPCSP</td>
<td>14.00 (0.83)</td>
<td>36.36 (9.73)</td>
<td>&lt; 1</td>
<td>2.51 (1.10)</td>
<td>5.04 (4.70)</td>
<td>&lt; 1</td>
<td>39.73 (27.17)</td>
<td>1.07 (1.00)</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 3.27: a) Microorganism or organic contaminant observed on the surface of CSP₂; and b) CSP₁ at 150x magnification on the edge of a perforation caused by environmental degradation.
Figure 3.27 b) is on the edge of a perforation that penetrated the entire depth of the sample. This was common in many locations along the invert. In fact, collecting a sample was made difficult due to the frequency of perforations and volume of the invert depleted. In this location a structure was put in place many years ago. The application is saltwater and the concentration of chlorides well exceeds the upper limit of 100 ppm as stated by AASHTO. When the structure began to show significant signs of corrosion a second culvert was placed as a liner to the first with a concrete grout filling the space between them. This was completed approximately 10 to 12 years before the sample was collected. Significant corrosion was again apparent on the inside liner. The corrosion products visible, on the underlying steel, were porous and not well adhered to the steel surface.

The sample in Figure 3.28 came from a structure in an environment containing low salts and negligible amounts of sulphates. The pH was also within the range stated in the environmental recommendations of Table 1.7. However, according to the titration strips, which lack precision and accuracy, but can be used to determine relative comparisons, the water was also soft. The resistivity value was measured as approximately 13,000 Ω-cm (98 μS/cm). The sample was significantly corroded and the invert of the structure contained many perforations. The image collected does a poor job of representing the corrosion products. However, it does depict a crater that penetrates deep into the depth of the sample.
The final sample analyzed with SEM is different from the first two as it is of structural plate, not CSP. Figure 3.29 depicts a corrosion product that is thin and with serrated edges, underneath which is a void, directly in the middle of the image. There are also a few deposits visible and the remainder was a thin tightly adhered layer that appeared black on the sample without the aid of a microscope.

All parameters satisfied those of the corrosion model constructed by the AASHTO and used to define the design criteria for galvanized steel structures. But again the invert was completely depleted and the sample obtained from the lower wall of the structure, rather than the bottom. Soft water, not originally a parameter defined in commonly used corrosion models, is common in these regions and reflected by the relative magnitude of the titration stripes detecting total hardness in the form of CaCO₃ concentration. The resistivity, 44,000 Ω-cm (23 μS/cm), was extremely high well exceeding the minimum resistivity recommended in Table 1.4, which has traditionally been used for the design of structures in both soil and aqueous environments.

3.1.1.3 Discussion

It is interesting to note the total hardness values had a direct relationship with resistivity; culvert watercourses that measured high resistivity (shown as low conductivity in Table 3.1), had low total hardness while watercourses with low resistivity (shown as high conductivity in Table 3.1) had high total hardness. While all structures, except the first line item in a saltwater application, met the environmental parameters defined by the UK durability guidelines as well as AASHTO which aid in
the design of North American galvanized steel structures in a broad range of applications, many of them were severely corroded to the point of no longer containing an invert.

3.1.2 Mechanically Stabilized Earth Walls
In 2009 it was discovered by visual observation that one particular wall, in a series of eight MSE retaining walls, was experiencing premature corrosion on the front face. In the process of widening the highway, that wall was deconstructed in the spring of 2012, along with two others, allowing for complete analysis.

3.1.2.1 Electrolyte Properties
Water samples were taken from both the creek on the upper side of the roadway as well as the creek on the lower side of the roadway in May, 2012. All snow from the winter months had been melted and deicing salts had not been applied since late March. The results of the water samples are provided in Table 3.3:
### Table 3.3: MSE Wall Water Properties

<table>
<thead>
<tr>
<th>Structure</th>
<th>Notes</th>
<th>Strips</th>
<th>Probes</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSE Wall</td>
<td>Watercourse upstream from wall. Wall face demonstrating significant red rust in bottom third.</td>
<td>pH ~ 7, Cl^- ~ 0, SO_4^{2-} &lt; 200, CaCO_3 ~ 25</td>
<td>Temp 20.2, pH 8.8, Cond 8, TDS 6, Sal 0.004</td>
</tr>
<tr>
<td>MSE Wall</td>
<td>Watercourse downstream from wall. Wall face demonstrating significant red rust in bottom third.</td>
<td>pH 8 - 9, Cl^- ~ 0, SO_4^{2-} &lt; 200, CaCO_3 ~ 50</td>
<td>Temp 19.9, pH 9.3, Cond 73, TDS 36, Sal 0.033</td>
</tr>
</tbody>
</table>

The values in terms of resistivity are 122,000 Ω-cm for upstream and 14,000 Ω-cm for downstream. As the two watercourses are only approximately 16 m apart, they were assumed to be naturally similar. However, the water properties demonstrated noticeable differences in resistivity, salinity and TDS. The increased salinity and corrosivity from the upstream side of the road to the downstream may have been the result of accumulation of ploughed snow and deicing salts from the winter months.

#### 3.1.2.2 Electrochemical Testing

The deconstruction, in the spring of 2012, involved a full analysis to determine the root cause of corrosion, extent of corrosion on the lateral reinforcements and to predict the service life of the remaining five MSE walls in that region. While on site, the author of this dissertation was given the opportunity to collect LPR readings from Walls B and C.
After calibrating the portable potentiostat, OCP was obtained from a 100 second stabilization period. The OCP vs. time plot is presented below as Figure 3.30.

Immediately following the determination of OCPs, a non-destructive electrochemical test was conducted to produce a LPR curve for each set of probes. Due to the interferences and “noise” of working outdoors, such as vibrations from vehicles traveling the road above, it was raining at the time of collection, etc., the scan rate slow at 0.1 mV/s to allow for stabilization between potential steps. The LPRs for both Walls B and C, using the preinstalled black steel and galvanized rods, are presented in Figure 3.31.
To determine the current density for the x-axis of Figure 3.31, the surface area involved in the LPR experiments is required. The rods used were W7 which translates to 7.58 mm, following galvanizing. Measurements of the rods were taken and averaged 7.42 mm and 7.58 mm in diameter for the black and galvanized rods, respectively. Each rod had 61 cm exposed in the engineered backfill. The surface areas for the black and galvanized rods are:

\[
A = 2\pi rh + \pi r^2
\]

(Equation 10)

Where:
\[
r = \text{radius; } \frac{1}{2} \text{ diameter (cm)}
\]
\[
h = \text{height (cm)}
\]

Black Rod:

\[
A = \left(2\pi \cdot \left(\frac{0.742}{2}\right) \cdot 60.96\right) + \left(\pi \cdot \left(\frac{0.742}{2}\right)^2\right) = 142.534 \text{ cm}^2
\]
3.0 Results & Discussion

Galvanized Rod:

\[
A = \left(2\pi \cdot \left(\frac{0.758}{2}\right) \cdot 60.96 \right) + \left(\pi \cdot \left(\frac{0.758}{2}\right)^2 \right) = 145.617 \text{ cm}^2
\]

3.1.2.3 Corrosion Rate

The slope of each line was determined using the Trendline function of Microsoft Excel with R\(^2\) values = 0.9938 ± 0.0135. The slope of the line represents the polarization resistance, by rearranging Ohm's Law: \(V = IR\). Following the determination of the polarization resistance, the Stern-Geary equation, (Equation 9), was utilized to calculate the corrosion current density, \(i_{corr}\). The Stern-Geary equation requires Tafel constants. To estimate the Tafel constants for the MSE wall probes, an average was taken of the Tafel constants from the laboratory PDP and Tafel plots of Sections 3.2.1.3 Corrosion Rate and 3.2.2.3 Corrosion Rate.

Following the determination of the corrosion current density, corrosion rate was calculated using:

\[
CR = K \frac{i_{corr}}{\rho} \left(\frac{M_{\text{atomic}}}{n}\right)
\]  

(Equation 11)

Where:

\(CR\) = corrosion rate (mpy)
\(K\) = conversion constant
\(i_{corr}\) = corrosion current density (A/cm\(^2\))
\(\rho\) = density (g/cm\(^3\))
\(M_{\text{atomic}}\) = atomic mass (amu)
\(n\) = valence electrons

The \(i_{corr}\) values determined from the Stern-Geary equation and LPR curves and are presented below in Table 3.4. The K constant used was 130 000 mpy·g/C for all calculations\(^{(76)}\), densities of the rods (\(\rho\)) were assumed 7.14 g/cm\(^3\) for the outer galvanized surfaces and 7.87 g/cm\(^3\) for the black steel rods, the atomic mass of the galvanized rods 65.38 amu and the black rods 55.85 amu with the transferring valence electrons assumed to be 2 for all\(^{(5)}\).
Table 3.4: Corrosion Rates of MSE Wall Lateral Reinforcement

<table>
<thead>
<tr>
<th>Test Location</th>
<th>$i_{corr}$ (A/cm$^2$)</th>
<th>Corrosion Rate (μm/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wall B Galv</td>
<td>$4.43 \times 10^{-8}$</td>
<td>0.7</td>
</tr>
<tr>
<td>Wall B Black</td>
<td>$2.02 \times 10^{-7}$</td>
<td>2.4</td>
</tr>
<tr>
<td>Wall C Galv</td>
<td>$1.42 \times 10^{-8}$</td>
<td>0.2</td>
</tr>
<tr>
<td>Wall C Black</td>
<td>$1.29 \times 10^{-7}$</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Walls B and C are located side by side. The retaining walls are at the same elevation and exposed to the same road and weather conditions and were backfilled with soil from the same stock pile. As a result the corrosion rates can be assumed to be $0.5 \pm 0.3 \mu$m/yr for galvanized steel and $2 \pm 0.5 \mu$m/yr for the underlying black steel following zinc depletion. However, it is to be reiterated that LPR produces instantaneous results that are not reflective of past trends or fluctuating conditions, but only measure the corrosion rates occurring in the instant that results are collected.

3.1.2.4 Steel Samples

The original welded wire reinforcement was made up of mats containing longitudinal and transverse wires of different diameters. The nominal thickness of the longitudinal wire and transverse wire, including galvanizing, was 7.76 mm and 6.25 mm, respectively. This was consistent for every mat except for the capping mat at the very top of the wall in which case both the longitudinal and transverse wires were 6.25 mm in diameter, including galvanizing.

Every wire section was measured from two vertical columns of wall A (vertical columns shown in Figure 2.19 through Figure 2.22). Three measurements were taken on every wire section. The average wire diameter was then calculated for each wire section. As there were no outlying measurements the average diameter for all longitudinal wires on a single mat was calculated as well as the average diameter for all transverse wires. These values were then plotted with respect to the depth of the mat down from the top of the wall, as presented in Figure 3.32.
From the above plot it can be easily seen that both vertical columns demonstrated the same trend in wire diameters. The measurements indicated that little to no galvanizing was lost during the 12 years of service and the wire diameters demonstrate negligible differences to the originals. In some cases the wire diameter measured was even greater than the original. This is due to the original stated diameter being a minimum with some variable tolerances on the steel as well as the galvanizing. In addition to that, there was evidence of zinc carbonate ($\text{ZnCO}_3$). $\text{ZnCO}_3$ is a layer formed on the outside of galvanized structures and is technically a corrosion product, but acts as a protector against degradation. The volume of $\text{ZnCO}_3$ is, in fact, greater than that of pure zinc, accounting for some minor diameter increase. While measurements were not taken on Walls B and C, the same visual observations were made – the galvanized layer was fully intact, the wire diameters had not visibly reduced, and there was some zinc carbonate present on the lateral reinforcements as evidenced by the white powdery appearance.

### 3.1.2.5 Discussion

The corrosion rates correctly convey the condition observed of the lateral reinforcements; the lateral reinforcements dug up from the three MSE retaining walls demonstrated little to no metal loss of the protective zinc coating and the underlying steel substrate remained completely hidden.
The corrosion rates in the table above, which are significantly less than those estimated by the AASHTO corrosion model used during the design process, reflect these observed conditions well. The wall faces showed significant premature corrosion while the lateral mats demonstrated little to no degradation. A few hypotheses have been made as to why the wall faces are degrading at a faster rate than the buried elements. However, the listed hypotheses have yet to be fully substantiated:

- Oxygen availability – corrosion requires oxygen to complete the electrochemical reaction. The buried elements are deprived of oxygen while the facing elements are exposed to excess available oxygen;
- Exposure to the elements – the buried lateral reinforcements are shielded from the elements by the layers of engineered backfill, while the facing elements experience continuous wet-dry cycles as well as more severe temperature fluctuations with changing seasons;
- Surface runoff and anthropogenic deicing salts – in this region the application of deicing salts is relied upon to maintain road safety. The anthropogenic additions of deicing salts were not considered during design. Splashing from traversing vehicles, surface runoff and accumulated snow from snow ploughing at the base of the MSE wall facings adds additional corrosive material the interior of the wall never encounters; and
- Drainage – the engineered backfill at the rear of the MSE retaining walls is supplemented with free draining material that is poorly compacted near the front facing. Groundwater and moisture from the road above that percolates into the retaining envelope below the asphalt surface is likely to travel the path of least resistance and drain to the facing, rather than infiltrating through the engineered backfill material.

### 3.2 Laboratory Experimentation

While field testing firmly presented a case that the AASHTO corrosion model is appropriate for use in unsaturated soil, as intended, it is not accurate at predicting corrosion rates in aqueous environments, articles subjected to cyclic wet-dry exposure or MSE wall faces in regions that experience high precipitation. However, as there are many influences in nature, laboratory experimentation was required to determine the primary contributing factors to the increased corrosion rates in these environments not covered by AASHTO. OCP and PDP were completed on a series of punched samples. One set of samples was mechanically galvanized to obtain baseline knowledge on the expected range of values for zinc while the second set of samples was HDG
structural steel plate taken directly from AIL inventory. Results and discussion of both sets of experiments are presented below.

3.2.1 MECHANICALLY GALVANIZED STEEL SAMPLES

The mechanically galvanized samples were commercial CS sheet Type B with a zinc coating $24 \pm 4 \mu m$ in thickness. As the samples were punched from a sheet, the edges were not coated in zinc. However, due to the nature of the testing this area was not exposed to the experimental environment and therefore did not impact the results.

3.2.1.1 Electrolyte Properties

As previously mentioned, in Section 2.2.1 Mechanically Galvanized, the properties of each solution were determined using both titration strips and a probe/meter. Table 3.5 displays the solutions created alongside the properties determined by testing them.

<table>
<thead>
<tr>
<th>Solution $(CO_3^{2-},Cl^-,SO_4^{2-})$ (ppm)</th>
<th>$CaCO_3$ (mg)</th>
<th>$CaCl_2$ (mg)</th>
<th>$CaSO_4$ (mg)</th>
<th>pH</th>
<th>T (°C)</th>
<th>Probe</th>
<th>$Cl^-$ (ppm)</th>
<th>$SO_4^{2-}$ (ppm)</th>
<th>$CaCO_3$ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0,50,0)</td>
<td>0.0</td>
<td>80.6</td>
<td>0.0</td>
<td>5.4</td>
<td>16.8</td>
<td>4 - 5</td>
<td>~ 43</td>
<td>&lt;200</td>
<td>120 - 250</td>
</tr>
<tr>
<td>(0,150,0)</td>
<td>0.0</td>
<td>235.1</td>
<td>0.0</td>
<td>6.0</td>
<td>15.8</td>
<td>4 - 5</td>
<td>~ 144</td>
<td>&lt;200</td>
<td>~ 425</td>
</tr>
<tr>
<td>(0,250,0)</td>
<td>0.0</td>
<td>390.1</td>
<td>0.0</td>
<td>6.3</td>
<td>15.9</td>
<td>4 - 5</td>
<td>~ 236</td>
<td>&lt;200</td>
<td>~ 425</td>
</tr>
<tr>
<td>(0,350,0)</td>
<td>0.0</td>
<td>546.4</td>
<td>0.0</td>
<td>6.6</td>
<td>15.8</td>
<td>5 - 6</td>
<td>~ 319</td>
<td>&lt;200</td>
<td>~ 425</td>
</tr>
<tr>
<td>(0,0,100)</td>
<td>0.0</td>
<td>0.0</td>
<td>140.4</td>
<td>5.4</td>
<td>16.8</td>
<td>5 - 6</td>
<td>~ 0</td>
<td>&lt;200</td>
<td>50 - 120</td>
</tr>
<tr>
<td>(0,0,300)</td>
<td>0.0</td>
<td>0.0</td>
<td>425.0</td>
<td>5.3</td>
<td>16.8</td>
<td>4 - 5</td>
<td>~ 0</td>
<td>&lt;400</td>
<td>~ 425</td>
</tr>
<tr>
<td>(0,0,500)</td>
<td>0.0</td>
<td>0.0</td>
<td>709.0</td>
<td>5.3</td>
<td>16.7</td>
<td>~ 5</td>
<td>~ 0</td>
<td>~400</td>
<td>~ 425</td>
</tr>
<tr>
<td>(0,0,700)</td>
<td>0.0</td>
<td>0.0</td>
<td>993.4</td>
<td>5.5</td>
<td>16.9</td>
<td>4 - 5</td>
<td>~ 0</td>
<td>&gt;800</td>
<td>~ 425</td>
</tr>
<tr>
<td>(30,0,0)</td>
<td>50.5</td>
<td>0.0</td>
<td>0.0</td>
<td>7.9</td>
<td>19.3</td>
<td>~ 6</td>
<td>~ 0</td>
<td>&lt;200</td>
<td>~ 50</td>
</tr>
<tr>
<td>(60,0,0)</td>
<td>100.4</td>
<td>0.0</td>
<td>0.0</td>
<td>8.8</td>
<td>18.5</td>
<td>6 - 7</td>
<td>~ 0</td>
<td>&lt;200</td>
<td>25 - 50</td>
</tr>
<tr>
<td>(90,0,0)</td>
<td>151.4</td>
<td>0.0</td>
<td>0.0</td>
<td>9.2</td>
<td>19.6</td>
<td>6 - 7</td>
<td>~ 0</td>
<td>&lt;200</td>
<td>~ 50</td>
</tr>
<tr>
<td>(120,0,0)</td>
<td>200.3</td>
<td>0.0</td>
<td>0.0</td>
<td>9.4</td>
<td>19.6</td>
<td>~ 6</td>
<td>~ 0</td>
<td>&lt;200</td>
<td>~ 25</td>
</tr>
<tr>
<td>(0,50,100)</td>
<td>0.0</td>
<td>78.3</td>
<td>143.0</td>
<td>5.9</td>
<td>19.8</td>
<td>4 - 5</td>
<td>~ 43</td>
<td>&lt;200</td>
<td>~ 250</td>
</tr>
<tr>
<td>(0,50,700)</td>
<td>0.0</td>
<td>76.4</td>
<td>991.3</td>
<td>5.7</td>
<td>19.6</td>
<td>5 - 6</td>
<td>~ 43</td>
<td>&gt;400</td>
<td>250 - 425</td>
</tr>
</tbody>
</table>
While the chloride strips demonstrated relative accuracy, the pH probe proved to be a more reliable reading than the pH titration strips. The sulphate strips left a little to be desired in their precision and the accuracy of the solution hardness is undetermined.

### 3.2.1.2 Electrochemical Testing

The relative corrosivity of each solution on a mechanically galvanized sample was calculated as well. A sample of an OCP plot for the (0,0,z) solutions is given in Figure 3.33. The remaining OCP plots can be found in Appendix A. As shown, the potential values were collected for one full hour to
obtain stabilization and the potential values are all versus the reference electrode used during experimentation, Ag/AgCl.

![OCP plot for (0,0,z) solutions](image)

*Figure 3.33: OCP plot for (0,0,z) solutions.*

The potentiodynamic plots were then constructed beginning 0.25 V below the previously determined OCP and carried out until 1.00 V above the OCP to obtain an Evan's Diagram of the entire Tafel region. The Tafel plots for all solutions used for the mechanically galvanized samples are provided below in Figure 3.34 through to Figure 3.40.
3.0 Results & Discussion

The above Tafel plots all follow the same general shape and pattern; all three curves appear relatively similar. While it was expected that solution (0,350,0) would have the greatest corrosion current density, it appears that solution (0,150,0) is greater. This was unexpected and is further discussed in Section 3.2.1.5 Discussion.
Again, all four curves appear similar in shape with the corrosion potential and corrosion current density in the same general vicinity. The transition from cathodic to anodic curves has been zoomed in on to clearly show that the solution containing 700 ppm CaSO₄, (0,0,700), has the greatest corrosion current density of the four curves. This is evident as the curve is the furthest to the right and closest to 0. This behaviour was expected as increasing amounts of sulphates have been proven to increase corrosion rates.

Once again, all four curves in the above plot demonstrate similar responses to the exposed solutions that contained increasing concentrations of calcium carbonate (CaCO₃). It is interesting to note that while the plots in Figure 3.34 and Figure 3.35, of samples exposed to calcium chloride (CaCl₂) and calcium sulphate (CaSO₄), respectively, had nearly horizontal plateaus in the anodic branch, or active regime, the curves in Figure 1.4 are far more exponential in shape. Finally, the corrosion potentials for solutions containing only CaCO₃ are between -0.6 and -0.8 V vs. Ag/AgCl while the corrosion potentials for solutions containing CaCl₂ or CaSO₄ are between -0.8 and -1.0 V vs. Ag/AgCl.
Combining CaCl₂ and CaSO₄ created four curves that once again take on the previously observed horizontal plateau in the anodic branch of the Tafel plot. It is also evident from the curves above that solution (0,350,700) has the greatest corrosion current density.

Introducing a combination of CaCO₃ and CaCl₂, which, according to literature, are to have opposing effects on the corrosive nature of the electrolytes, produced the four curves presented in Figure 3.38. While the corrosion current density does not appear to differ significantly between the four
curves, there is some variance in the corrosion potential. In addition, the two curves with significant amounts of CaCl₂, solutions (30,350,0) and (120,350,0) also indicate a fair amount of noise in the transpassive region.

![Figure 3.39: Potentiodynamic plots for (x,0,z) solutions.](image)

While the corrosion current densities for all curves in the above plot do not vary by orders of magnitude, the shape of the curves provides some insight into the behaviour of corrosion. The two solution containing less CaSO₄, solutions (30,0,100) and (120,0,100), have shapes similar to those found for electrolytes containing only CaCO₃ while solutions containing more CaSO₄, solutions (30,0,700) and (120,0,700), are more indicative of curves containing CaSO₄ only by the flatter active anodic branch.
3.0 Results & Discussion

Figure 3.40: Potentiodynamic plots for (x,y,z) solutions.

It is evident that the majority of the plots follow similar shape offering smooth anodic branches in the active region with either little noise in the transpassive region or the transpassive region was not yet reached in the scan. However, solutions (30,50,100) and (30,350,100) do not have the same horizontal plateau as the remaining curves with significantly less negative corrosion potentials. These two solutions both contain 30 ppm CO$_3^{2-}$ and 100 ppm SO$_4^{2-}$ but varying concentrations of Cl$^-$. 

3.2.1.3 Corrosion Rate

From the above plots the Tafel region was studied in more depth for analysis. From all data collected for a single sample and solution, the minimum current was found and assumed to be the exchange current ($i_0$) for initial purposes. After relating this to the corresponding exchange potential ($E_{eq}$) a range of ± 50 mV from the $E_{eq}$ was assumed the Tafel plot for further analysis. Once the Tafel region was determined and plotted, the Butler-Volmer equation, following simplification (Equation 8), was used to evaluate the results and determine the rate of corrosion for each sample and related solution.

(Equation 8)

\[ i = i_0 \cdot \left\{ \exp \left[ \frac{OP}{\beta_a} \right] - \exp \left[ \frac{OP}{\beta_c} \right] \right\} \]

The analysis was conducted in Excel using the Solver function – the slopes ($\beta_a$ and $\beta_c$) of the Tafel plot of a computer generated Butler-Volmer curve were manipulated to minimize the error
between that and the collected raw data to determine corrosion current density ($i_{corr}$). The generated Butler-Volmer curve created for each solution determined the Tafel constants, $\beta_a$ and $\beta_c$, as well as the corrosion potential, $E_{corr}$, and corrosion current density, $i_{corr}$. The same procedure was conducted for determining the corrosion current density for each and every solution tested with a mechanically galvanized sample. Following the determination of the corrosion current density, corrosion rate was calculated using (Equation 11) presented in 3.1.2.3 Corrosion Rate.

Again, the $K$ constant used was 130 000 mpy·g/C$^{(71)}$. The density, atomic mass and valence electrons for zinc are 7.14 g/cm$^3$, 65.38 amu and 2$^{(5)}$, respectively.

The following, Table 3.6, presents all variables determined from the Butler-Volmer equation and Tafel plot analysis as well as the overall corrosion rate calculated for the mechanically galvanized samples in each solution.

From a brief overview of the corrosion rates, the solution with the greatest corrosivity towards a mechanically galvanized sample is (0,350,700). This solution contains 0 ppm CaCO$_3$, 350 ppm CaCl$_2$ and 700 ppm CaSO$_4$. The solution that was least aggressive against a mechanically galvanized sample was solution (90,0,0), containing 90 ppm CaCO$_3$, 0 ppm CaCl$_2$ and 0 ppm CaSO$_4$. These results were as expected as soluble salts, Cl$^-$ and SO$_4^{2-}$, have proven to be aggressive towards galvanized steel while CO$_3^{2-}$ is needed to form the protective scale on the outer surface.
### Table 3.6: Corrosion Rate of Mechanically Galvanized Steel Samples

<table>
<thead>
<tr>
<th>Solution</th>
<th>$E_{corr}$ (V vs. Ag/AgCl)</th>
<th>$\beta_a$ (mV/decade)</th>
<th>$\beta_c$ (mV/decade)</th>
<th>$i_{corr}$ (A/cm²)</th>
<th>Corrosion Rate (µm/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0,50,0)</td>
<td>-0.8390</td>
<td>0.0125</td>
<td>0.0400</td>
<td>9.45x10^{-8}</td>
<td>1</td>
</tr>
<tr>
<td>(0,150,0)</td>
<td>-0.8538</td>
<td>0.0091</td>
<td>10.0000</td>
<td>1.79x10^{-6}</td>
<td>27</td>
</tr>
<tr>
<td>(0,250,0)</td>
<td>-0.8950</td>
<td>0.0080</td>
<td>10.0000</td>
<td>1.53x10^{-7}</td>
<td>2</td>
</tr>
<tr>
<td>(0,350,0)</td>
<td>-0.9153</td>
<td>0.0070</td>
<td>10.0000</td>
<td>3.94x10^{-7}</td>
<td>6</td>
</tr>
<tr>
<td>(0,0,100)</td>
<td>-0.9141</td>
<td>0.0125</td>
<td>10.0000</td>
<td>5.38x10^{-7}</td>
<td>8</td>
</tr>
<tr>
<td>(0,0,300)</td>
<td>-0.9521</td>
<td>0.0100</td>
<td>10.0000</td>
<td>4.11x10^{-7}</td>
<td>6</td>
</tr>
<tr>
<td>(0,0,500)</td>
<td>-0.9694</td>
<td>0.0095</td>
<td>10.0000</td>
<td>2.76x10^{-7}</td>
<td>4</td>
</tr>
<tr>
<td>(0,0,700)</td>
<td>-0.9622</td>
<td>0.0075</td>
<td>10.0000</td>
<td>1.18x10^{-6}</td>
<td>18</td>
</tr>
<tr>
<td>(30,0,0)</td>
<td>-0.7174</td>
<td>0.0370</td>
<td>0.0500</td>
<td>3.07x10^{-7}</td>
<td>5</td>
</tr>
<tr>
<td>(60,0,0)</td>
<td>-0.7289</td>
<td>0.0350</td>
<td>0.0425</td>
<td>5.20x10^{-8}</td>
<td>0.8</td>
</tr>
<tr>
<td>(90,0,0)</td>
<td>-0.6988</td>
<td>0.0250</td>
<td>0.0500</td>
<td>4.64x10^{-8}</td>
<td>0.7</td>
</tr>
<tr>
<td>(120,0,0)</td>
<td>-0.7591</td>
<td>0.0350</td>
<td>0.0600</td>
<td>2.23x10^{-7}</td>
<td>3</td>
</tr>
<tr>
<td>(0,50,100)</td>
<td>-0.9368</td>
<td>0.0120</td>
<td>10.0000</td>
<td>1.97x10^{-7}</td>
<td>3</td>
</tr>
<tr>
<td>(0,50,700)</td>
<td>-0.9784</td>
<td>0.0100</td>
<td>0.0500</td>
<td>7.87x10^{-8}</td>
<td>1</td>
</tr>
<tr>
<td>(0,350,100)</td>
<td>-0.9391</td>
<td>0.0100</td>
<td>10.0000</td>
<td>6.74x10^{-7}</td>
<td>10</td>
</tr>
<tr>
<td>(0,350,700)</td>
<td>-0.9366</td>
<td>0.0093</td>
<td>10.0000</td>
<td>8.06x10^{-7}</td>
<td>122</td>
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<tr>
<td>(30,50,0)</td>
<td>-0.8274</td>
<td>0.0250</td>
<td>0.6000</td>
<td>5.63x10^{-7}</td>
<td>9</td>
</tr>
<tr>
<td>(30,350,0)</td>
<td>-0.2265</td>
<td>0.0350</td>
<td>10.0000</td>
<td>2.11x10^{-7}</td>
<td>3</td>
</tr>
<tr>
<td>(120,50,0)</td>
<td>-0.8726</td>
<td>0.0350</td>
<td>0.1000</td>
<td>1.84x10^{-7}</td>
<td>3</td>
</tr>
<tr>
<td>(120,350,0)</td>
<td>-0.8922</td>
<td>0.0125</td>
<td>10.0000</td>
<td>2.02x10^{-7}</td>
<td>3</td>
</tr>
<tr>
<td>(30,0,100)</td>
<td>-0.9457</td>
<td>0.0450</td>
<td>10.0000</td>
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<td>(30,0,700)</td>
<td>-0.9441</td>
<td>0.0100</td>
<td>10.0000</td>
<td>1.51x10^{-6}</td>
<td>23</td>
</tr>
<tr>
<td>(120,0,100)</td>
<td>-0.8839</td>
<td>0.0175</td>
<td>10.0000</td>
<td>8.68x10^{-7}</td>
<td>13</td>
</tr>
<tr>
<td>(120,0,700)</td>
<td>-0.9328</td>
<td>0.0085</td>
<td>10.0000</td>
<td>4.26x10^{-7}</td>
<td>6</td>
</tr>
</tbody>
</table>
3.0 Results & Discussion

### Tafel Plot

<table>
<thead>
<tr>
<th>Solution</th>
<th>$E_{corr}$ (V vs. Ag/AgCl)</th>
<th>$\beta_a$ (mV/decade)</th>
<th>$\beta_c$ (mV/decade)</th>
<th>$i_{corr}$ (A/cm²)</th>
<th>Corrosion Rate (µm/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(30,50,100)</td>
<td>-0.3307</td>
<td>0.0350</td>
<td>10.0000</td>
<td>2.16x10^{-7}</td>
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</tr>
<tr>
<td>(30,50,700)</td>
<td>-1.1430</td>
<td>0.0350</td>
<td>10.0000</td>
<td>2.97x10^{6}</td>
<td>45</td>
</tr>
<tr>
<td>(30,350,100)</td>
<td>-0.3634</td>
<td>0.0800</td>
<td>10.0000</td>
<td>8.28x10^{-7}</td>
<td>13</td>
</tr>
<tr>
<td>(30,350,700)</td>
<td>-0.9441</td>
<td>0.0073</td>
<td>10.0000</td>
<td>7.73x10^{-7}</td>
<td>12</td>
</tr>
<tr>
<td>(120,50,100)</td>
<td>-0.8832</td>
<td>0.0170</td>
<td>10.0000</td>
<td>2.56x10^{6}</td>
<td>39</td>
</tr>
<tr>
<td>(120,50,700)</td>
<td>-1.0245</td>
<td>0.0350</td>
<td>10.0000</td>
<td>1.00x10^{-7}</td>
<td>2</td>
</tr>
<tr>
<td>(120,350,100)</td>
<td>-0.9025</td>
<td>0.0073</td>
<td>10.0000</td>
<td>1.39x10^{6}</td>
<td>21</td>
</tr>
<tr>
<td>(120,350,700)</td>
<td>-0.9252</td>
<td>0.0078</td>
<td>10.0000</td>
<td>1.79x10^{6}</td>
<td>27</td>
</tr>
</tbody>
</table>

#### 3.2.1.4 Steel Samples

Following electrochemical experimentation, the samples were retained to investigate the extent of corrosion and corrosion products formed. Samples were measured for overall thickness, coating thickness and weight both prior to testing and following drying after testing. The results are presented in Table 3.7. The precision of the overall thickness gauge and coating thickness gauge are 25.4 µm and 0.254 µm, respectively. Due to this, the accuracy of the difference in overall thickness and coating thickness before and after testing leaves a little to be desired. Therefore, the most valuable column in Table 3.7 is the difference in sample mass prior to and following electrochemical experimentation.

According to the mass difference results, the mass of all samples decreased following the electrochemical testing due to small amounts of metal loss except for the samples exposed to solutions containing only CaCO₃. This reiterates that a protective scale is formed, ZnCO₃, on the outer surface to protect against metal loss.
### Table 3.7: Before and After Mechanically Galvanized Steel Samples

<table>
<thead>
<tr>
<th>Solution</th>
<th>Before Testing</th>
<th>After Testing</th>
<th>Mass Diff</th>
<th>Thick Diff</th>
<th>Coat Diff</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mass (mg)</td>
<td>Thick (mm)</td>
<td>Coats (μm)</td>
<td>Mass (mg)</td>
<td>Thick (mm)</td>
</tr>
<tr>
<td>(0,50,0)</td>
<td>478.0</td>
<td>1.956</td>
<td>24.1</td>
<td>477.4</td>
<td>2.362</td>
</tr>
<tr>
<td>(0,150,0)</td>
<td>477.7</td>
<td>2.007</td>
<td>24.6</td>
<td>473.0</td>
<td>2.184</td>
</tr>
<tr>
<td>(0,250,0)</td>
<td>477.7</td>
<td>1.956</td>
<td>21.1</td>
<td>475.8</td>
<td>1.981</td>
</tr>
<tr>
<td>(0,350,0)</td>
<td>475.3</td>
<td>2.134</td>
<td>22.4</td>
<td>470.5</td>
<td>2.769</td>
</tr>
<tr>
<td>(0,0,100)</td>
<td>481.1</td>
<td>1.905</td>
<td>24.6</td>
<td>480.8</td>
<td>1.981</td>
</tr>
<tr>
<td>(0,0,300)</td>
<td>482.0</td>
<td>1.981</td>
<td>23.6</td>
<td>480.1</td>
<td>2.057</td>
</tr>
<tr>
<td>(0,0,500)</td>
<td>480.6</td>
<td>1.956</td>
<td>24.9</td>
<td>477.5</td>
<td>2.235</td>
</tr>
<tr>
<td>(0,0,700)</td>
<td>479.1</td>
<td>1.905</td>
<td>28.4</td>
<td>472.7</td>
<td>2.362</td>
</tr>
<tr>
<td>(30,0,0)</td>
<td>479.5</td>
<td>1.981</td>
<td>21.6</td>
<td>480.4</td>
<td>2.032</td>
</tr>
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<td>(60,0,0)</td>
<td>474.4</td>
<td>1.880</td>
<td>22.4</td>
<td>475.2</td>
<td>1.981</td>
</tr>
<tr>
<td>(90,0,0)</td>
<td>475.9</td>
<td>1.880</td>
<td>22.1</td>
<td>476.9</td>
<td>1.956</td>
</tr>
<tr>
<td>(120,0,0)</td>
<td>472.0</td>
<td>1.854</td>
<td>22.9</td>
<td>472.8</td>
<td>1.930</td>
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<tr>
<td>(0,50,100)</td>
<td>478.0</td>
<td>1.930</td>
<td>22.9</td>
<td>477.1</td>
<td>2.007</td>
</tr>
<tr>
<td>(0,50,700)</td>
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<td>1.930</td>
<td>23.6</td>
<td>470.4</td>
<td>2.261</td>
</tr>
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<td>2.134</td>
<td>24.6</td>
<td>473.0</td>
<td>2.946</td>
</tr>
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<td>(0,350,700)</td>
<td>479.0</td>
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<td>22.9</td>
<td>471.0</td>
<td>2.184</td>
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<td>(30,50,0)</td>
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<td>2.108</td>
<td>21.6</td>
<td>474.2</td>
<td>2.007</td>
</tr>
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<td>(30,350,0)</td>
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<td>2.108</td>
<td>22.9</td>
<td>474.4</td>
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<td>22.9</td>
<td>476.3</td>
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<td>19.8</td>
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<td>478.5</td>
<td>2.007</td>
<td>24.6</td>
<td>476.6</td>
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<td>(30,0,700)</td>
<td>475.2</td>
<td>2.007</td>
<td>23.6</td>
<td>470.4</td>
<td>2.362</td>
</tr>
<tr>
<td>(120,0,100)</td>
<td>479.4</td>
<td>2.057</td>
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<td>2.057</td>
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<tr>
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<td>2.007</td>
<td>27.4</td>
<td>471.8</td>
<td>2.083</td>
</tr>
</tbody>
</table>
3.0 Results & Discussion

3.2.1.5 Discussion

While the correlation is not exact due to the formation of corrosion products, the general trend was that the greater the mass loss, the greater the corrosion rate. The calculated corrosion rates varied from 1 to 122 μm/yr. Of the electrolytes created to comply with the AASHTO environmental recommendations only two solutions, or 15%, responded with corrosion rates that exceeded that of the corresponding corrosion model which conservatively estimates 15 μm/yr for the first two years of zinc degradation. Those solutions are (30,0,100) and (120,50,100) with calculated corrosion rates of 21 μm/yr and 39 μm/yr, respectively.

The United Kingdom guidelines estimate a zinc loss rate of 14 μm/yr for aggressive environments containing 50 to 250 ppm chlorides and 240 to 600 ppm sulphates (Table 1.9 and Table 1.8, respectively). Of the solutions created to simulate these environments, 25% returned corrosion rates greater than 14 μm/yr and 40% of the solutions created to extend beyond the design criteria of both AASHTO and the UK durability guidelines returned corrosion rates greater than 15 μm/yr.

The effects of adding CaCO₃ to electrolytes are presented in Table 3.8:
Table 3.8: Impact of CaCO₃ Additions

<table>
<thead>
<tr>
<th>Electrolyte (ppm)</th>
<th>Corrosion Rate (μm/yr)</th>
<th>Mass Difference (mg)</th>
<th>Electrolyte (ppm)</th>
<th>Corrosion Rate (μm/yr)</th>
<th>Mass Difference (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0,50,0)</td>
<td>1</td>
<td>-0.5</td>
<td>(30,50,0)</td>
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<td>-0.7</td>
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<tr>
<td></td>
<td></td>
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<td>-4.7</td>
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<td>-1.0</td>
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<td>-5.4</td>
</tr>
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<tr>
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<td></td>
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<td>13</td>
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</tr>
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<td>(30,350,100)</td>
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<td>12</td>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(120,350,700)</td>
<td>27</td>
<td>-9.4</td>
</tr>
</tbody>
</table>

Solutions containing only CaCO₃, (30,0,0), (60,0,0), (90,0,0) and (120,0,0), had slow corrosion rates in comparison and were the only four samples to increase in mass following testing. However, the addition of CaCO₃ to the other solutions demonstrated no consistency in the affect on corrosion rates or mass difference.
3.2.2 **HOT-DIP GALVANIZED STEEL SAMPLES**

The HDG samples were taken from a flat sheet of AIL inventory. Samples complied with Canadian Standards Association (CSA) G401-07 for corrugated steel pipe with a zinc coating of 64 μm nominal thickness. Again, as the samples were cut from a sheet the edges were not coated but this did not affect the test results.

3.2.2.1 **Electrolyte Properties**

The properties of each solution were determined by testing a sample of each solution with titration strips as well as probes and accompanying multimeter, as discussed in Section 2.2.2 Hot-Dip Galvanized Steel Samples. The solutions and measured properties are presented in Table 3.9.
### Table 3.9: Solution Properties

<table>
<thead>
<tr>
<th>Solution (\text{CO}_3^{2-},\text{Cl}^-,\text{SO}_4^{2-}) (ppm)</th>
<th>(\text{CaCO}_3) (mg)</th>
<th>(\text{CaCl}_2) (mg)</th>
<th>(\text{CaSO}_4) (mg)</th>
<th>(\text{pH})</th>
<th>(T) (°C)</th>
<th>TDS (ppm)</th>
<th>Conductivity (μS/cm)</th>
<th>Salinity (ppt)</th>
<th>Probe</th>
<th>Strips</th>
<th>pH (ppm)</th>
<th>Cl(^-) (ppm)</th>
<th>SO(_4^{2-}) (ppm)</th>
<th>CaCO(_3) (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0,50,0)</td>
<td>0.0</td>
<td>76.7</td>
<td>0.0</td>
<td>7.85</td>
<td>22.6</td>
<td>134</td>
<td>267</td>
<td>0.126</td>
<td>~ 8</td>
<td>~ 85</td>
<td>&lt; 200</td>
<td>120 - 250</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0,150,0)</td>
<td>0.0</td>
<td>235.3</td>
<td>0.0</td>
<td>7.84</td>
<td>22.5</td>
<td>245</td>
<td>489</td>
<td>0.235</td>
<td>~ 8</td>
<td>~ 164</td>
<td>&lt; 200</td>
<td>~ 250</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0,250,0)</td>
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<td>395.0</td>
<td>0.0</td>
<td>8.21</td>
<td>23.5</td>
<td>407</td>
<td>812</td>
<td>0.396</td>
<td>8 - 9</td>
<td>~ 307</td>
<td>&lt; 200</td>
<td>~ 425</td>
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<tr>
<td>(0,350,0)</td>
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<td>0.0</td>
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<td>2540</td>
<td>5070</td>
<td>2.730</td>
<td>6 - 7</td>
<td>&gt; 643</td>
<td>&lt; 200</td>
<td>~ 425</td>
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<td></td>
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<tr>
<td>(0,0,100)</td>
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<td>0.0</td>
<td>179.5</td>
<td>7.05</td>
<td>23.3</td>
<td>149</td>
<td>299</td>
<td>0.142</td>
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<td>~ 36</td>
<td>&lt; 200</td>
<td>~ 250</td>
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<td></td>
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<td>536.4</td>
<td>7.01</td>
<td>23.2</td>
<td>229</td>
<td>454</td>
<td>0.221</td>
<td>~ 7</td>
<td>36 - 42</td>
<td>200 - 400</td>
<td>~ 250</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0,0,500)</td>
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<td>0.0</td>
<td>897.7</td>
<td>6.77</td>
<td>20.6</td>
<td>298</td>
<td>599</td>
<td>0.291</td>
<td>~ 7</td>
<td>36 - 42</td>
<td>400 - 800</td>
<td>~ 250</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0,0,700)</td>
<td>0.0</td>
<td>0.0</td>
<td>1253.7</td>
<td>7.31</td>
<td>22.7</td>
<td>442</td>
<td>884</td>
<td>0.434</td>
<td>~ 7</td>
<td>36 - 42</td>
<td>400 - 800</td>
<td>250 - 425</td>
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</tr>
<tr>
<td>(30,0,0)</td>
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<td>0.0</td>
<td>0.0</td>
<td>8.50</td>
<td>23.8</td>
<td>91</td>
<td>182</td>
<td>0.085</td>
<td>7 - 8</td>
<td>~ 46</td>
<td>&lt; 200</td>
<td>120 - 250</td>
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<td>(60,0,0)</td>
<td>98.8</td>
<td>0.0</td>
<td>0.0</td>
<td>8.47</td>
<td>23.6</td>
<td>94</td>
<td>188</td>
<td>0.088</td>
<td>7 - 8</td>
<td>~ 53</td>
<td>&lt; 200</td>
<td>120 - 250</td>
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<td></td>
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<td>(90,0,0)</td>
<td>152.8</td>
<td>0.0</td>
<td>0.0</td>
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<td>23.3</td>
<td>99</td>
<td>199</td>
<td>0.094</td>
<td>~7</td>
<td>~ 46</td>
<td>&lt; 200</td>
<td>120 - 250</td>
<td></td>
<td></td>
</tr>
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<td>0.0</td>
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<td>22.2</td>
<td>104</td>
<td>209</td>
<td>0.099</td>
<td>~ 7</td>
<td>~ 36</td>
<td>&lt; 200</td>
<td>120 - 250</td>
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<td>78.2</td>
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<td>22.3</td>
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<td>388</td>
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<td>~ 85</td>
<td>&lt; 200</td>
<td>~ 250</td>
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<td></td>
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<tr>
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<td>488</td>
<td>955</td>
<td>0.477</td>
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<td>75 - 85</td>
<td>400 - 800</td>
<td>250 - 425</td>
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<tr>
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<td>442</td>
<td>881</td>
<td>0.401</td>
<td>~ 7</td>
<td>~ 345</td>
<td>&lt; 200</td>
<td>250 - 425</td>
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<tr>
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<td>550.5</td>
<td>1254.5</td>
<td>7.14</td>
<td>21.1</td>
<td>643</td>
<td>1293</td>
<td>0.650</td>
<td>6 - 7</td>
<td>~ 345</td>
<td>400 - 800</td>
<td>250 - 425</td>
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<td></td>
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</tbody>
</table>
## 3.0 Results & Discussion

<table>
<thead>
<tr>
<th>Solution $(CO_3^{2-}, Cl^-, SO_4^{2-})$ (ppm)</th>
<th>CaCO$_3$ (mg)</th>
<th>CaCl$_2$ (mg)</th>
<th>CaSO$_4$ (mg)</th>
<th>Probe</th>
<th>Strips</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH</td>
<td>T (°C)</td>
<td>TDS (ppm)</td>
<td>Conductivity (μS/cm)</td>
<td>Salinity (ppt)</td>
</tr>
<tr>
<td>(30,50,0)</td>
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<td>22.8</td>
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<td>7.63</td>
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<td>20.6</td>
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<td>545.3</td>
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<td>6.97</td>
<td>15.7</td>
</tr>
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<td>(30,0,100)</td>
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<td>0.0</td>
<td>181.3</td>
<td>8.03</td>
<td>22.4</td>
</tr>
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<td>(30,700)</td>
<td>51.0</td>
<td>0.0</td>
<td>1252.9</td>
<td>7.75</td>
<td>21.9</td>
</tr>
<tr>
<td>(120,0,100)</td>
<td>203.1</td>
<td>0.0</td>
<td>180.6</td>
<td>7.68</td>
<td>22.0</td>
</tr>
<tr>
<td>(120,700)</td>
<td>201.0</td>
<td>0.0</td>
<td>1255.0</td>
<td>8.11</td>
<td>22.3</td>
</tr>
<tr>
<td>(30,50,100)</td>
<td>49.8</td>
<td>80.2</td>
<td>181.4</td>
<td>8.05</td>
<td>22.8</td>
</tr>
<tr>
<td>(30,50,700)</td>
<td>49.7</td>
<td>81.0</td>
<td>1255.8</td>
<td>7.92</td>
<td>23.0</td>
</tr>
<tr>
<td>(30,350,100)</td>
<td>50.5</td>
<td>549.1</td>
<td>180.1</td>
<td>8.14</td>
<td>23.4</td>
</tr>
<tr>
<td>(30,350,700)</td>
<td>49.7</td>
<td>548.1</td>
<td>1253.2</td>
<td>7.94</td>
<td>23.3</td>
</tr>
<tr>
<td>(120,50,100)</td>
<td>199.6</td>
<td>77.8</td>
<td>179.2</td>
<td>7.64</td>
<td>22.6</td>
</tr>
<tr>
<td>(120,50,700)</td>
<td>200.3</td>
<td>79.6</td>
<td>1254.6</td>
<td>7.97</td>
<td>24.0</td>
</tr>
<tr>
<td>(120,350,100)</td>
<td>201.5</td>
<td>548.1</td>
<td>181.4</td>
<td>7.74</td>
<td>24.0</td>
</tr>
<tr>
<td>(120,350,700)</td>
<td>199.6</td>
<td>547.7</td>
<td>1252.9</td>
<td>7.70</td>
<td>23.8</td>
</tr>
</tbody>
</table>
As with the solutions used for the mechanically galvanized samples, the titration strips did not offer the same precision or accuracy as the handheld multimeter and accompanying probes, with exception to the chloride strips.

### 3.2.2.2 Electrochemical Testing

Again following the settlement period and determination of the OCP (included in Appendix B), PDP were conducted following the parameters stated in Section 2.2.2 Hot-Dip Galvanized Steel Samples.

The reproducibility of the Ivium CompactStat portable potentiostat and SCE reference electrode was confirmed by conducting a series of three experiments under the same conditions. Below is an example with an electrolyte containing 30 ppm CaCO₃ and 350 ppm CaCl₂. The results obtained, presented in Figure 3.41 are within an acceptable range of variance; the corrosion potentials are within 50 mV and the corrosion current density within 10 dA.

![Reproducibility plots](image)

*Figure 3.41: Reproducibility plots.*

The raw potentiodynamic plots for the remainder of the data are presented in Figure 3.42 through to Figure 3.48.
3.0 Results & Discussion

The surfaces of the HDG samples are not as smooth or homogenous as those of mechanically galvanized samples. While they provide more insight into actual field behaviour, the plots are not as neat or clean cut. However, general trends and behaviour can be determined.

All four curves in Figure 3.43 are the same general shape, again demonstrating the characteristic horizontal plateau observed of the mechanically galvanized samples in Section 3.2.1.2
Electrochemical Testing. Also, it can be observed from the above plot that the corrosion current density increases with increasing concentration of CaSO$_4$.

Figure 3.44: Potentiodynamic plots for (x,0,0) solutions.

The curves for electrolytes (30,0,0) and (60,0,0) demonstrate greater slopes in the anodic branch of the Tafel plots and the corrosion potential less negative than those corresponding to electrolytes containing CaCl$_2$ or CaSO$_4$. Sample (30,0,0) actually has two equilibrium points. As solutions containing CaCO$_3$ are believed to produce ZnCO$_3$, the first (lower) equilibrium point could be the formation of protective scale while the second equilibrium point (higher) the degradation of that same coating as only 30 ppm CaCO$_3$ are readily available.
The curves in Figure 3.45 are distinctly separated into pairs. The solutions containing greater amounts of CaCl$_2$, solutions (0,350,100) and (0,350,700), have corrosion current densities indicative of lower corrosion rates but also less negative corrosion potentials. This was unexpected and will be further discussed in Section 3.1.2.5 Discussion. The shapes of the curves are more exponential in the anodic branch than the shallower slopes of the solutions containing only 50 ppm CaCl$_2$. The fluctuating concentrations of CaSO$_4$ appear to have negligible effects on corrosion potential and slope shape. However, the corrosion current density increases slightly with increasing CaSO$_4$ concentration.
Solutions containing 120 ppm CaCO$_3$ yielded curves similar in shape, corrosion potential and corrosion current density; the concentration of CaCl$_2$ negligibly affected results. Curves with only 30 ppm CaCO$_3$ were far more influenced by chloride concentration. The electrolyte that contained 350 ppm CaCl$_2$ returned a greater corrosion current density/corrosion rate than the electrolyte containing only 50 ppm.

It is important to note that while the higher concentrations of CaCO$_3$ can return greater corrosion current densities, indicative of faster corrosion rate and generally assumed greater metal loss, the corrosion current density relates only to the rate of reaction. In the case of high concentration of CaCO$_3$ the most likely reaction to occur is the formation of ZnCO$_3$, the protective scale or zinc patina. So while the rate of reaction is greater, it does not necessarily indicate that the solution is rapidly attacking the metal surface exposed, but in these cases it is more likely that the high concentrations of CaCO$_3$ is encouraging the rapid formation of ZnCO$_3$. This phenomenon is further emphasized with SEM images and EDS analyses.
3.0 Results & Discussion

Again, all curves have steep anodic curves as has been previously determined characteristic of solutions containing CaCO₃. In addition, the corrosion potential is more negative for solutions containing a greater concentration, 120 ppm, of CaCO₃. The corrosion current density is significantly affected by an increase in concentration of CaSO₄, from 100 ppm to 700 ppm, for solutions containing 30 ppm CaCO₃ and only mildly affected for the solutions containing a greater concentration of CaCO₃, (120,0,100) and (120,0,700).

Figure 3.47: Potentiodynamic plots for \((x,0,z)\) solutions.

Figure 3.48: Potentiodynamic plots for \((x,y,z)\) solutions.
The above plot, Figure 3.48, presents eight curves of varying concentrations of CaCO$_3$, CaCl$_2$ and CaSO$_4$. While there is a fair bit occurring in the plot, it is obvious that the electrolyte with the greatest corrosion current density, and therefore reaction rate, is solution (120,350,700).

### 3.2.2.3 Corrosion Rate

Tafel plots, the Butler-Volmer equation and the equation for corrosion rate were again used to determine the relative corrosivity of the solutions with respect to a HDG steel sample. The calculated corrosion rates are presented in Table 3.10:

<table>
<thead>
<tr>
<th>Solution (CO$_3^{2-}$,Cl$^-$,SO$_4^{2-}$) (ppm)</th>
<th>Tafel Plot</th>
<th>Corrosion Rate μm/yr</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{corr}$ (V vs. SCE)</td>
<td>$\beta_a$ (mV/decade)</td>
<td>$\beta_c$ (mV/decade)</td>
</tr>
<tr>
<td>(0,50,0)</td>
<td>-1.0005</td>
<td>0.0200</td>
</tr>
<tr>
<td>(0,150,0)</td>
<td>-0.3439</td>
<td>0.0900</td>
</tr>
<tr>
<td>(0,250,0)</td>
<td>-0.9557</td>
<td>0.0125</td>
</tr>
<tr>
<td>(0,350,0)</td>
<td>-0.3169</td>
<td>0.1000</td>
</tr>
<tr>
<td>(0,0,100)</td>
<td>-1.0077</td>
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<tr>
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</tr>
<tr>
<td>(0,700)</td>
<td>-0.9724</td>
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</tr>
<tr>
<td>(90,0,0)</td>
<td>-0.9586</td>
<td>0.0300</td>
</tr>
<tr>
<td>(120,0,0)</td>
<td>-1.0381</td>
<td>0.0400</td>
</tr>
<tr>
<td>(0,50,100)</td>
<td>-0.9399</td>
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</tr>
<tr>
<td>(0,350,700)</td>
<td>-0.4800</td>
<td>0.1000</td>
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</table>
### 3.0 Results & Discussion

<table>
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<tr>
<th>Solution (CO$_3^{2-}$,Cl$^-$,SO$_4^{2-}$) (ppm)</th>
<th>E$_{corr}$ (V vs. SCE)</th>
<th>$\beta_a$ (mV/decade)</th>
<th>$\beta_c$ (mV/decade)</th>
<th>i$_{corr}$ (A/cm$^2$)</th>
<th>Corrosion Rate µm/yr</th>
</tr>
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<td>0.0800</td>
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<tr>
<td>(30,50,700)</td>
<td>-0.4261</td>
<td>0.0600</td>
<td>0.1000</td>
<td>2.22x10$^{-7}$</td>
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<tr>
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<td>0.1000</td>
<td>6.98x10$^{-8}$</td>
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<td>(120,350,100)</td>
<td>-0.4328</td>
<td>0.0400</td>
<td>0.0300</td>
<td>1.05x10$^{-8}$</td>
<td>0.2</td>
</tr>
<tr>
<td>(120,350,700)</td>
<td>-1.0139</td>
<td>0.0250</td>
<td>1.0000</td>
<td>9.78x10$^{-7}$</td>
<td>15</td>
</tr>
</tbody>
</table>

Briefly glancing at the results, the highest corrosion rate was discovered with solution (0,0,700), containing 0 ppm CaCO$_3$, 0 ppm CaCl$_2$ and 700 ppm CaSO$_4$. The solutions that yielded the slowest reaction rate towards the HDG steel samples were solutions (30,0,100) (120,0,100) and (120,0,700). The corrosion rates and how they correlate with the various electrolytes is further discussed in Section 3.1.2.5 Discussion.
3.2.2.4 Steel Samples

The HDG steel samples were measured for overall thickness, coating thickness and mass both prior to testing and following drying after testing had been completed. The results are presented below. Again, the precision on the overall thickness and coating thickness gauges were less than ideal, leaving the results, presented in Table 3.11, slightly erroneous.

### Table 3.11: Before and After Hot-Dip Galvanized Steel Samples

<table>
<thead>
<tr>
<th>Solution (CO$_3^{2-}$,Cl$^-$,SO$_4^{2-}$) (ppm)</th>
<th>Before Testing</th>
<th>After Testing</th>
<th>Thick Diff (mg)</th>
<th>Coat Diff (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass (mg)</td>
<td>Thick (mm)</td>
<td>Coat (μm)</td>
<td>Mass (mg)</td>
<td>Thick (mm)</td>
</tr>
<tr>
<td>(0,50,0)</td>
<td>2038.6</td>
<td>1.346</td>
<td>58.4</td>
<td>2043.1</td>
</tr>
<tr>
<td>(0,150,0)</td>
<td>2024.7</td>
<td>1.321</td>
<td>63.5</td>
<td>2030.0</td>
</tr>
<tr>
<td>(0,250,0)</td>
<td>2031.5</td>
<td>1.321</td>
<td>69.3</td>
<td>2036.5</td>
</tr>
<tr>
<td>(0,350,0)</td>
<td>2022.0</td>
<td>1.321</td>
<td>60.2</td>
<td>2028.1</td>
</tr>
<tr>
<td>(0,0,100)</td>
<td>2033.8</td>
<td>1.550</td>
<td>55.9</td>
<td>2034.3</td>
</tr>
<tr>
<td>(0,0,300)</td>
<td>2070.5</td>
<td>1.473</td>
<td>55.1</td>
<td>2067.2</td>
</tr>
<tr>
<td>(0,0,500)</td>
<td>2056.8</td>
<td>1.499</td>
<td>61.0</td>
<td>2053.8</td>
</tr>
<tr>
<td>(0,0,700)</td>
<td>1692.7</td>
<td>1.422</td>
<td>66.8</td>
<td>1690.6</td>
</tr>
<tr>
<td>(30,0,0)</td>
<td>1697.0</td>
<td>1.321</td>
<td>74.4</td>
<td>1700.5</td>
</tr>
<tr>
<td>(60,0,0)</td>
<td>2071.4</td>
<td>1.575</td>
<td>54.6</td>
<td>2076.2</td>
</tr>
<tr>
<td>(90,0,0)</td>
<td>1690.9</td>
<td>1.778</td>
<td>55.9</td>
<td>1689.0</td>
</tr>
<tr>
<td>(120,0,0)</td>
<td>2046.9</td>
<td>2.388</td>
<td>78.0</td>
<td>2048.8</td>
</tr>
<tr>
<td>(0,50,100)</td>
<td>1694.7</td>
<td>2.210</td>
<td>73.7</td>
<td>1690.2</td>
</tr>
<tr>
<td>(0,50,700)</td>
<td>2056.8</td>
<td>2.032</td>
<td>59.2</td>
<td>2049.5</td>
</tr>
<tr>
<td>(0,350,100)</td>
<td>2023.6</td>
<td>1.473</td>
<td>56.6</td>
<td>2028.1</td>
</tr>
<tr>
<td>(0,350,700)</td>
<td>2062.2</td>
<td>1.473</td>
<td>56.6</td>
<td>2066.8</td>
</tr>
<tr>
<td>(30,50,0)</td>
<td>2039.4</td>
<td>1.397</td>
<td>73.7</td>
<td>2043.1</td>
</tr>
<tr>
<td>(30,350,0)</td>
<td>1694.1</td>
<td>1.270</td>
<td>59.2</td>
<td>1697.7</td>
</tr>
</tbody>
</table>
### Results & Discussion

<table>
<thead>
<tr>
<th>Solution (CO$_3^{2-}$,Cl$^-$,SO$_4^{2-}$) (ppm)</th>
<th>Before Testing</th>
<th>After Testing</th>
<th>Thick</th>
<th>Coat Diff</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass (mg)</td>
<td>Thick (mm)</td>
<td>Coat (μm)</td>
<td>Mass (mg)</td>
<td>Thick (mm)</td>
</tr>
<tr>
<td>(120,50,0)</td>
<td>2032.3</td>
<td>1.778</td>
<td>64.3</td>
<td>2032.6</td>
</tr>
<tr>
<td>(120,350,0)</td>
<td>2034.2</td>
<td>1.727</td>
<td>62.7</td>
<td>2027.2</td>
</tr>
<tr>
<td>(30,0,100)</td>
<td>1689.6</td>
<td>1.829</td>
<td>56.6</td>
<td>1693.6</td>
</tr>
<tr>
<td>(30,0,700)</td>
<td>1983.8</td>
<td>1.473</td>
<td>62.7</td>
<td>1987.9</td>
</tr>
<tr>
<td>(120,0,100)</td>
<td>1699.3</td>
<td>2.057</td>
<td>64.3</td>
<td>1702.2</td>
</tr>
<tr>
<td>(120,0,700)</td>
<td>1689.1</td>
<td>1.346</td>
<td>69.3</td>
<td>1692.9</td>
</tr>
<tr>
<td>(30,50,100)</td>
<td>1696.6</td>
<td>1.676</td>
<td>57.7</td>
<td>1700.1</td>
</tr>
<tr>
<td>(30,50,700)</td>
<td>1693.1</td>
<td>1.705</td>
<td>71.9</td>
<td>1696.2</td>
</tr>
<tr>
<td>(30,350,100)</td>
<td>2037.0</td>
<td>2.667</td>
<td>59.2</td>
<td>2042.0</td>
</tr>
<tr>
<td>(30,350,700)</td>
<td>2053.6</td>
<td>2.311</td>
<td>61.7</td>
<td>2047.2</td>
</tr>
<tr>
<td>(120,50,100)</td>
<td>1683.1</td>
<td>1.880</td>
<td>65.3</td>
<td>1687.1</td>
</tr>
<tr>
<td>(120,50,700)</td>
<td>1687.1</td>
<td>2.235</td>
<td>64.3</td>
<td>1690.5</td>
</tr>
<tr>
<td>(120,350,100)</td>
<td>1690.4</td>
<td>2.083</td>
<td>62.7</td>
<td>1693.8</td>
</tr>
<tr>
<td>(120,350,700)</td>
<td>1696.3</td>
<td>1.397</td>
<td>74.4</td>
<td>1681.8</td>
</tr>
</tbody>
</table>

Unlike the mechanically galvanized samples, the HDG samples appear to increase in mass following testing for the majority of the electrolytes. This is further addressed in Section 3.1.2.5 Discussion.

Samples were also analyzed with a SEM and energy dispersive x-ray spectroscopy (EDS) to gain insight on the gross morphology of the sample surfaces as well as the corrosion products present. To obtain baseline knowledge, SEM and EDS were also conducted on an HDG surface not exposed to any solution to represent how a structure would appear at the time of initial installation. A sample EDS spectrum is provided in Figure 3.49 and SEM image in Figure 3.50 a).
It should be noted that there are three different peaks appearing for zinc (Zn) in the above EDS spectrum. This is due to the location of the emitted electrons and the shells from which the vacancies were filled; the energy in the emitted x-ray is characteristic of the two involved shells. Having more than one peak for an element indicates that different valence shells were involved in x-ray emitting.

Each EDS scan took 100 seconds to complete and created plots of intensity versus energy. The computer software, Quartz Xone – X-Ray Microanalysis System, quantified the results by calculating weight percent of the surface area dedicated to each element. Analyses were conducted on three randomly selected locations on each sample, of which averages were calculated to generate Table 3.12.
3.0 Results & Discussion

### Table 3.12: EDS Elemental Quantities

<table>
<thead>
<tr>
<th>Electrolyte ((\text{CO}_3^{2-}, \text{Cl}^-, \text{SO}_4^{2-})) (ppm)</th>
<th>Elemental Weight Percent (wt%) ((\sigma; \text{wt}%))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O</td>
</tr>
<tr>
<td>N/A</td>
<td>9.28 (0.63)</td>
</tr>
<tr>
<td>(0,250,0)</td>
<td>28.81 (1.77)</td>
</tr>
<tr>
<td>(0,0,700)</td>
<td>23.56 (1.16)</td>
</tr>
<tr>
<td>(90,0,0)</td>
<td>28.88 (3.43)</td>
</tr>
<tr>
<td>(0,50,100)</td>
<td>26.62 (4.95)</td>
</tr>
<tr>
<td>(120,350,0)</td>
<td>44.30 (0.70)</td>
</tr>
<tr>
<td>(120,0,100)</td>
<td>14.91 (1.79)</td>
</tr>
<tr>
<td>(120,350,700)</td>
<td>33.67</td>
</tr>
</tbody>
</table>

EDS was used as an analysis method to obtain general knowledge on the corrosion products and relative extent of zinc attack. This was accomplished by relative comparison of the weight percents for each sample, rather than taking their exact numerical value. As explained in 1.4.5.6 Energy Dispersive X-Ray Spectroscopy, EDS is not accurate at detecting light elements, such as carbon (C), boron (B), beryllium (Be), lithium (Li) and hydrogen (H). Carbon was detected on every sample surface, regardless of its presence in the electrolyte. Due to the erroneous results, carbon was removed and the remaining elements elemental weight percents normalized. Oxygen (O) is the most prominent element in corrosion products as it is the primary element of oxides (O\(^2\)), hydroxides (OH\(^-\)) and carbonates (CO\(_3^{2-}\)). Many of the other elements appearing in Table 3.12 are alloying elements in the galvanized zinc coating, such as aluminum (Al), silicon (Si), etc. Sulphur (S) appears on the samples that were submersed in electrolytes containing CaSO\(_4\)\(_2\) solutions (0,0,z). Calcium (Ca) was in every electrolyte, as the electrolytes were created from CaCO\(_3\), CaCl\(_2\) and CaSO\(_4\), but not always detected. In some cases peaks of one element will overlap those of another in the spectrum. When this happens the wrong element can be picked up or an element missed altogether if the peaks are less prominent. Iron (Fe) was only detected on samples on which the zinc layer had been depleted enough to expose the underlying steel substrate. These galvanized samples still have significant amounts of zinc present, indicating that the zinc layer has not completely degraded, but only exposed the steel in defined areas, further explained with the assistance of SEM images below.

SEM images were captured on all of the samples highlighted in Table 3.12. The images appear in Figure 3.50 a) through to Figure 3.51 d). Images were collected at 150x magnification to compare
surface morphologies caused by electrochemical reactions with different electrolytes. A second image of each sample, at 600x magnification, is provided in Appendix C.
3.0 Results & Discussion

Figure 3.50: a) HDG sample to demonstrate the surface morphology prior to exposure of an electrolyte; All remaining images are HDG sample surfaces, at 150x magnification, following electrochemical testing in b) solution (0,250,0); c) solution (0,0,700); and d) solution (90,0,0).
3.0 Results & Discussion

Figure 3.51: All images are HDG sample surfaces, at 150x magnification, following electrochemical testing in a) solution (0,50,100); b) solution (120,350,0); c) solution (120,0,100); and d) and solution (120,350,700).
3.0 Results & Discussion

Figure 3.50 a) of a HDG surface, not exposed to an electrolyte, comes from near the punched outer edge. This is the reason for the cracking that was observed to follow the grain boundaries. Otherwise the surface appears relatively smooth and homogenous with no deposits present. b) demonstrates a porous corrosion product covering the entire surface imaged. The corrosion is widespread and uniform, penetrating down to the steel substrate in some locations, as observed on the left side of the image. Some grain boundaries are visible in c) where the cracks extend down to the steel substrate below, as shown by the hole in the top center of the image. Again, the entire surface demonstrates evidence of electrochemical attack. d), on the other hand, is different. Iron does not show up in Table 3.12 and this is further emphasized in the SEM image. With exception to the areas that appear to have lost a thin layer of the outermost material, the surface resembles that in Figure 3.50 a) with minor cracks and little deposit. As this is of a sample exposed to solution containing only CaCO₃, the EDS and SEM further confirm that a protective scale is produced to protect the underlying zinc coated steel substrate.

Figure 3.51 a), the SEM image for an HDG sample subjected to PDP in a solution containing 50 ppm CaCl₂ and 100 ppm CaSO₄, shows the first evidence of localized pitting in the bottom left corner of the image. The areas of penetration extend to the steel substrate, while approximately half of the surface appears to be unaffected by degradation. Again, there are cracks around many of the grain boundaries. In image b) there is an extensive amount of deposit on the surface. The deposit is semi-spherical and porous in structure. There is also an inexplicable stringy cluster on the surface. While this may be a result of the electrochemical reaction, it is more likely a contaminant introduced to the sample prior to entering the SEM vacuum chamber. Other than some minor cracks along grain boundaries and superficial degradation of the outermost material, image c) closely reflects the unaffected surface of Figure 3.50 a). Again, this is a sample containing high CaCO₃ content. The surface in image d) has some deposit, both spherical and porous as well as platelet degradation, on the surface. The degradation appears over the entire surface and penetrates through many layers of the galvanized coating and reaches the underlying steel in some locations. This sample appears to have experienced the most extensive degradation which is consistent with the corrosion rate presented in Table 3.10.
3.0 Results & Discussion

3.2.2.5 Discussion

Trends were not as easy to distinguish for the HDG samples as they were for the mechanically galvaniz ed samples. The fluctuations in mass difference from before to after testing were surprising. However, the corrosion rates were easier to interpret for many of the sample sets and resistivity was also incorporated into the evaluation.

Referring back to Table 3.10 and the PDP plots in 3.2.2.2 Electrochemical Testing, the (0,0,0) samples did not increase in corrosion rate as expected. The Tafel plots are divided with (0,50,0) and (0,250,0) paired together with greater corrosion rates and more negative corrosion potentials than (0,150,0) and (0,350,0). It was expected that increasing the concentration of CaCl₂ would increase the corrosion rate. Conversely, the measured resistivity for (0,50,0) was above the acceptable AASHTO minimum of 3,000 Ω-cm. As the solubility of CaCl₂ is 74.5 g/100 g water (67), the amount of CaCl₂ present in an electrolyte influences resistivity; increasing the CaCl₂ content decreased resistivity resulting in the other three solutions returning resistivity values less than 3,000 Ω-cm.

The (0,0,z) samples acted precisely as anticipated. With increasing CaSO₄ concentration, the corrosion rate increased. The Tafel curves are all closely plotted with the corrosion potential within 18 mV of each other, floating around the vicinity of -1.0 V vs. SCE. The experimentation returned results reflecting the AASHTO soil model where solution (0,0,100) has an acceptable resistivity, but as concentration of CaSO₄ increased, resistivity decreased to unacceptable values. Again this is a function of solubility which is 0.255 g/100 g water for CaSO₄ (67).

Solutions (x,0,0) were again separated into pairs. Solutions (30,0,0) and (60,0,0) have less negative corrosion potentials and slower reaction rates than (90,0,0) and (120,0,0). The resistivity values for all (x,0,0) solutions exceeded the minimum recommended by AASHTO. Taking mass difference into account, the first two solutions had a greater increase in mass than the latter. This may indicate a buildup of scale at lesser concentrations with the reaction rate increasing at greater concentrations of CaCO₃. This was further emphasized with the SEM image in Figure 3.50 d). A smooth surface appeared under a layer of corrosion products or scale.

Combining CaCl₂ and CaSO₄ yielded intriguing results. The corrosion rate and decrease in mass were greater for solutions containing 50 ppm CaCl₂ than for solutions containing 350 ppm CaCl₂. While no solutions met the resistivity requirements, (0,50,100) was the closest to being acceptable.
Electrolytes containing CaCO₃ and CaCl₂ also yielded interesting results. When the concentration of CaCO₃ was 30 ppm, the influence of CaCl₂ was far greater. The electrolyte containing 350 ppm CaCl₂ returning a corrosion rate greater than 100 μm/yr while corrosion rate of the electrolyte containing only 50 ppm CaCl₂ returned a corrosion rate less than 1 μm/yr. However, when the concentration of CaCO₃ was 120 ppm, the amount of CaCl₂ had negligible effects on corrosion rate. While the mass differences did not follow the expected trends, the more rapid reaction rate at higher concentrations of CaCO₃ is consistent with the remaining results. The resistivity results were as expected; both (30,50,0) and (120,50,0) met the generic AASHTO requirements while solutions (30,350,0) and (120,350,0) did not.

Combining CaCO₃ and CaSO₄, solutions (x,0,z), created electrolytes yielding anticipated results; when the concentration of CaCO₃ was 120 ppm, the fluctuating concentration of CaSO₄ had little effect on corrosion rate, mass difference and corrosion potential. However, solution (30,0,100) and (30,0,700) did not follow the same trends or satisfy the resistivity requirements. In these samples the increase in CaSO₄ content significantly affected the corrosion rate, while still having little to no affect on the mass difference. In addition, the corrosion potential between the 120 ppm CaCO₃ and 30 ppm CaCO₃ increased from approximately -1.0 V vs. SCE to -0.38 V vs. SCE.

In summary, 38% of solutions created to satisfy AASHTO’s design criteria returned corrosion rates that exceeded the predicted maximum 15 μm/yr of zinc metal loss in the first two years of exposure. Of the electrolytes created to simulate environments that met AASHTO, 70% of solutions containing CaCO₃ had corrosion rates less than 15 μm/yr while only 33% of solutions not containing CaCO₃ yielded acceptable results. Of the solutions created to simulate UK aggressive environments, 75% exceeded the predicted maximum metal loss of 14 μm/yr, none of which contained CaCO₃. However, 90% of solutions that simulated electrolytes which exceeded the maximum recommended allowances on chlorides and sulphates, but contained CaCO₃, returned corrosion rates less than 15 μm/yr while only 60% of solutions that did not contain CaCO₃ gave rates in this predictable range.

The addition of CaCO₃, which is not currently an environmental parameter considered, was of great interest. As a result, a quick summary table has been constructed and is presented as Table 3.13:
### Table 3.13: Impact of CaCO<sub>3</sub> Additions

<table>
<thead>
<tr>
<th>Without CaCO&lt;sub&gt;3&lt;/sub&gt;</th>
<th>With CaCO&lt;sub&gt;3&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Electrolyte</strong> (CO&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;2-&lt;/sup&gt;, Cl&lt;sup&gt;-&lt;/sup&gt;, SO&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;2-&lt;/sup&gt;) (ppm)</td>
<td><strong>Corr Rate</strong> (μm/yr)</td>
</tr>
<tr>
<td>(0,50,0)</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>(0,350,0)</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>(0,0,100)</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>(0,0,700)</td>
<td>252</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>(0,50,100)</td>
<td>43</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>(0,50,700)</td>
<td>65</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>(0,350,100)</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>(0,350,700)</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The following can be said about solutions (x,y,z):

- For solutions containing CaCl<sub>2</sub>, reaction rate increased with the addition of CaCO<sub>3</sub> for all cases except one;
- For solutions containing CaSO<sub>4</sub>, corrosion rate decreased with increasing additions of CaCO<sub>3</sub>;
• For solutions containing 50 ppm CaCl₂ and either 100 or 700 ppm CaSO₄, corrosion rate decreased with increasing additions of CaCO₃;
• Without CaCO₃, (0,0,100), (0,0,700), (0,50,100) and (0,50,700) all exceeded the estimated corrosion rate of zinc in the first two years of service, 15 μm/yr;
• With CaCO₃, only (120,50,0), (30,350,0) and (120,350,0) exceeded 15 μm/yr; and
• As CaCO₃ has very low solubility (7.0 x 10⁻⁴ g/100 g water⁶⁷) resistivity was generally unaffected by the addition of CaCO₃.
4.0 Conclusions

The focus of the dissertation was waterside corrosion of galvanized soil-steel structures, specifically corrugated steel pipe (CSP), structural plate corrugated steel pipe (SPCSP) and mechanically stabilized earth (MSE) retaining walls. Discussion and experimentation were concerned with water environments and contributing factors that cause corrosion of galvanized steel.

AASHTO defined durability design criteria for unsaturated soil conditions for buried steel structures. As evident on the lateral reinforcements of the MSE walls and crowns of the culverts analyzed, AASHTO’s corrosion model demonstrates conservative coherence in these environments. However, it has become common practice for AASHTO’s design criteria and associated corrosion model to be used in all buried steel applications. The results in this dissertation provide evidence to conclude that the environmental parameters and associated corrosion model developed by AASHTO are not appropriate for use in the design of CSP/SPCSP servicing watercourses or soil-steel structures in wet-dry cyclic conditions.

This bold statement was most evident by field observations and testing then substantiated with laboratory experimentation. Many of the CSP sites were consistent with the crown of the structures, exposed only to unsaturated soil and atmosphere, in excellent condition while the inverts, exposed to wet-dry cyclic conditions or constant submersion, demonstrating clear signs of premature degradation. This was represented in Figure 3.26. These trends were again reiterated by the MSE walls with severe corrosion to the face of the wall but buried elements demonstrating similar appearances to a new install. The water samples collected at these locations were tested for compliance with the original design criteria and satisfied all environmental conditions.

Laboratory testing was completed to substantiate field findings. The following conclusions were made:

1. Due to the formation of corrosion products on sample surfaces, mass difference was not an appropriate method to measure corrosion on the HDG samples (Table 3.11);
2. As stated in literature, the resistivity of an electrolyte is directly related to the soluble salts contained within it; increasing concentrations of CaCl₂ and CaSO₄, with solubility of 74.5
g/100 g water and 0.255 g/100 g water, respectively, decreased resistivity while increasing CaCO$_3$, with low solubility of 7.0 \times 10^{-4} \text{g/100 g water}, had relatively little effect (Table 3.9);  

3. Electrolytes containing a high concentration of CaCO$_3$ with no other constituents or only low concentrations of CaCl$_2$ or CaSO$_4$ demonstrated the least amount of surface degradation most closely resembling the HDG surface not subjected to accelerated corrosion testing (Figure 3.50 and Figure 3.51); and  

4. While not the case every time, a general trend was observed in the relationship between corrosion rate and resistivity: as resistivity increases, corrosion rate decreases. This is demonstrated by the oscillating results of Figure 4.52

![Figure 4.52: Corrosion rate and resistivity.](image)

The addition of CaCO$_3$ had the following effects on HDG samples in a laboratory setting:

- Adding 30 ppm CaCO$_3$ to solutions containing only CaCl$_2$ – (0,y,0) to (30,y,0) – decreased the corrosion rates. However, adding 120 ppm CaCO$_3$ – (0,y,0) to (120,y,0) – increased the reaction rates of those same baseline solutions;
4.0 Conclusions

- Adding CaCO$_3$ to solutions containing only CaSO$_4$ – (0,0,z) to (x,0,z) – decreased corrosion rates; and
- Adding CaCO$_3$ to solutions containing CaSO$_4$ and 50 ppm CaCl$_2$ – (0,50,z) to (x,50,z) – decreased the corrosion rates. However, adding CaCO$_3$ to solutions containing CaSO$_4$ and 350 ppm CaCl$_2$ – (0,350,z) to (x,350,z) – increased reaction rates.

While in some cases the corrosion current density increased with the addition of CaCO$_3$, this does not necessarily indicate rapid metal degradation but an increased reaction rate for the formation of ZnCO$_3$, the protective scale or zinc patina on the outer surface of galvanized articles to protect against further degradation.

The CPSI has modified the United Kingdom’s durability guidelines to propose that resistivities greater than 8,000 $\Omega$-cm are indicative of soft water and thus promote corrosion, rather than inhibit as is implied in AASHTO’s durability design criteria for soils. The resistivities of laboratory simulated electrolytes did not reach extreme highs, with the largest resistivity recorded at 6,300 $\Omega$-cm. Additionally, the solubility of CaCO$_3$ is very low ($7.0 \times 10^{-4}$ g/100 g water$^{(67)}$) having little effect on resistivity. However, field testing was able to demonstrate this phenomenon. With exception to the first line item in a saltwater application, the CSP analyzed all satisfied the AASHTO design criteria. Resistivities reached a maximum 63,500 $\Omega$-cm and the structure was heavily corroded to the point of losing the invert to degradation in less than 20 years of service life. Further work is required in this area to substantiate.

While valid for unsaturated soil conditions, as solely intended and demonstrated by the condition of the buried welded wire reinforcements and crowns of the CSP structures, the results in this dissertation thus challenge the appropriateness of the AASHTO durability design criteria for use in aqueous applications, saturated soils and wet-dry cyclic conditions. Results also indicated that the primary constituents to waterside corrosion are not limited to chlorides (Cl$^-$) and soluble sulphates (SO$_4^{2-}$) but also include water hardness in the form of CaCO$_3$. 
5.0 **Recommendations & Future Considerations**

The work completed for this dissertation made only a small dent in the required research to construct an updated corrosion model that is suited to North American climates. While it was discovered that the current AASHTO model is not appropriate for use in the design of structures subjected to wet-dry cyclic conditions and aqueous environments, extensive work is necessary to quantify corrosion rates and establish corrosion allowances for these applications.

Recommendations for future work include the following:

1. Accelerated corrosion testing of black steel and collecting performance data of ungalvanized structures in service, or structures that no longer have any galvanized thickness remaining. Following depletion of zinc, the underlying steel substrate is exposed. Gaining an understanding of how black steel responds to these environments would provide insight on estimating the necessary sacrificial thickness for design purposes;

2. The experimentation carried out for this dissertation demonstrates that hard water is beneficial to inhibit metal loss while soft water hinders the formation of the zinc patina, the steps of increasing CaCO$_3$ concentration were too great to define the optimal hardness range or where the turning point is;

3. The AASHTO design criteria and corresponding corrosion model were originally developed in Florida, United States. While Florida is humid and coastal, it does not see the winters experienced in Canada. Canadian winters bring about a series of additional variables such as the application of anthropogenic contaminants (deicing salts), accumulation of snow ploughed against structures and months of wet-dry cyclic conditions. To develop a model appropriate for use in Canada, seasonal field investigations are required; and

4. As proposed by CSPI, an upper limit on resistivity values is recommended for aqueous environments. It is believed that high resistivities are reflective of soft water. Experimentation that simulates these high resistivities would be beneficial when evaluating the necessity of this limit as a design criterion.
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APPENDIX A

OCP from Mechanically Galvanized Samples

Figure A.53: OCP for solutions \((x,0,0)\).

Figure A.54: OCP for solutions \((0,y,0)\).
Figure A.55: OCP for solutions \((x,y,0)\).

Figure A.56: OCP for solutions \((x,0,z)\).
Figure A.57: OCP for solutions (0,y,z).

Figure A.58: OCP for solutions (x,y,z).
APPENDIX B

OCP from HDG Samples

Figure B.59: OCP for solutions (x,0,0).

Figure B.60: OCP for solutions (0,y,0).
Figure B.61: OCP for solutions (0,0,z).

Figure B.62: OCP for solutions (x,y,0).
Appendix B

Figure B.63: OCP for solutions \((x,0,z)\).

Figure B.64: OCP for solutions \((0,y,z)\).
Figure B.65: OCP for solutions $(x,y,z)$. 
APPENDIX C

SEM Images Captured at 600x of HDG Samples

Figure C.66: HDG sample from (90,0,0).

Figure C.67: HDG sample from (0,250,0).
Appendix C

Figure C.68: HDG sample from (0,0,700).

Figure C.69: HDG sample from (120,350,0).
Figure C.70: HDG sample from (120,0,100).

Figure C.71: HDG sample from (0,50,100).
Figure C.72: HDG sample from (120,350,700).
APPENDIX D

SEM Images Captured at 600x of CSP

Figure D.73: CSP1.

Figure D.74: CSP2.
Figure D.75: SPCSP.