

SUMMARY REPORT FOR BRINE CORROSION RESEARCH STUDY

Prepared for:

City of Edmonton

Prepared By:

**Corrpro Canada, Inc.
Edmonton, AB**

**Permit to Practice No.:
P05933**



CORRPRO DOCUMENT No.: 0119-4632-CED-REN-001-2

2	30-JUL-19	Final Report	K. Duncan, E.I.T. Corrosion Engineer	D. Jungert, E.I.T. Corrosion Engineer	S. Gibson, M.Sc., P.Eng. Project Manager
1	04-JUL-19	Draft Final Report	K. Duncan, E.I.T. Corrosion Engineer	D. Jungert, E.I.T. Corrosion Engineer	S. Gibson, M.Sc., P.Eng. Project Manager
0	15-MAY-19	Preliminary Report	K. Duncan, E.I.T. Corrosion Engineer	D. Jungert, E.I.T. Corrosion Engineer	S. Gibson, M.Sc., P.Eng. Project Manager
REV	DATE (DD-MMM-YY)	COMMENTS	ORIGINATOR	REVIEWER	APPROVER

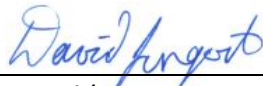
This document has been prepared by Corrpro Canada, Inc. (Corrpro) and is intended solely for the City of Edmonton (the City). This document and all copies are the property of Corrpro and the City. The documents are created specifically for the City and any other use is prohibited.

**Originated
By:**



Kristen Duncan, E.I.T.
Email: kduncan@aegion.com

Reviewed By:



David Jungert, E.I.T.
Email: djungert@aegion.com

Approved By:



Stephen Gibson, M.Sc., P.Eng.
Email: sgibson@aegion.com



AEGION[®]

Stronger. Safer. Infrastructure.™

corrpro[®]

BRINE CORROSION RESEARCH STUDY

SUMMARY REPORT

Edmonton

REVISION LOG

REV	REVISION / CHANGE DESCRIPTION
2	Final Report
1	Draft Final Report
0	Preliminary Report

EXECUTIVE SUMMARY

The City of Edmonton (the “City”) commissioned Corrpro Canada, Inc. (Corrpro) to conduct a targeted corrosion research project related to their newly implemented anti-icing pilot project.

The City began their anti-icing pilot project in 2017 to improve the overall efficiency and effectiveness of their winter road maintenance program. The City’s existing winter road maintenance program (the “existing program”) involves the use of sodium chloride (NaCl) for de-icing purposes. The anti-icing pilot involves the added use of corrosion-inhibited calcium chloride (CaCl₂) brine as an anti-icing agent (in addition to NaCl). The inhibited CaCl₂ brine is sprayed on the road as a thin layer prior to snowfall to improve the efficiency of snow plowing. This research project involves an investigation into the corrosion impacts of NaCl and CaCl₂ on a selection of metals expected to be most exposed to municipal anti-icing and de-icing solutions. The metals tested and reasons for inclusion are detailed below:

- Carbon steel (heavily utilized in vehicle, bicycle and municipal infrastructure construction)
- Galvanized steel (light poles, sign poles, etc.)
- Aluminum (bicycle frames and some vehicles)
- Stainless steel (some vehicle/bicycle components)

The scope of work for this research project included a literature review followed by field and laboratory testing.

The field testing program included the installation and monitoring of corrosion coupons on buses and municipal infrastructure. The coupons were placed in areas where the application of the anti-icing and de-icing products is well known. Half of the coupons were placed in areas that were exposed to NaCl salt only (existing program), whereas the remaining coupons were placed in areas exposed to both NaCl salt and CaCl₂ brine (anti-icing pilot). After exposure to Edmonton winter conditions (winter 2018/2019) and retrieval from the field, the corrosion effects of the anti-icing and de-icing products were evaluated.

The laboratory portion of this research study was based on an industry standard corrosion test method (NACE TM0169). The corrosion effects of NaCl and CaCl₂ solutions on carbon steel, stainless steel, aluminum, and galvanized steel were evaluated.

The major findings from the literature review, field program, and laboratory programs in this research study are summarized below:

- Anti-icing and de-icing products, including CaCl₂, NaCl and other chloride salts, are used globally for winter road maintenance in areas that experience icy conditions.
- Research studies and pilot programs have been introduced worldwide to determine the impact of anti-icing and de-icing products on metal infrastructure and vehicles. However,

the results of research programs found in literature review have been inconsistent. Both laboratory and field programs are highly dependent on several factors, such as metal type, temperature, humidity, amount of exposure, and many more. Literature review has shown significant variations between the corrosion effects of NaCl and CaCl₂.

- Literature review of various case studies has proven that laboratory and field testing results do not always correlate with each other. Unknown factors in real world results cannot be easily replicated in laboratory testing.
- Aqueous solutions containing chloride salts, such as NaCl, CaCl₂ and MgCl₂, are known to cause corrosion to metal infrastructure and vehicles. Regular cleaning and maintenance of protective coatings (i.e. paint) is recommended to minimize corrosion.
- The amount/length of exposure to corrosive environments was a major contributing factor to amount of corrosion observed on laboratory and field coupons. In general, more exposure to corrosive environments leads to more corrosion.
- The amount of corrosion observed varied with coupon material type. Carbon steel was the most easily corroded material, while stainless steel was the most resistant to corrosion.
- With regards to the comparison of anti-icing/de-icing programs, the field testing produced inconclusive results due to insufficient time in the field, varied/atypical application of inhibited CaCl₂ brine in winter 2018/2019, and due to the high correlation between exposure amount and amount of corrosion observed. Additional testing time in the field is recommended to further investigate the corrosion effects of the anti-icing pilot.
- In the lab program, the corrosivity of various liquids was tested. The liquids tested included distilled water, tap water, concentrated NaCl and CaCl₂ brines, inhibited CaCl₂ brine plus multiple brine mixtures and dilutions. The corrosion observed on the coupons varied with liquid type:
 - Tap water was one of the most corrosive liquids, while distilled water was one of the least corrosive liquids. These results display the large effect that impurities have on the corrosivity of water.
 - Salt concentrations had a large effect on corrosivity of the liquids:
 - The addition of NaCl or CaCl₂ brines to distilled water significantly increased corrosivity. It is anticipated the effect would be the same on environmental moisture (rain and snow/ice melt).
 - The results indicate that very concentrated aqueous salt solutions (brines) become more corrosive as they are diluted (in the absence of a corrosion inhibitor).
 - Further research is required to better compare the corrosivity of different aqueous salt solution types.
 - The addition of inhibitor had a varied effect on the corrosion observed:
 - The addition of inhibitor appeared to greatly reduce the corrosivity of *diluted* CaCl₂ brine, but slightly increased the corrosivity of *concentrated* CaCl₂ brine. However, a diluted state of the inhibited CaCl₂ brine may be

more typical of exposure conditions in Edmonton (as part of the anti-icing pilot project).

- When reviewing the corrosivity of all liquids tested, it appears that the inhibitor may only be effective over a range of inhibitor and salt concentrations. Further research is recommended to better understand the range of effectiveness.
- Biological products formed in solutions that contained diluted inhibited CaCl_2 brine. While further research is recommended to understand the impact of these biological products on corrosion, this result does indicate that the corrosion inhibitor would biodegrade over time once released into the environment.
- The results indicate that carbon steel, zinc and aluminum can corrode when exposed to typical environmental conditions found in Edmonton. It is recommended that additional corrosion prevention methods be applied to metal surfaces exposed to corrosive environments. Examples methods include limitation of actual exposure to moisture (keeping surfaces dry), the application and maintenance of high-performance corrosion protection coatings (e.g. paint on a car) or lubrication (e.g. for bicycle chains/cassettes).
- There are many factors that can influence the corrosive effects of anti-icing/de-icing programs. Many of these factors could be investigated further for additional clarification.

Table of Contents

1.0	Project Introduction	1
1.1	Project Deliverables	1
2.0	Literature Review.....	1
2.1	Summary	1
2.2	Metals Commonly Used in Civil Infrastructure & Vehicles.....	2
2.3	Anti-Icing & De-Icing Chemicals.....	3
2.3.1	<i>Corrosion Theory of Chloride-Based Anti-icing & De-Icing Chemicals</i>	<i>3</i>
2.3.2	<i>Properties of Chloride-Based Anti-Icing Chemicals.....</i>	<i>4</i>
2.3.3	<i>Corrosion Inhibitors.....</i>	<i>5</i>
2.4	Laboratory Corrosion Testing Standards	5
2.4.1	<i>PNS Specifications</i>	<i>6</i>
2.4.2	<i>NACE TM0169</i>	<i>6</i>
2.4.3	<i>ASTM B117.....</i>	<i>7</i>
2.4.4	<i>SAE J2334</i>	<i>7</i>
2.5	Laboratory Testing Case Studies.....	8
2.5.1	<i>Colorado Department of Transportation</i>	<i>8</i>
2.5.2	<i>Iowa Highway Research Board</i>	<i>10</i>
2.6	Field Testing Case Studies.....	10
2.6.1	<i>Washington State Department of Transportation Salt Pilot Project</i>	<i>10</i>
2.6.2	<i>Colorado Department of Transportation Field Testing.....</i>	<i>11</i>
2.6.3	<i>Ontario Ministry of Transportation Field Testing</i>	<i>12</i>
3.0	Field Program.....	12
3.1	Chosen Field Program	12
3.2	Coupon Procurement.....	13
3.3	Coupon Installation	14
3.3.1	<i>Vehicle-Related</i>	<i>14</i>
3.3.2	<i>Infrastructure-Related.....</i>	<i>17</i>
3.3.3	<i>Bicycle-Related</i>	<i>19</i>
3.4	Retrieval of Field Coupons	21
3.4.1	<i>Vehicle-Related</i>	<i>21</i>
3.4.2	<i>Infrastructure & Bicycle-Related</i>	<i>21</i>
3.5	Field Program Analysis.....	24
3.5.1	<i>Vehicle-Related</i>	<i>24</i>
3.5.2	<i>Infrastructure-Related.....</i>	<i>28</i>
3.5.3	<i>Bicycle-Related</i>	<i>29</i>
3.5.4	<i>Environmental Control</i>	<i>30</i>
4.0	Laboratory Program	31

4.1	Chosen Laboratory Program	31
4.2	Coupon Procurement.....	31
4.3	Laboratory Procedure	32
4.4	Laboratory Program Analysis.....	35
4.4.1	<i>Standard Test</i>	35
4.4.2	<i>Modified Test</i>	41
4.4.2.1	<i>Effect of Water</i>	45
4.4.2.2	<i>Effect of Salt Concentration</i>	45
4.4.2.3	<i>Effect of Biological Products</i>	47
4.4.2.4	<i>Effect of Inhibitor</i>	50
4.4.2.5	<i>Corrosion of Carbon Steel Coupons</i>	51
4.4.2.6	<i>Corrosion of Stainless Steel Coupons</i>	53
4.4.2.7	<i>Corrosion of Aluminum Coupons</i>	55
4.4.2.8	<i>Corrosion of Galvanized Steel Coupons</i>	57
5.0	Conclusions	61
	References.....	67

List of Tables

Table 1 - Project Deliverables	1
Table 2 - Field Coupon Compositions and Quantities.....	13
Table 3 - Break-down of Coupon Placement	14
Table 4 - Bus Numbers Used in Field Program.....	16
Table 5 - Average Measured Change in Mass on Buses	27
Table 6 - Average Measured Change in Mass on Metal Infrastructure	28
Table 7 - Average Measured Change in Mass on Bicycles	29
Table 8 - Average Measured Change in Mass on the Environmental Control Coupons.....	30
Table 9 - Lab Coupons Compositions and Quantities	32
Table 10 - Winter 2017/2018 Anti-Icing/De-Icing Material Usage [17]	34
Table 11 - Anti-Icing/De-Icing Solutions Tested.....	35
Table 12 - Measured Change in Mass from 72-Hour NACE TM0169 Test	38
Table 13 - Ranking of Standard Test Solutions in Terms of Mass Loss (Highest to Lowest)	39
Table 14 - Measured Change in Mass from Modified NACE TM0169 Test.....	44
Table 15 - Ranking of Modified Test Solutions in Terms of Mass Loss (Highest to Lowest)	44

List of Figures

Figure 1 - Phase Diagrams for NaCl and CaCl ₂ [6]	4
Figure 2 - As-Received Field Coupons	13
Figure 3 - Coupon Mounting Locations on Buses	15
Figure 4 - Coupons Mounted Behind the Wheel Well of Buses.....	15
Figure 5 - Coupons Mounted on Bus Mud Flaps.....	16
Figure 6 - Field Coupon Mounting Apparatus.....	18
Figure 7 - Coupon Installed on a Lamp post	18
Figure 8 - Coupon Installed on Bicycle Lane Signpost.....	19
Figure 9 - Field Coupon Locations	20
Figure 10 - As-Retrieved Corroded Field Coupons Installed on Buses.....	21
Figure 11 - Infrastructure-Related Field Coupons Retrieved from 122 nd Street (Existing Program)	22
Figure 12 - Infrastructure-Related Field Coupons from 178 th Street (Anti-Icing Pilot Program)	23

Figure 13 - Control Coupons Outside the Corrpro Office (Environmental Control)	23
Figure 14 - Packaged Coupons After Cleaning & Weighing	24
Figure 15 - Lightly Cleaned Field Coupons Recovered from Spruce Grove Buses (Existing Program)	25
Figure 16 - Lightly Cleaned Field Coupons Recovered from City of Edmonton Buses (Anti-Icing Pilot Program)	25
Figure 17 - Crevice Corrosion on Field Coupons Installed on Buses (Carbon Steel on Left, Aluminum on Right)	26
Figure 18 - As-Received Laboratory Coupons	32
Figure 19 – Side View of the Laboratory Setup (Coupons Out of Solution)	33
Figure 20 – Side View of the Laboratory Setup (Coupons Immersed in Solution)	33
Figure 21 - Standard NACE TM0169 Coupons from Solution 1 (Saturated NaCl)	35
Figure 22 - Standard NACE TM0169 Coupons from Solution 2 (As-Received CaCl ₂ Brine)	36
Figure 23 - Standard NACE TM0169 Coupons from Solution 3 (As-Received Inhibited CaCl ₂ Brine)	36
Figure 24 - Standard NACE TM0169 Coupons from Solution 4 (Mixed Solution of Saturated NaCl and Inhibited CaCl ₂ Brine (95:5))	36
Figure 25 - Standard NACE TM0169 Coupons from Solution 5 (Solution 4 Diluted 1:1 with Distilled Water)	36
Figure 26 - Standard NACE TM0169 Coupons from Solution 6 (Solution 4 Diluted 3:97 with Distilled Water)	37
Figure 27 - Standard NACE TM0169 Coupons from Solution 7 (Tap Water)	37
Figure 28 - Standard NACE TM0169 Coupons from Solution 8 (Distilled Water)	37
Figure 29 - Standard NACE TM0169 Coupons from Solution 9 (CaCl ₂ Brine Diluted 3:97 with Distilled Water)	37
Figure 30 - Standard NACE TM0169 Coupons from Solution 10 (Inhibited CaCl ₂ Brine Diluted 3:97 with Distilled Water)	38
Figure 31 - Biological Products Appearing in Inhibited CaCl ₂ Solutions	40
Figure 32 - Biological Buildup on Coupons in Inhibited CaCl ₂ Brine Solutions	40
Figure 33 - Modified NACE TM0169 Coupons from Solution 1 (Saturated NaCl)	41
Figure 34 - Modified NACE TM0169 Coupons from Solution 2 (As-Received CaCl ₂ Brine)	41
Figure 35 - Modified NACE TM0169 Coupons from Solution 3 (As-Received Inhibited CaCl ₂ Brine)	41
Figure 36 - Modified NACE TM0169 Coupons from Solution 4 (Mixed Solution of Saturated NaCl and	

Inhibited CaCl ₂ Brine (95:5)).....	42
Figure 37 - Modified NACE TM0169 Coupons from Solution 5 (Solution 4 Diluted 1:1 with Distilled Water)	42
Figure 38 - Modified NACE TM0169 Coupons from Solution 6 (Solution 4 Diluted 3:97 with Distilled Water)	42
Figure 39 - Modified NACE TM0169 Coupons from Solution 7 (Tap Water)	42
Figure 40 - Modified NACE TM0169 Coupons from Solution 8 (Distilled Water)	43
Figure 41 - Modified NACE TM0169 Coupons from Solution 9 (CaCl ₂ Brine Diluted 3:97 with Distilled Water)	43
Figure 42 - Modified NACE TM0169 Coupons from Solution 10 (Inhibited CaCl ₂ Brine Diluted 3:97 with Distilled Water)	43
Figure 43 - Graphical Representation of Coupon Mass Change	45
Figure 44 - Corrosion of Carbon Steel in Various NaCl Mixtures [20].....	47
Figure 45 - Effect of Diluted Inhibited CaCl ₂ Brine Solutions (Solution 10) on Aluminum.....	48
Figure 46 - Effect of As-Received Inhibited CaCl ₂ Brine (Solution 3) on Carbon Steel.....	49
Figure 47 - Graphical Representation of Carbon Steel Coupon Mass Change.....	51
Figure 48 - Corroded Carbon Steel Coupons (From Left to Right: Solution 6, 7, and 9).....	52
Figure 49 - Significant Mass Loss in Carbon Steel Coupons	53
Figure 50 - Graphical Representation of Stainless Steel Coupons Mass Change.....	54
Figure 51 - Stainless Steel Coupon Exposed to CaCl ₂ Brine	55
Figure 52 - Graphical Representation of Aluminum Coupon Mass Change	56
Figure 53 - Pitting Corrosion on Aluminum Coupons	57
Figure 54 - Graphical Representation of Galvanized Steel Coupons Mass Loss	58
Figure 55 - Zinc Coating Entirely Consumed from Inhibited CaCl ₂ Brine (Solution 3).....	59
Figure 56 - Zinc Coating Break-down on Galvanized Steel Coupons	60

1.0 PROJECT INTRODUCTION

Corrpro was selected by the City to conduct a targeted corrosion research project related to road anti-icing and de-icing programs. Specifically, the project involves an investigation into the corrosion impacts of calcium chloride (CaCl_2) and sodium chloride (NaCl) on metals. Laboratory testing, field testing, and literature review were included in the scope of work for this research study.

1.1 PROJECT DELIVERABLES

The project phases and deliverables are listed in 'Table 1'.

Table 1 - Project Deliverables

Phase	Deliverable
1	Proposed Lab Program
	Literature Review Summary
2	Field Coupon Procurement
	Field Coupon Installation
3	Final Lab Program
	Lab Coupon Procurement
	Preliminary Report
4	Field Coupon Retrieval
	Final Report

2.0 LITERATURE REVIEW

2.1 SUMMARY

- Anti-icing and de-icing chemicals are used globally for winter road maintenance in areas that experience icy conditions.
- Winter road maintenance is a highly researched subject for many cities that experience winter road conditions. Many cities globally have introduced research studies and pilot programs to determine the impact of anti-icing and de-icing chemicals on metal infrastructure. However, there have been inconclusive results from research studies on the corrosion of anti-icing and de-icing chemicals.

- There are many different laboratory tests used to determine the corrosion effect of anti-icing and de-icing chemicals, the most common corrosion tests used are NACE TM0169, ASTM B117, and SAE J2334 [1].
- Pacific Northwest Snowfighters (PNS) are an organization that have created standards and testing methods to assess the corrosion impacts of anti-icing and de-icing chemicals. PNS uses a modified NACE TM0169 test to see if commercially produced anti-icing and de-icing products meet specific criteria [2].
- Review of literature resources clearly shows that laboratory test results are highly dependent on the test method, type of metal used, concentration of anti-icing or de-icing solution used, duration of the test, oxygen exposure, and complexity of the test method. Testing has shown significant variation between the corrosion effect of NaCl and CaCl₂. In immersion or arid environments, NaCl is more corrosive than CaCl₂, but in humid environments, CaCl₂ is more corrosive than NaCl [3].
- Field and laboratory results have proven not be comparable in many case studies. The anti-icing and de-icing chemicals that initially meet the PNS criteria when tested in the laboratory often fail this criterion when tested in the field [4].
- Field testing generally consists of attaching metallic coupons to metal infrastructure and vehicles. The initial and final weight of the coupons are compared to determine the extent of corrosion.
- The results of field testing often lead to inconclusive findings due to significant variation of corrosion rates of the anti-icing chemical between areas of roadways tested [4], [5], [6], [7], [8], [9], [3].
- Weather conditions and the environment have a significant impact on the corrosivity of anti-icing and de-icing chemicals [8].

2.2 METALS COMMONLY USED IN CIVIL INFRASTRUCTURE & VEHICLES

Some metals commonly used in civil infrastructure and vehicles include carbon steel, aluminum, galvanized steel, and stainless steel. Cast iron, titanium and other specialized

metals are also used, but in limited quantities. Steel is often used to create the chassis or cage beneath the body of a vehicle, or on door beams, car roofs and body panels. Aluminum is commonly used because of its high strength to weight ratio. In cars, aluminum is typically used in body panels and wheel rims. Additionally, aluminum is used for bicycle frames and street signs. Stainless steel is commonly used in exhaust pipes on cars due to its higher resistance to corrosive environments. Light posts are typically made of galvanized steel [10].

Most metals used in civil infrastructure and vehicles have a protective coating applied to them, whether it is paint on your car or a galvanized coating. Coatings will increase the lifespan of the metal by acting as a barrier between the metal and corrosive environments. It is important to note that coatings on metals do not last forever; proper maintenance of the coating must be maintained to avoid localized corrosion. Ensure cars are properly coated, regularly cleaned, and the coating is maintained to minimize corrosion.

2.3 ANTI-ICING & DE-ICING CHEMICALS

Anti-icing and de-icing chemicals are commonly used for road maintenance in areas that experience icy winter driving conditions. Anti-icing is primarily a preventative strategy, while de-icing is primarily a reactive strategy. In many jurisdictions, these two strategies are used in combination to improve overall effectiveness of winter road maintenance programs. The most common anti-icing and de-icing chemicals used include NaCl, CaCl₂, abrasives (sand), magnesium chloride (MgCl₂), agricultural-based, and others. This literature review section will cover the impact that chloride-based anti-icing and de-icing chemicals have on metal infrastructure in the transportation industry.

2.3.1 CORROSION THEORY OF CHLORIDE-BASED ANTI-ICING & DE-ICING CHEMICALS

According to the adsorption theory, when chloride based anti-icing and de-icing chemicals are in contact with metal, the chloride ions (Cl⁻) are adsorbed on the metal surface [3]. The chloride ions increase the rate of metal dissolution, or the rate that metal ions enter

into solution. In other words, the chloride ions in salt and other anti-icing and de-icing chemicals produce electrochemically active solutions when dissolved in water [5]. The chloride ions do not chemically react with metals, instead they assume a role as a catalyst in the electrochemical process. Chloride anions help remove the metal cations accumulated on the anode by forming soluble compounds, which contributes to an accelerated anodic reaction and an increased corrosion rate [3].

2.3.2 PROPERTIES OF CHLORIDE-BASED ANTI-ICING CHEMICALS

'Figure 1' shows the phase diagrams for the NaCl – H₂O and CaCl₂ – H₂O systems [6].

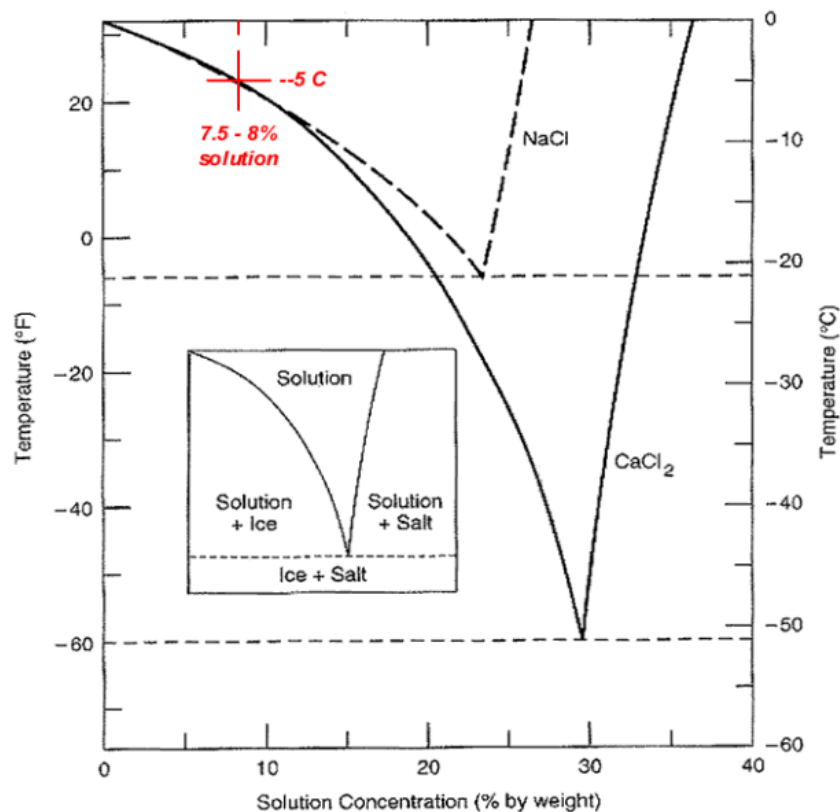


Figure 1 - Phase Diagrams for NaCl and CaCl₂ [6]

There is little difference between the two melting curves at warmer temperatures, above approximately -21°C. However, when the temperature drops below -21°C CaCl₂ significantly outperforms NaCl. Testing of the ice melting capacities of anti-icing and

de-icing chemicals is typically determined using the SHRP H-332 test method. At warmer temperatures the ice melting capacity of CaCl_2 is slightly higher than NaCl . But at lower temperatures, the ice melting performance of CaCl_2 is much higher compared to NaCl [6]. Therefore, less CaCl_2 product is needed to achieve the same ice melting results of NaCl , especially at lower temperatures.

CaCl_2 has a higher viscosity compared to NaCl , meaning it adheres to the road more easily than NaCl . NaCl has the tendency to dry up and get swept off the roads. Mixtures of NaCl and CaCl_2 have been found to stay on the roads longer as compared to NaCl salt alone [6].

2.3.3 CORROSION INHIBITORS

To reduce the corrosive effects of anti-icing and de-icing chemicals, corrosion inhibitors can be added. Many inhibitors are derived from agriculturally based products, such as molasses and beets. Inhibitors are chemicals which can reduce the corrosion rate when added in small, but critical amounts. Inhibitors are only effective for general corrosion, not localized corrosion [11].

2.4 LABORATORY CORROSION TESTING STANDARDS

The objective of laboratory corrosion testing is to create a similar degradation environment in a shorter period of time compared to the natural period, without changing the failure mechanism. There are many different laboratory tests used to determine the corrosion of metals, such as immersion tests, continuous spray tests, and cyclic tests. Most corrosion studies compare anti-icing and de-icing chemicals using NaCl as an index. Carbon steel is used most frequently as the metal to be tested, though many other metals have been examined as well [3].

2.4.1 PNS SPECIFICATIONS

PNS association has developed standardized specifications, testing methods and laboratories to use for testing anti-icing and de-icing chemicals [1]. The specifications developed by the PNS take into consideration human safety, environment, corrosion protection, cost-effectiveness, and performance [2]. PNS has developed a pre-approved list of anti-icing and de-icing chemicals [12].

One of the criteria PNS uses to determine acceptable corrosivity of an anti-icing/de-icing chemical is that “only corrosion inhibited chemical products that are at least 70% less corrosive than reagent grade NaCl may be used” [2]. This criterion is determined by comparing the mass loss of the coupon caused by the selected anti-icing/de-icing chemical with a standard NaCl solution in the PNS modified version of the NACE TM0169 immersion laboratory test.

2.4.2 NACE TM0169

The NACE TM0169 corrosion test method is an immersion test than alternates between the coupons being submerged in the salt solution and being air dried outside of the solution [13].

The anti-icing/de-icing chemical is mixed with distilled water and put into a flask, approximately half filled. The flask is stoppered with a rubber stopper that has been drilled to allow a line to run through it. If the hole is too large (> 4mm), the flask will vent excessively and skew the results. One end is attached to a plastic frame that holds the metal coupons. The other end of the line is attached to a bar that can be moved up and down on its frame. The bar is controlled by an electric timer that lowers the coupons into the solution for 10 minutes then raises them for 50 minutes. The design keeps the coupons inside the contained environment in the flask for the duration of the testing. The

total duration of the test is 72 hours. This corrosion test is conducted at room temperature (21-23°C) and the solution is not agitated during testing [13].

In order to be approved for the PNS Qualified Products list, the anti-icing solutions are tested with the NACE TM0169. The anti-icing or de-icing product tested must be at least 70% less corrosive than NaCl to be acceptable [2].

Modified versions of the NACE test with extended duration have often had to be implemented because 72 hours is not long enough to see significant amount of corrosion in most metals. The test duration is often extended to weeks or even months to see visible/measurable corrosion results [3].

2.4.3 ASTM B117

The ASTM B117 method of salt spray testing is a continuous salt spray testing method where the coupons are exposed to the salt solution spray for several hours. ASTM B117 is the oldest and most commonly used standard laboratory corrosion testing method. ASTM B117 outlines the apparatus, procedure, and conditions required to create and maintain the salt spray test environment. Test specimens, dimensions, shape or exposure periods are not specified in the ASTM B117 test method. The spray time for the ASTM B117 test is 800 hours [14].

2.4.4 SAE J2334

SAE J2334 is a cyclic corrosion test involving repeated exposure to salt solution, humidity, and drying conditions. The test cycle consists of three basic stages: the humidity stage at 50°C and 100% relative humidity for six hours, the salt application stage at ambient temperature for 15 minutes, and the dry stage at 60°C and 50% relative humidity for 17 hours and 45 minutes. The salt application stage can be completed by various methods, such as immersion, salt spray or atomized fog. The test is repeated daily for a minimum of 60 cycles [15].

The biggest challenge for implementing the SAE J2334 test is the need to precisely control the relative humidity and temperature of the testing environment during each stage of the testing.

2.5 LABORATORY TESTING CASE STUDIES

2.5.1 COLORADO DEPARTMENT OF TRANSPORTATION

The Colorado Department of Transportation (CDOT) did extensive laboratory testing on various anti-icing and de-icing chemicals to determine their corrosion effects on metal infrastructure. Experimental results of the ASTM B117 test showed that NaCl was more corrosive than $MgCl_2$. However, the ASTM B117 test was determined not to be an ideal representation of real-life conditions of the corrosion of metal on vehicles because there are only wet conditions. In real life, there will be situations in which the anti-icing solution will be allowed to dry on the metal surface [3].

The NACE test determined that NaCl was more corrosive than $MgCl_2$ on carbon steel coupons. However, significant corrosion of other metals, such as stainless steel and aluminum, were not observed during the NACE test. The CDOT laboratory testing concluded that the duration of 72 hours was not enough time for the metals to corrode sufficiently. The coupons were left in the solutions for longer periods of times to determine the long-term corrosion effects. The coupons were observed after 69 days, significant corrosion was present on all metal types [3].

Experimental results determined by the CDOT of the SAE J2334 test method showed the opposite effect, that $MgCl_2$ was more corrosive than NaCl on carbon steel. The corrosion of the metals in the SAE J2334 test was much more significant than the other tests. The likely reason for this was the role of oxygen in the corrosion reaction. The ASTM B117 and NACE tests are conducted in an enclosed test chamber, whereas the SAE test is not in a sealed environment [3].

The corrosion rate of NaCl did not change dramatically from the NACE to the SAE test, whereas the corrosion rate of the MgCl_2 increased significantly during the SAE test compared to the NACE test. The major difference between these tests is the testing temperature and relative humidity. The NACE test is conducted at ambient temperature, while the SAE test is conducted at varying elevated temperatures. Generally, higher temperature results in higher reaction or corrosion rate. The CDOT conducted a modified NACE test at elevated temperature (50°C) to see the effect of temperature on the corrosion rate. It was determined that the temperature was not the parameter responsible for the difference between the NACE test and SAE test. The immersion time, duration of testing, and the concentration of the anti-icing chemicals also did not significantly contribute to differences between the NACE and SAE tests. Further testing concluded that the difference in relative humidity between the NACE and SAE tests was responsible for the varied corrosion rate of MgCl_2 . MgCl_2 has high viscosity; therefore, it can easily stick to metal surfaces unlike NaCl, which has much lower viscosity. Consequently, there is more condensed solid MgCl_2 on the surface of the metals compared to NaCl during the 'dry' stage of the testing. This does not affect the results of the NACE test because there is no moisture on the surface to cause corrosion during the 'dry' stage. However, during the high humidity or 'wet' stage of the SAE test, the MgCl_2 on the surface will absorb the moisture, due to its high hydrophilicity, and become solution. This results in corrosion to occur on the metal surface even though the coupons are not dipped into the solution. This phenomenon is also seen in NaCl, but to a lesser extent due to its lower viscosity and lesser absorbability into water [3].

CDOT determined that under high humidity conditions, such as under the hood or door of a vehicle, MgCl_2 is more corrosive than NaCl. In immersion or arid environments, NaCl is more corrosive than MgCl_2 . However, a vehicle may be exposed to specific and complex situations which can not be represented by any of the controlled laboratory tests [3].

These results are not necessarily true when considering various types of metals. CDOT laboratory tests have found CaCl_2 and MgCl_2 to be more corrosive to aluminum compared to NaCl in the NACE test. MgCl_2 has similar corrosivity and viscosity to CaCl_2 when compared to NaCl [3].

2.5.2 IOWA HIGHWAY RESEARCH BOARD

The purpose of this laboratory testing was to further investigate the effect of the concentration of the anti-icing chemical on the corrosion of the metal. The PNS modified NACE TM0169 test method was used to compare the corrosivity of a variety of anti-icing chemicals at three different concentrations (1.5%, 3% and 6%). Several anti-icing chemicals were examined, including NaCl and CaCl_2 . The concentrations were achieved by mixing the anti-icing chemical with distilled water. Cylindrical flat carbon steel washers were used as the mass loss coupons. At the 1.5% and 3% concentrations, it was determined that the CaCl_2 was more corrosive compared to NaCl. Whereas, at the 6% concentration the corrosion rates of CaCl_2 significantly decreased to rates similar to NaCl. Therefore, it was determined that the corrosion rate of the anti-icing chemicals can vary significantly with concentration [16].

2.6 FIELD TESTING CASE STUDIES

2.6.1 WASHINGTON STATE DEPARTMENT OF TRANSPORTATION SALT PILOT PROJECT

Washington State Department of Transportation (WSDOT) conducted a field test to compare NaCl and corrosion-inhibited anti-icing chemicals, such as CaCl_2 and MgCl_2 , for snow and ice control on highways [8]. Sections of highways were designated for the NaCl solution. Other similar sections of the highways were designated for corrosion-inhibited anti-icing chemicals (CaCl_2 , MgCl_2). Corrosion was evaluating by exposing samples of steel, sheet aluminum, and cast aluminum to each anti-icing solution. The metal coupons were attached to maintenance trucks, supervisor pick-up trucks, and roadside guardrails posts.

WSDOT chose anti-icing chemicals which met the PNS corrosion criterion prior to use in the field [4].

The coupons were attached to galvanized and painted steel racks, which were then attached to the trucks. Coupons were also attached to guardrail posts to be exposed to stormwater ‘splash’ from vehicles driving on the highway [8].

The corrosion-inhibited chemicals did not meet the PNS specification for any of the regions based on the field-testing results. This indicates that the specification and related laboratory testing does not have a direct and predictable relationship to the corrosion rates that occur on the roadways [8].

The mass loss of the coupons was measured as an average amount due to the number of coupons tested. The mass loss in the steel was on the order of grams. The mass loss of the aluminum was on the order of tenths of grams. Generally, the use of the corrosion inhibited chemicals appeared to reduce the amount of corrosion in the steel in motor vehicles, but it also appeared to increase corrosion rates in aluminum. However, the corrosion of the metals varied significantly depending on the region of Washington in which they were tested. The corrosion-reducing effects of the inhibited chemicals that were seen in the eastern part of the state were not apparent in the western part of the state. WSDOT concluded that the weather conditions and the environment have a very significant impact on the corrosion of these metals. The overall findings of this field test were determined to be inconclusive [8].

2.6.2 COLORADO DEPARTMENT OF TRANSPORTATION FIELD TESTING

Field testing was conducted on Colorado highways for one winter season in 1999. The purpose of this field testing was to verify the results of their extensive laboratory testing. Various types of metal coupons were utilized during this testing including carbon steel,

stainless steel and aluminum. The coupons were attached to a plexiglass sheet, which were mounted on to trucks to be exposed to highways [1].

There was significant variance in corrosion rate of the coupons depending on the truck they were attached to. This was mainly attributed to exposure times. However, detailed records of the salt application on these roads were not available; therefore, the field test did not lead to conclusive results [1].

2.6.3 ONTARIO MINISTRY OF TRANSPORTATION FIELD TESTING

Ontario Ministry of Transportation conducted field testing of corrosion inhibitors on both steel and aluminum in 2006-07. Field tests evaluated NaCl, MgCl₂, and a brine with a mixture of NaCl, CaCl₂, and MgCl₂. The first phase of the field testing determined that in some cases inhibitors reduced corrosion, but in other cases the inhibitors increased corrosion. A second phase field test was conducted with a larger number of field sites and coupons. The results of the second phase were also determined to be inconclusive. The inhibited anti-icing solutions functioned well at reducing corrosion in the laboratory tests, but the corrosion in field tests increased as the concentration of inhibitor increased [8].

3.0 FIELD PROGRAM

3.1 CHOSEN FIELD PROGRAM

Field testing was suggested by Corrpro to determine the corrosion effect of NaCl salt and inhibited CaCl₂ brine in Edmonton's weather and traffic conditions. Field testing in Edmonton was important as the corrosion effect of anti-icing/de-icing chemicals can vary significantly based on weather conditions [8]. Corrpro's recommended field program included the installation and monitoring of a number of coupons on buses and metal infrastructure in Edmonton. To better determine the effect of different anti-icing/de-icing solutions, Corrpro conducted testing in areas where the conditions are well known. Information on anti-icing/de-icing chemical applications in Edmonton was provided by the City.

3.2 COUPON PROCUREMENT

A total of 180 field coupons were ordered on January 11, 2019. The field coupons were received on January 31, 2019. The quantities and compositions of field coupons are detailed in 'Table 2'.

Table 2 - Field Coupon Compositions and Quantities

Coupon Composition	Quantity
Carbon Steel (C1010)	60
Stainless Steel (316L)	60
Aluminum (1100)	60
Total	180

'Figure 2' shows the as-received condition of the field coupons for each metal type. The dimensions of the coupons are 0.5" wide, 3" long, and 0.063" thick.



Figure 2 - As-Received Field Coupons

3.3 COUPON INSTALLATION

The coupons were installed on vehicle-related, infrastructure-related, and bicycle-related structures and equipment throughout Edmonton. 'Table 3' shows the breakdown of the location and number of coupons that were installed.

Table 3 - Break-down of Coupon Placement

Structure & Equipment	Number of Field Coupons	Percentage of Total
Vehicle-related	72	40%
Infrastructure-related	54	30%
Bicycle-related	36	20%
Outside Corrpro Office (No Exposure to Anti-icing/De-icing Chemicals)	3	2%
Extra Coupons	15	8%
Total	180	100%

3.3.1 VEHICLE-RELATED

The coupons were installed on buses during the week of February 3 – 9, 2019. Two sets of each metal coupon (six coupons per bus) were mounted onto 12 buses; six City of Edmonton buses and six Spruce Grove buses were used. The Spruce Grove buses were expected to be exposed primarily to the existing program (NaCl salt). The City of Edmonton buses were exposed to the anti-icing pilot program (NaCl salt and inhibited CaCl_2 brine). The coupons were attached near the rear, curb-side wheel of the buses in the locations indicated (circled) on 'Figure 3'.



Figure 3 - Coupon Mounting Locations on Buses

The coupons attached to wiring behind the back curb-side wheel well were secured with heavy duty plastic cable ties. 'Figure 4' shows images of the coupons after they were installed behind the back wheel well.



Figure 4 - Coupons Mounted Behind the Wheel Well of Buses

The coupons were also attached to the mud flaps and secured with stainless steel bolts, washers, and lock nuts. Nylon insulators were installed between the coupons and the mounting hardware to eliminate metal-to-metal contact. 'Figure 5' shows the coupons

after they were installed on the mud flaps. The coupons were placed in the upper corner of the mud flap to minimize the chances of damage or loss.



Figure 5 - Coupons Mounted on Bus Mud Flaps

'Table 4' indicates the bus numbers of the City of Edmonton and Spruce Grove buses that were used for this field program.

Table 4 - Bus Numbers Used in Field Program

City of Edmonton Buses	Spruce Grove Buses
7031	6900
4536	6901
4366	6902
4879	6903
4374	6904
4916	6905

The mechanics at City of Edmonton fleet services periodically checked the specified buses to see if the coupons were still attached and undamaged.

3.3.2 INFRASTRUCTURE-RELATED

Installation of the infrastructure and bicycle-related field coupons was completed on February 26, 2019. The infrastructure-related structures used in this field program were mounted on specified routes in the city. The routes that were to be primarily exposed to the existing program are:

- 122nd Street, between 51st Street and 62nd Avenue
- Groat Road, between 87th Avenue and Groat Bridge

The routes that were to be primarily exposed to the anti-icing pilot program are:

- 178th Street, between Stony Plain Road and Whitemud Drive
- 111th Avenue, between Groat Road and 120th Street

The coupons were mounted to a neoprene sheet with nylon bolts, washers and nuts. Holes were drilled into the neoprene to allow for heavy duty cable ties to secure the apparatus to metal infrastructure. 'Figure 6' and 'Figure 7' show the field coupon mounting apparatus and examples of how they were mounted to various metal infrastructure on the specified routes.



Figure 6 - Field Coupon Mounting Apparatus



Figure 7 - Coupon Installed on a Lamp post

3.3.3 BICYCLE-RELATED

For winter 2018/2019, the bicycle lanes in Edmonton received regular applications of CaCl_2 brine and NaCl salt. The application of the anti-icing and de-icing products is much higher on bicycle lanes as compared to roads. For the bicycle-related structures, the coupons were mounted downtown on the streets with designated bicycle lanes; the routes are as follows:

- 106th Street
- 102nd Avenue
- 103rd Street
- 100th Avenue

‘Figure 8’ shows an example of how the bicycle-related coupon were installed the bicycle lanes downtown.



Figure 8 - Coupon Installed on Bicycle Lane Signpost

An additional mounting apparatus with a set of coupons was placed outside the Corrpro office. This set of coupons was not in contact with any anti-icing/de-icing chemicals or road splash; therefore, it will serve as a control to see the amount of corrosion based solely on the weather and the environment.

The corresponding locations of the field coupons are shown in the Google Earth map in 'Figure 9'.

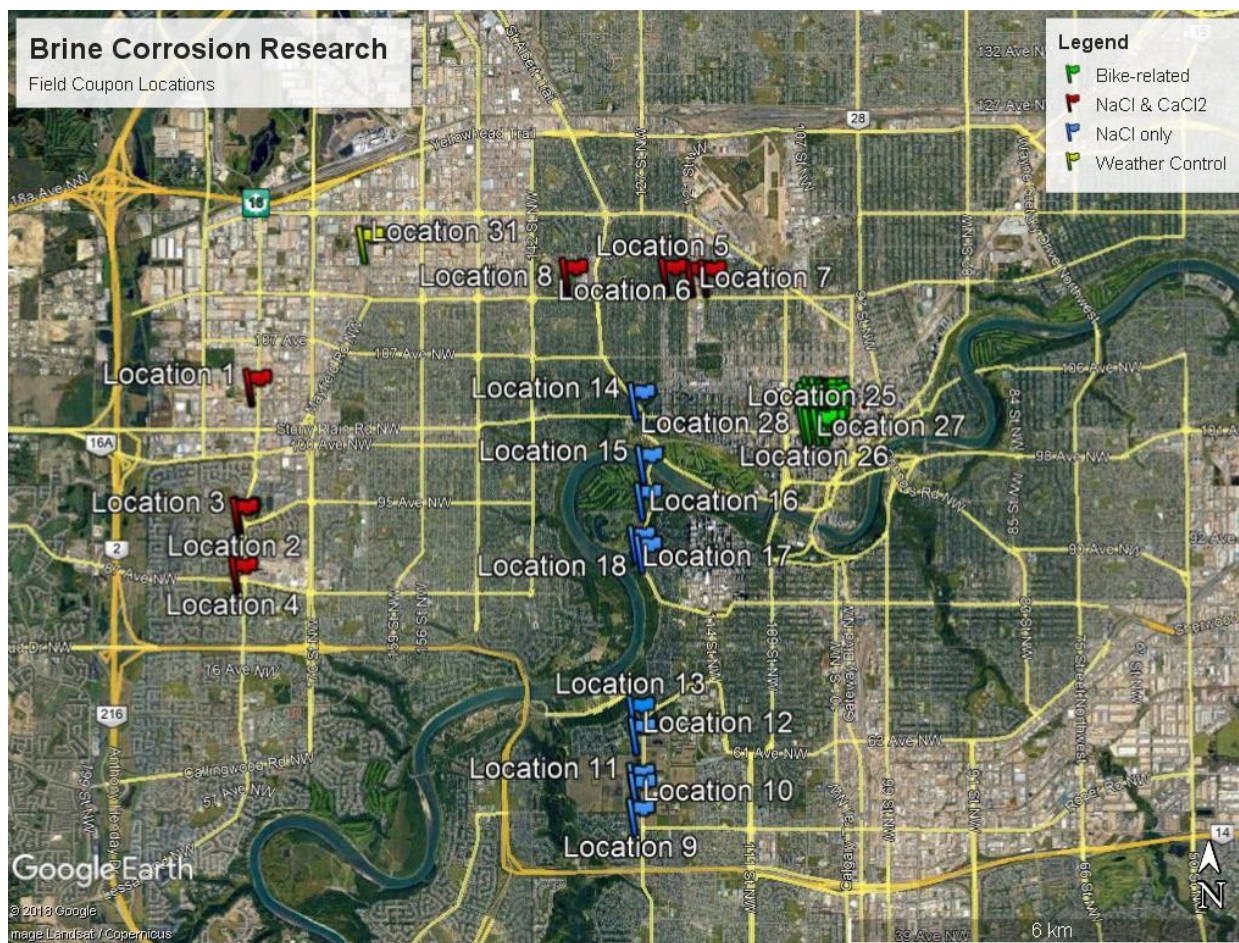


Figure 9 - Field Coupon Locations

3.4 RETRIEVAL OF FIELD COUPONS

3.4.1 VEHICLE-RELATED

The field coupons installed on City of Edmonton and Spruce Grove Buses were all retrieved by June 18, 2019. All coupons installed on buses were recovered.

'Figure 10' shows the coupons retrieved from the buses. Visual inspection of corrosion could not be conducted initially because the coupons were completely covered in dirt.



Figure 10 - As-Retrieved Corroded Field Coupons Installed on Buses

3.4.2 INFRASTRUCTURE & BICYCLE-RELATED

The field coupons installed on metal infrastructure and bicycle lanes were retrieved on May 14, 2019. Two of the coupon installments (6 coupons total) that were attached to the bicycle lanes downtown were not recovered. These coupon installments were either stolen or lost during the winter season.

Photos of the as-received field coupons are shown in 'Figure 11', 'Figure 12', and 'Figure 13'. The coupons shown in these photos were installed in areas exposed the existing program, the anti-icing pilot program, and no anti-icing/de-icing chemicals (environmental control test), respectively.



Figure 11 - Infrastructure-Related Field Coupons Retrieved from 122nd Street (Existing Program)

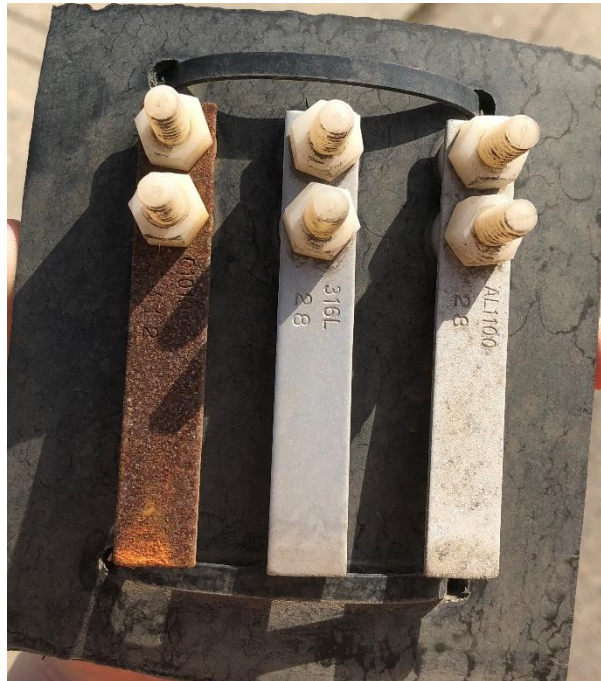


Figure 12 - Infrastructure-Related Field Coupons from 178th Street (Anti-Icing Pilot Program)



Figure 13 - Control Coupons Outside the Corrpro Office (Environmental Control)

Additional measures were taken to preserve the coupons to allow for an additional testing the next winter season if agreed upon by Corrpro and the City. To preserve the field

coupons, after cleaning and weighing, the coupons were placed in a paper towel soaked in mineral oil. Then the coupons were packaged in plastic to shield them from the environment. The coupons will have to be cleaned and reweighed before going back out into the field. 'Figure 14' shows the individually packaged coupons after cleaning.



Figure 14 - Packaged Coupons After Cleaning & Weighing

3.5 FIELD PROGRAM ANALYSIS

3.5.1 VEHICLE-RELATED

The coupons installed on buses were wiped with a damp cloth to remove some of the dirt before a full cleaning. 'Figure 15' and 'Figure 16' show the lightly cleaned coupons.



Figure 15 - Lightly Cleaned Field Coupons Recovered from Spruce Grove Buses (Existing Program)



Figure 16 - Lightly Cleaned Field Coupons Recovered from City of Edmonton Buses (Anti-Icing Pilot Program)

The carbon steel coupons showed the most significant surface corrosion (approx. 100% of surface corroded), the aluminum coupons showed only some visible corrosion (approx. 20-30% of surface corroded), and the stainless steel showed no observed corrosion (approx. 0% of surface corroded). There is not a visible difference between the corrosion on the Spruce Grove buses (exposed to existing program) compared to the City of Edmonton buses (exposed to anti-icing pilot program).

Significant corrosion typically occurred near the holes where the coupons were secured with the bolts. This localized corrosion is likely caused by the crevice between the nylon insulators and the coupon (crevice corrosion). 'Figure 17' shows a closer view of the corrosion near the mounting holes in the coupons.



Figure 17 - Crevice Corrosion on Field Coupons Installed on Buses (Carbon Steel on Left, Aluminum on Right)

After the dirt and corrosion products were cleaned off the field coupons, the average mass change of each metal coupon installed on the buses was recorded. The results are shown in 'Table 5'.

Table 5 - Average Measured Change in Mass on Buses

Bus Route	Program Exposed To	Location on Bus	Carbon Steel		Stainless Steel		Aluminum	
			Average Measured Change in Mass (g)	Total Coupon Mass Change (%)	Average Measured Change in Mass (g)	Total Coupon Mass Change (%)	Average Measured Change in Mass (g)	Total Coupon Mass Change (%)
Spruce Grove Buses	Existing	Mud Flap	- 0.249	2.615	- 0.001	0.003	- 0.014	0.389
		Wheel Well	- 0.127	1.334	0.000	0.000	- 0.006	0.164
		Combined	- 0.188	1.975	0.000	0.003	- 0.010	0.276
City of Edmonton Buses	Anti-Icing Pilot	Mud Flap	- 0.367	3.852	0.000	0.003	- 0.018	0.491
		Wheel Well	- 0.230	2.404	0.000	0.000	- 0.010	0.282
		Combined	- 0.299	3.128	0.000	0.001	- 0.014	0.386

The coupons attached to the mud flaps generally experienced greater change in mass, likely due to higher exposure. There were scratches on the mud flap coupons compared to the coupons attached to the wheel well, likely due to rocks and debris impacting the coupons while in service.

The stainless steel coupons were not observed to corrode at all while in service. The carbon steel and aluminum coupons on the City of Edmonton buses (anti-icing pilot program) have a greater metal loss compared to the Spruce Grove buses (existing program). However, in winter 2018/2019 there were not many applications of the inhibited CaCl_2 brine on Edmonton roads due to weather conditions. There were only approximately two full applications of inhibited CaCl_2 brine during winter 2018/2019. When temperatures drop too low, anti-icing/de-icing chemicals will freeze, making the road conditions worse. Therefore, there was not a big distinction between the anti-icing/de-icing chemicals applied to the specified routes, leading to similar corrosion rates of the coupons. The difference between the mass losses of the coupons could be due to several factors. A factor that could influence the corrosion significantly was the amount of time the buses were in service. Buses that go to Spruce Grove are only driven at specified times; however, City of Edmonton buses do not have a set schedule. Therefore, the exposure times may not have been the same. As well, a Spruce Grove bus

was out of service for a few weeks while conducting this field testing, possibly skewing the results. Omitting the coupons attached to this bus does not affect the mass change of the stainless steel and aluminum coupons but gives a mass change of - 0.200 g for the carbon steel coupons. Corrosion due to the type of anti-icing/de-icing chemicals could be the influencing factor; however, other factors such as exposure times may also affect the corrosion of the coupons.

3.5.2 INFRASTRUCTURE-RELATED

The average mass change of the metal types for the metal infrastructure routes are shown in 'Table 6'.

Table 6 - Average Measured Change in Mass on Metal Infrastructure

Location	Program Exposed To	Carbon Steel		Stainless Steel		Aluminum	
		Average Measured Change in Mass (g)	Total Coupon Mass Change (%)	Average Measured Change in Mass (g)	Total Coupon Mass Change (%)	Average Measured Change in Mass (g)	Total Coupon Mass Change (%)
178 th Street	Anti-icing Pilot	- 0.127	1.342	0.000	0.004	- 0.011	0.300
111 th Avenue	Anti-icing Pilot	- 0.103	1.092	0.000	0.006	- 0.012	0.317
122 nd Street	Existing	- 0.111	1.166	0.000	0.002	- 0.017	0.470
Groat Road	Existing	- 0.127	1.329	0.000	0.005	- 0.015	0.420

As with the bus-mounted coupons, no mass loss was measured for the stainless steel coupons installed on metal infrastructure. As expected, the carbon steel coupons experienced the largest mass change. The aluminum coupons installed on metal infrastructure showed minimal mass change. The mass change measurements agree with the visual observations of the corrosion after retrieving the coupons.

There was not a significant difference in the measured mass changes for any of the metal types tested whether they were exposed to the existing program or to the anti-icing pilot program. This observation infers that there is not a difference between the corrosion

effect of NaCl salt and inhibited CaCl_2 brine. However, there may be other factors affecting the corrosion rates of the anti-icing/de-icing chemicals. The amount of exposure is a very significant factor that can affect the extent of corrosion on the coupons. Exposure can be affected by the amount of splashing on the coupons, distance from the road, traffic conditions, duration of test, etc. Therefore, the coupons installed on metal infrastructure may not have had enough exposure to the anti-icing/de-icing chemicals to give accurate results. The corrosion seen on the coupons could be due to water (from snow/rain) splashing on the coupons rather than the anti-icing/de-icing chemicals.

3.5.3 BICYCLE-RELATED

'Table 7' shows the mass change related to the coupons installed on bicycle lane downtown.

Table 7 - Average Measured Change in Mass on Bicycles

Location	Program Exposed To	Carbon Steel		Stainless Steel		Aluminum	
		Average Measured Change in Mass (g)	Total Coupon Mass Change (%)	Average Measured Change in Mass (g)	Total Coupon Mass Change (%)	Average Measured Change in Mass (g)	Total Coupon Mass Change (%)
Downtown (Bicycle Lane)	Anti-icing Pilot	- 0.035	0.372	0.000	0.001	- 0.014	0.375

The mass change for the carbon steel coupons attached to the bicycle lanes was lower as compared to the coupon attached to metal infrastructure. The stainless steel and aluminum coupons attached to bicycle lanes experienced similar mass loss to those attached to metal infrastructure. The bicycle lanes downtown received regular applications of inhibited CaCl_2 brine as compared to the roads. Therefore, there was a much greater concentration of inhibited CaCl_2 brine on bicycle lanes compared to roads. This result could indicate that the inhibited CaCl_2 brine is not very corrosive to bicycles. However, the factor of exposure also must be considered. Bicycle lanes are typically less

utilized compared to roads in Edmonton during the winter due to weather condition. As well, bicycles do not generate as much splash on these coupons compared to cars because of their smaller size and reduced speed. Therefore, bicycle-related coupons would have significantly less exposure to splash and anti-icing/de-icing chemicals as compared to the metal infrastructure and vehicle-related coupons.

3.5.4 ENVIRONMENTAL CONTROL

'Table 8' shows the mass change related to the environmental control coupons installed outside the Corrpro office.

Table 8 - Average Measured Change in Mass on the Environmental Control Coupons

Location	Program Exposed To	Carbon Steel		Stainless Steel		Aluminum	
		Average Measured Change in Mass (g)	Total Coupon Mass Change (%)	Average Measured Change in Mass (g)	Total Coupon Mass Change (%)	Average Measured Change in Mass (g)	Total Coupon Mass Change (%)
Outside Corrpro Offices	Environmental Control	- 0.009	0.097	0.000	0.000	- 0.014	0.374

Compared with the coupons installed on city infrastructure near roadways and on buses, less corrosion was observed and measured on the environmental control coupons. Based on the installation location, these coupons would not have experienced any splashing from roadways and would have received minimal exposure to anti-icing and de-icing chemicals. Consequently, the corrosion would have been due to regular environmental conditions in Edmonton (snow, rain, wind, fluctuating temperatures, etc.). This highlights the corrosive nature of the local environments found around roadways in Edmonton.

4.0 LABORATORY PROGRAM

4.1 CHOSEN LABORATORY PROGRAM

Laboratory testing was considered for this research study to determine the corrosion effect of anti-icing/de-icing chemicals in known conditions. Unlike field-testing, variables such as temperature, humidity and exposure can be easily controlled in laboratory testing. The corrosion test recommended by Corrpro was the NACE TM0169 test. PNS uses a modified version of the NACE TM0169 corrosion test as a standard for selecting suitable anti-icing/de-icing chemicals for its Qualified Products list [2]. Ease of use, reproducibility, and flexibility in test duration length were additional reasons the NACE TM0169 test was chosen for this laboratory program. The metal types chosen for the coupons were carbon steel, stainless steel, aluminum, and galvanized steel. There are a wide range of metals used in civil infrastructure and vehicles, but the metals chosen are some of the most commonly used [10]. The coupons were exposed to various mixtures of NaCl, CaCl₂ brine, inhibited CaCl₂ brine, tap water, and distilled water. The City provided Corrpro with the anti-icing/de-icing chemicals used on Edmonton roads for laboratory testing. Anti-icing/de-icing mixtures and dilutions were discussed by Corrpro and City representatives to best reflect possible in-service scenarios on Edmonton roads.

4.2 COUPON PROCUREMENT

A total of 100 laboratory coupons were ordered on February 5, 2019 and procured by Corrpro on March 22, 2019. The quantities and compositions of coupons ordered are detailed in 'Table 9'. The dimensions of the coupons were 1" wide, 2" long, and 0.063" thick.

Table 9 - Lab Coupons Compositions and Quantities

Coupon Composition	Quantity Ordered
Carbon Steel (C1010)	25
Stainless Steel (316L)	25
Aluminum (1100)	25
Carbon Steel with Hot-Dipped Galvanized Finish (HD GALV)	25
Total	100

‘Figure 18’ shows the as-received condition of the laboratory coupons for each metal type. The order of the coupons from left to right in the image is carbon steel, stainless steel, aluminum, and galvanized steel.



Figure 18 - As-Received Laboratory Coupons

The standard NACE TM0169 immersion test was started on April 2, 2019 and was completed on April 5, 2019 (72 hours). The longer duration (modified NACE TM0169) test was started on April 6, 2019 and was completed on June 13, 2019.

4.3 LABORATORY PROCEDURE

The experimental set up of this testing is based on NACE TM0169 and is shown in ‘Figure 19’ and ‘Figure 20’.



Figure 19 – Side View of the Laboratory Setup (Coupons Out of Solution)



Figure 20 – Side View of the Laboratory Setup (Coupons Immersed in Solution)

One end of the fishing line is attached to the coupon, the other end is attached a custom-built wood frame. The string was threaded through the hole in the lid to allow for the testing environment to be enclosed. The custom-built wooden frame was positioned directly above the plastic containers, so the coupons could hang straight down into their corresponding plastic container. In order to avoid unintended galvanic coupling and corrosion, the individual coupons were installed and tested in a way that ensured separation and electrical isolation from all other coupons and conductive materials. The wooden frame was attached to four linear actuators and a timer relay, which automatically move the coupons up and down at specified intervals. The NACE test alternates between the coupons being immersed in the solution for 10 minutes and air drying for 50 minutes [13]. This test will be conducted inside the Corrpro office at room temperature. There will be no significant variations in temperature or humidity for the duration of this testing.

The ratio of chlorides from NaCl salt and CaCl₂ brine that was actually deposited onto the roads in winter 2017/2018 was utilized to help select sample liquid/solution compositions. This ratio is outlined in 'Table 10'.

Table 10 - Winter 2017/2018 Anti-Icing/De-Icing Material Usage [17]

Anti-Icing/De-Icing Chemicals	Amount	Units
NaCl salt	36,800	tonnes
Chloride from the NaCl	22,317	tonnes
CaCl ₂ brine	4,673,100	L
Chloride from the CaCl ₂	1,050	tonnes
Total chlorides	23,367	tonnes
Percent of total chloride from CaCl ₂ brine	4.5	%
Ratio of NaCl salt to CaCl ₂ brine	7.875	g/mL

Collectively, the term 'solution' is used for all liquids in this experiment for simplicity, even though distilled water is not technically a solution. A total of 10 liquids/solutions were investigated during this laboratory program, their corresponding solution numbers are outline in 'Table 11'.

Table 11 - Anti-Icing/De-Icing Solutions Tested

Solution Number	Description
1	Saturated NaCl
2	As-received CaCl ₂ brine
3	As-received inhibited CaCl ₂ brine
4	Saturated NaCl mixed with inhibited CaCl ₂ brine based on ratio in 'Table 10' (95:5)
5	Solution 4 diluted 1:1 by volume with distilled water
6	Solution 4 diluted 3:97 by volume with distilled water
7	Tap water
8	Distilled water
9	CaCl ₂ brine diluted 3:97 by volume with distilled water
10	Inhibited CaCl ₂ brine diluted 3:97 by volume with distilled water

4.4 LABORATORY PROGRAM ANALYSIS

4.4.1 STANDARD TEST

The standard version of the NACE test had a total test duration of 72 hours. 'Figure 21' to 'Figure 30' show pictures of the corroded coupons after the 72-hour test. The order of the coupons from left to right in each image is carbon steel, stainless steel, aluminum, and galvanized steel.



Figure 21 - Standard NACE TM0169 Coupons from Solution 1 (Saturated NaCl)



Figure 22 - Standard NACE TM0169 Coupons from Solution 2 (As-Received CaCl_2 Brine)



Figure 23 - Standard NACE TM0169 Coupons from Solution 3 (As-Received Inhibited CaCl_2 Brine)



Figure 24 - Standard NACE TM0169 Coupons from Solution 4 (Mixed Solution of Saturated NaCl and Inhibited CaCl_2 Brine (95:5))



Figure 25 - Standard NACE TM0169 Coupons from Solution 5 (Solution 4 Diluted 1:1 with Distilled Water)



Figure 26 - Standard NACE TM0169 Coupons from Solution 6 (Solution 4 Diluted 3:97 with Distilled Water)



Figure 27 - Standard NACE TM0169 Coupons from Solution 7 (Tap Water)



Figure 28 - Standard NACE TM0169 Coupons from Solution 8 (Distilled Water)



Figure 29 - Standard NACE TM0169 Coupons from Solution 9 (CaCl₂ Brine Diluted 3:97 with Distilled Water)



Figure 30 - Standard NACE TM0169 Coupons from Solution 10 (Inhibited CaCl_2 Brine Diluted 3:97 with Distilled Water)

Visual corrosion was evident on many of carbon steel, aluminum and galvanized steel coupons. The mass loss of the metal types in each solution after the 72-hour test are shown in 'Table 12'.

Table 12 - Measured Change in Mass from 72-Hour NACE TM0169 Test

Solution	Description	Measured Change in Mass (g)			
		Carbon Steel	Stainless Steel	Aluminum	Galvanized Steel
1	Saturated NaCl	- 0.047	0.000	- 0.004	- 0.198
2	As-received CaCl_2 brine	- 0.029	0.000	- 0.001	- 0.016
3	As-received inhibited CaCl_2 brine	- 0.027	0.001	- 0.022	- 0.515
4	Saturated NaCl mixed with inhibited CaCl_2 brine (95:5)	- 0.029	0.000	- 0.005	- 0.022
5	Solution 4 diluted 1:1 by volume with distilled water	- 0.040	0.001	- 0.006	- 0.016
6	Solution 4 diluted 3:97 by volume with distilled water	- 0.155	0.000	- 0.001	- 0.014
7	Tap water	- 0.029	0.001	- 0.001	- 0.031
8	Distilled water	- 0.004	0.000	- 0.001	- 0.012
9	CaCl_2 brine diluted 3:97 by volume with distilled water	- 0.171	0.000	- 0.000	- 0.019
10	Inhibited CaCl_2 brine diluted 3:97 by volume with distilled water	- 0.040	0.001	- 0.004	- 0.023

As seen in 'Table 12', the stainless steel coupons show some mass gain; however, this can be considered as the error margin in the mass measurements and can be assumed to be a zero. The error may be due to different scales used, residual corrosion products on the coupons, mineral deposition from the solution onto the coupons, or residual water on the

coupons. The mass losses of the coupons were low in the 72-hour test, especially for the stainless steel and aluminum coupons. The mass losses make it hard to determine which solution is causing the most corrosion to the metals, considering the margin of error. The longer duration test may yield larger mass losses and allow for better differentiation between the corrosiveness of the anti-icing/de-icing chemicals.

‘Table 13’ shows a ranking of the corrosivity of the solutions based on mass losses for each metal type in the standard test for better representation of the data.

Table 13 - Ranking of Standard Test Solutions in Terms of Mass Loss (Highest to Lowest)

	Solutions with Carbon Steel	Solutions with Stainless Steel	Solutions with Aluminum Coupons	Solutions with Galvanized Steel
Increasing Corrosivity ↑	9	—*	3	3
	6	—	5	1
	1	—	4	7
	10	—	10	10
	5	—	1	4
	4	—	2	9
	7	—	8	5
	2	—	7	2
	3	—	6	6
	8	—	9	8

*The stainless steel coupons showed zero mass change.

There is not a clear solution that is the most corrosive to all the metals. However, it seems that the corrosivity of each anti-icing/de-icing chemical may vary based on metal type.

Biological product appeared in the solutions containing the inhibited CaCl_2 brine, particularly in diluted and inhibited CaCl_2 brine (solution 10), as shown in ‘Figure 31’. There was some biological product buildup observed on a number of coupons immersed in solution 10, as shown in ‘Figure 32’. The presence of the biological product could influence the corrosion rate of the coupons, though the exact impact on the test results is unknown.

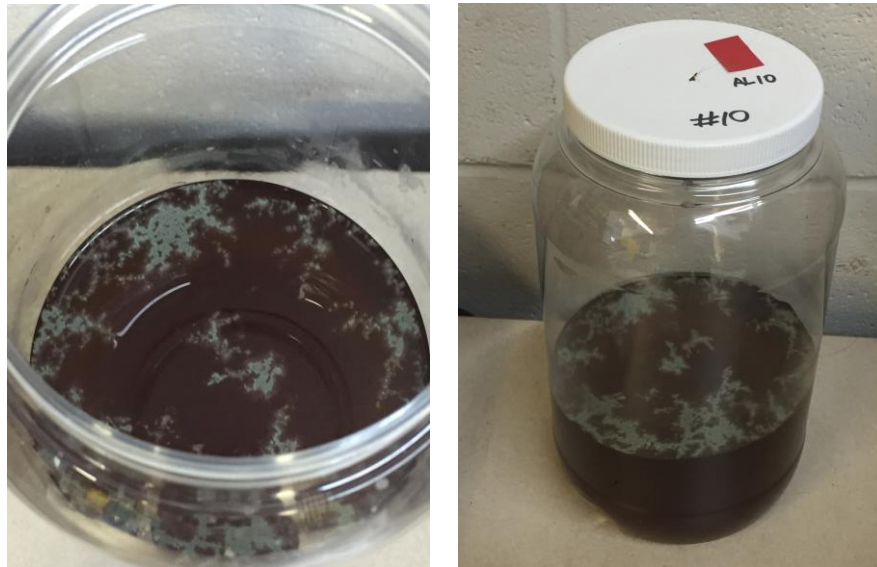


Figure 31 - Biological Products Appearing in Inhibited CaCl_2 Solutions



Figure 32 - Biological Buildup on Coupons in Inhibited CaCl_2 Brine Solutions

Based on the results of the 72-hour test, a ranking of the corrosivity of the solutions tested cannot be finalized. It was anticipated that a longer test length was needed to better determine the corrosivity of the NaCl salt and CaCl_2 brine solutions tested in this research study.

4.4.2 MODIFIED TEST

A modified test was completed based on the NACE TM0169 with an extended test duration. The modified laboratory test was concluded on June 13, 2019. The modified version of the NACE test had a total test duration of 69 days, or 1656 hours. 'Figure 33' to 'Figure 42' show pictures of the corroded coupons after the modified test. The order of the coupons from left to right in each image is carbon steel, stainless steel, aluminum, and galvanized steel.



Figure 33 - Modified NACE TM0169 Coupons from Solution 1 (Saturated NaCl)



Figure 34 - Modified NACE TM0169 Coupons from Solution 2 (As-Received CaCl₂ Brine)

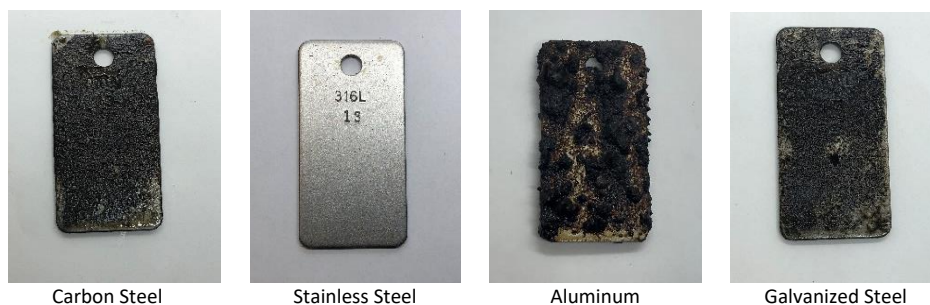


Figure 35 - Modified NACE TM0169 Coupons from Solution 3 (As-Received Inhibited CaCl₂ Brine)

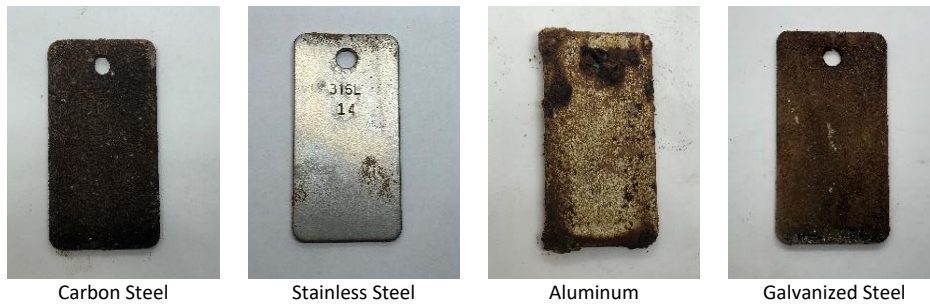


Figure 36 - Modified NACE TM0169 Coupons from Solution 4 (Mixed Solution of Saturated NaCl and Inhibited CaCl₂ Brine (95:5))



Figure 37 - Modified NACE TM0169 Coupons from Solution 5 (Solution 4 Diluted 1:1 with Distilled Water)



Figure 38 - Modified NACE TM0169 Coupons from Solution 6 (Solution 4 Diluted 3:97 with Distilled Water)



Figure 39 - Modified NACE TM0169 Coupons from Solution 7 (Tap Water)



Figure 40 - Modified NACE TM0169 Coupons from Solution 8 (Distilled Water)



Figure 41 - Modified NACE TM0169 Coupons from Solution 9 (CaCl₂ Brine Diluted 3:97 with Distilled Water)

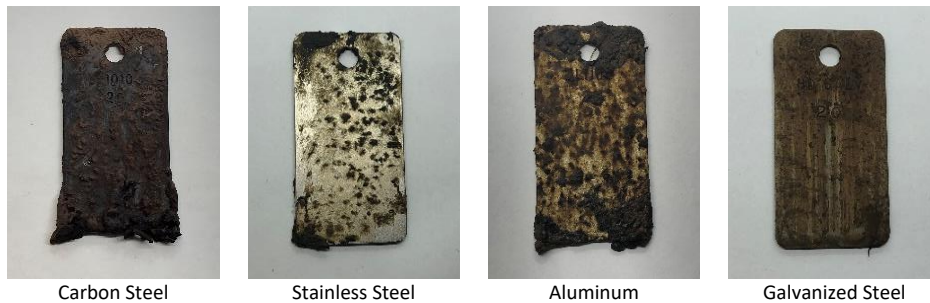


Figure 42 - Modified NACE TM0169 Coupons from Solution 10 (Inhibited CaCl₂ Brine Diluted 3:97 with Distilled Water)

Overall, there was significantly more corrosion on the coupons used in the modified test compared to the 72-hour test. The measured mass loss per metal coupon type is shown in 'Table 14'.

Table 14 - Measured Change in Mass from Modified NACE TM0169 Test

Solution	Description	Measured Change in Mass (g)			
		Carbon Steel	Stainless Steel	Aluminum	Galvanized Steel
1	Saturated NaCl	- 0.589	0.000	- 0.032	- 0.781
2	As-received CaCl ₂ brine	- 0.122	- 0.051	- 0.080	- 0.330
3	As-received inhibited CaCl ₂ brine	- 0.584	0.000	- 0.238	- 0.821
4	Saturated NaCl mixed with inhibited CaCl ₂ brine (95:5)	- 0.085	0.000	- 0.058	- 0.402
5	Solution 4 diluted 1:1 by volume with distilled water	- 0.270	0.000	- 0.026	- 0.571
6	Solution 4 diluted 3:97 by volume with distilled water	- 2.844	0.000	- 0.032	- 0.278
7	Tap water	- 2.285	0.000	- 0.035	- 0.351
8	Distilled water	- 0.090	0.000	- 0.024	- 0.128
9	CaCl ₂ brine diluted 3:97 by volume with distilled water	- 2.798	0.000	- 0.043	- 0.326
10	Inhibited CaCl ₂ brine diluted 3:97 by volume with distilled water	- 0.218	- 0.001	- 0.009	- 0.313

'Table 15' shows the ranking of the solutions based on mass losses for each metal type in the modified test for better representation of the data.

Table 15 - Ranking of Modified Test Solutions in Terms of Mass Loss (Highest to Lowest)

	Solutions with Carbon Steel	Solutions with Stainless Steel	Solutions with Aluminum	Solutions with Galvanized Steel
Increasing Corrosivity ↑	6	2*	3	3
	9	-	2	1
	7	-	4	5
	1	-	9	4
	3	-	7	7
	5	-	6	2
	10	-	1	9
	2	-	5	10
	8	-	8	6
	4	-	10	8

*For stainless steel coupons, significant mass loss was only measured in solution 2.

'Figure 43' shows a graphical representation of the mass change observed in the coupons.

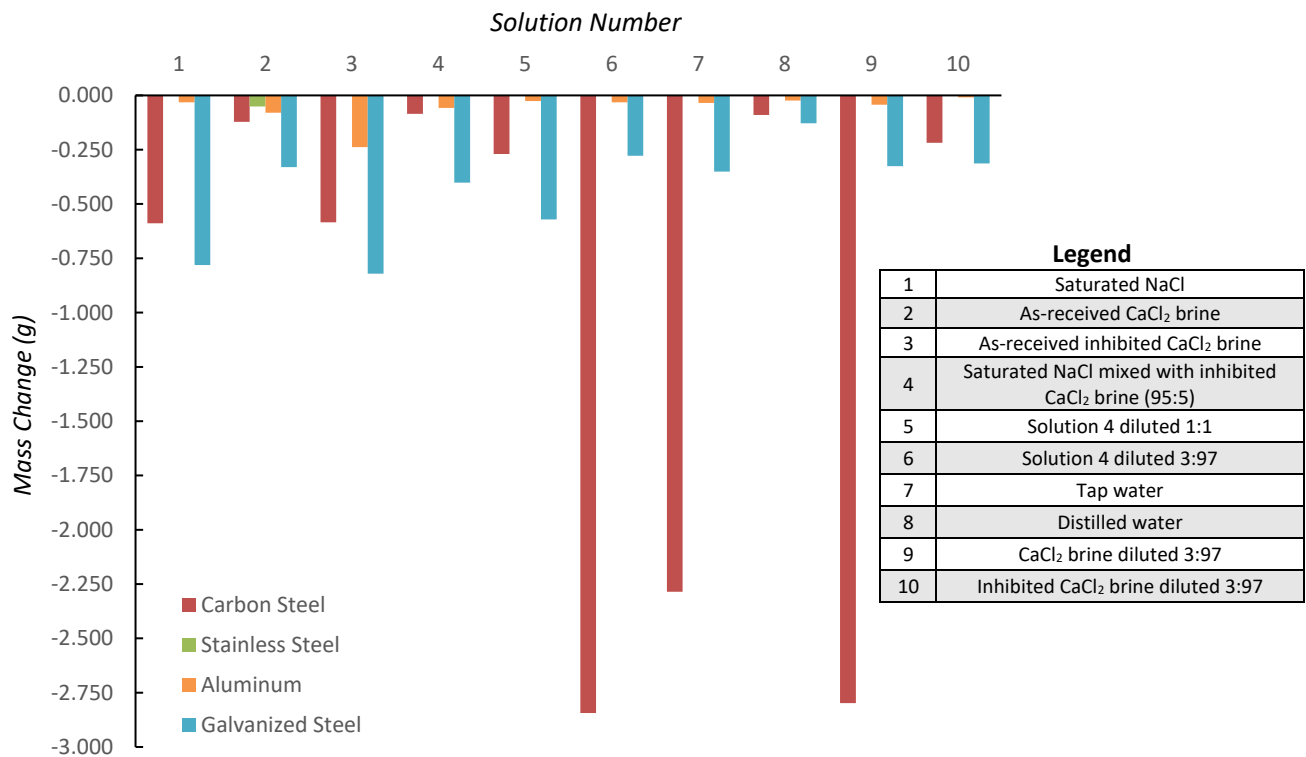


Figure 43 - Graphical Representation of Coupon Mass Change

4.4.2.1 EFFECT OF WATER

Distilled water was one of the least corrosive substances to all the metals investigated in the laboratory testing. However, tap water was the third most corrosive to carbon steel and the fifth most corrosive to the aluminum and galvanized steel coupons. This observation illustrates that impurities in water (e.g. those present in tap water) can contribute significantly to the corrosivity of water. Based on a comparison of the results from the standard (72-hour) and modified TM0169 tests, the overall amount/length of exposure to moisture appeared to be a significant contributor to the amount of corrosion observed on the coupons.

4.4.2.2 EFFECT OF SALT CONCENTRATION

Generally increasing salt content will speed up corrosion by acting as a catalyst in the electrochemical process, according to the adsorption theory [3]. In any chemical

reaction, such as corrosion, a transfer of electrons occurs. Water that contains salt (NaCl, CaCl₂, etc.) has a higher conductivity, so the electrons can move more freely around the solution. A higher rate of transfer of electrons leads to a higher rate of corrosion of the metal [18].

The saturated NaCl (solution 1) and the as-received brine (solution 2 and 3) would be considered as concentrated solutions. Concentrated solutions have unique thermodynamic and physical properties, such as strong acidity or alkalinity, high viscosity, and complicated ionic interactions. The chemical components in concentrated solutions do not completely dissociate since the ions are too close together. The activity coefficient in these solutions is suppressed, which results in decreased ion activity. Decreasing the ion activity in these solutions can cause the solutions to be less reactive or less corrosive. High salt concentrations dissolved in water can also reduce the amount of dissolved oxygen. This is because water molecules are highly attracted to the dissolved ions from the salt, which decreases the attraction of the water molecules to the non-polar oxygen molecules. Since oxygen is a required reactant in the corrosion chemical reaction, this can slow down the rate of reaction. However, this theory is only applicable when the metal is completely submerged in unaerated water [19].

Literature has shown that a solution with 3.5% salt content produces the most corrosive chloride salt solution possible. The combination of the high conductivity and oxygen solubility is at a maximum at this point [20]. 'Figure 44' shows the relationship between corrosion rate and NaCl content for carbon steels.

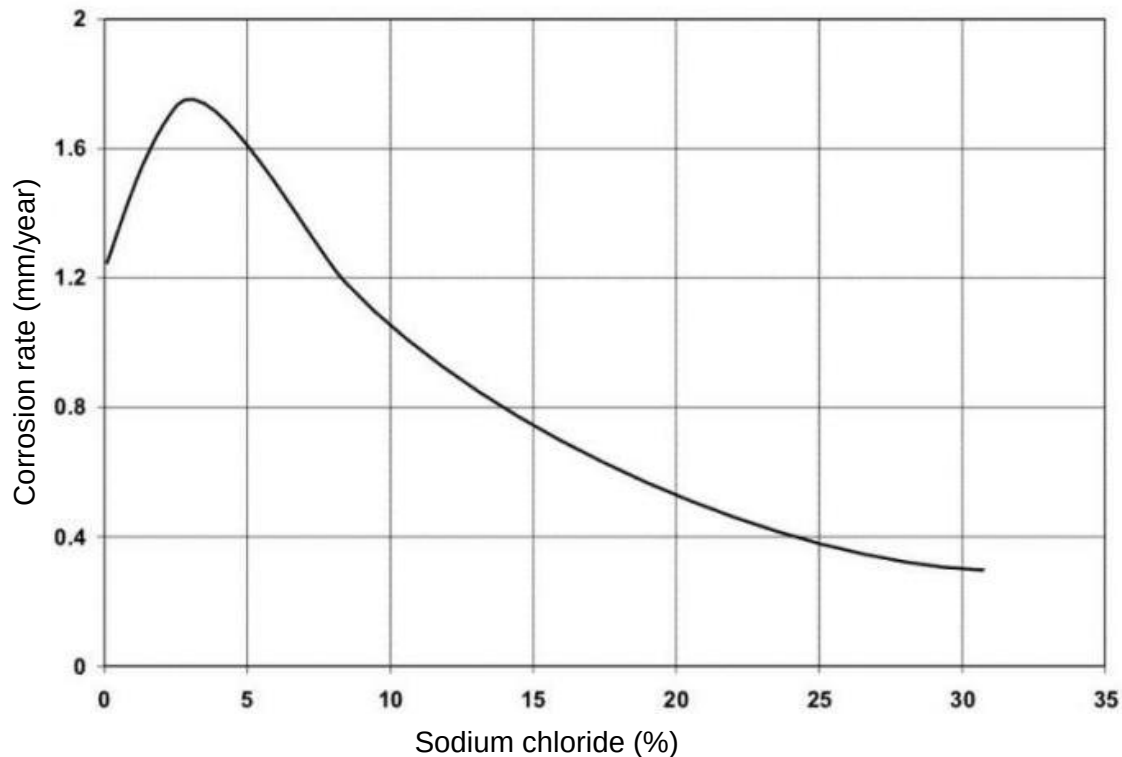


Figure 44 - Corrosion of Carbon Steel in Various NaCl Mixtures [20]

In this laboratory testing, the solutions with very high concentrations of salt (solution 1, 2, 3, 4, and 5), the salt could have reduced the amount of dissolved oxygen while the coupons were submerged. Though the adsorption theory would still apply for solutions with very high concentrations of salt, the reduction of available dissolved oxygen and suppressed ionic activity could minimize its effect. Whereas in solutions with a lower salt concentration (solution 6, 9, and 10), the salt could be a critical amount where it sped up corrosion but did not decrease the available dissolved oxygen when the coupon was submerged in the solution.

4.4.2.3 EFFECT OF BIOLOGICAL PRODUCTS

Biological products were observed in the solutions that contained the diluted inhibited CaCl_2 brine (solution 4, 5, 6, & 10). The biological products formed a film on the surface of these solution as well as buildup on the coupons. Another indicator that biological products were growing in these solutions was the smell of degradation. Since the

solutions were left in room temperature for a period of time, it is likely that the biodegradation of the organic inhibitor lead to the development of the biological products. Biodegradation of the inhibitor is expected in humid or wet environments when the concentrations are low enough [21]. 'Figure 45' shows the biological product that formed in the solution and on the coupons.

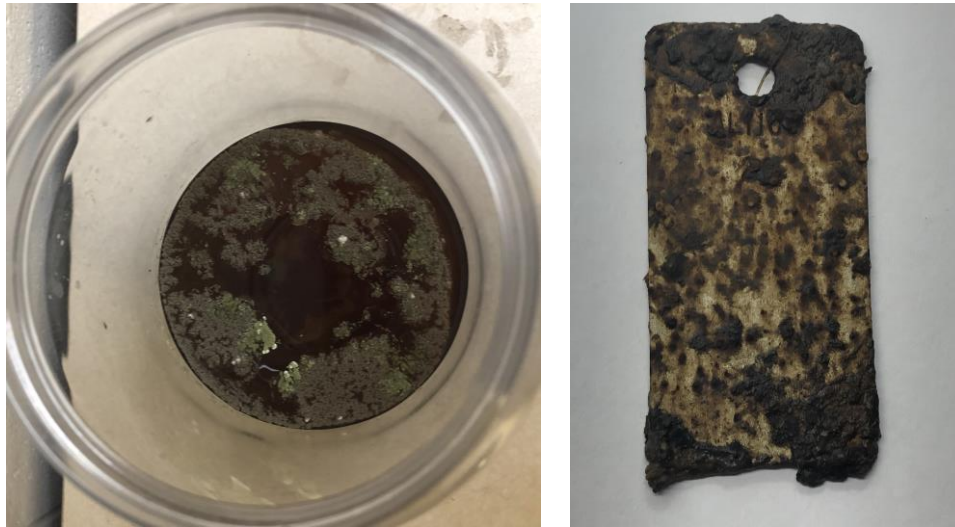


Figure 45 - Effect of Diluted Inhibited CaCl_2 Brine Solutions (Solution 10) on Aluminum

The as-received inhibited CaCl_2 brine (solution 3) did not form a film of biological products on the surface of the solution; however, a black slime-like corrosion product or biological product formed on all coupons exposed to inhibited CaCl_2 brine. The smell of degradation was also apparent on the as-received inhibited CaCl_2 brine (solution 3).



Figure 46 - Effect of As-Received Inhibited CaCl_2 Brine (Solution 3) on Carbon Steel

All microbial products set up an oxygen concentration on the metal's surface. In the concentration cell, the oxygen content is very low, creating an anodic region which is susceptible to metal loss [22]. Underneath the areas where biological products grow, localized corrosion or break-down of protective films will preferentially occur.

Some biological products, such as mold, absorb oxygen and produce carbon dioxide [23]. This results in a decrease in the amount of dissolved oxygen in the solutions, which could slow down the rate of the corrosion reaction.

Certain fungi can produce organic acids which can corrode steel and aluminum. Fungi may produce anaerobic sites for sulphate reducing bacteria which can lead to corrosion problems [20].

Further testing is recommended to determine what the biological product is and the full extent of its effect on the corrosion of the various metal types.

4.4.2.4 EFFECT OF INHIBITOR

The corrosion inhibitor affected the corrosivity of the CaCl_2 brine solution for different metals in different ways. For stainless steel, the as-received uninhibited CaCl_2 brine solution was significantly more corrosive compared to the inhibited brine (solution 3). For carbon steel, aluminum and galvanized steel, the as-received inhibited CaCl_2 brine solution (solution 3) appeared to be more corrosive compared to the as-received CaCl_2 brine (solution 2).

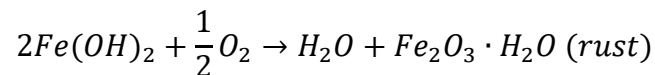
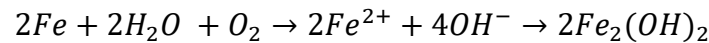
However, when the diluted brine solutions (solution 9 & 10) are compared for the carbon steel coupons, the CaCl_2 brine (solution 9) is significantly more corrosive than the inhibited CaCl_2 brine (solution 10). These conclusions indicate that the inhibitor may only be effective when the brine solution is diluted. Concentrated solutions may have too high chloride content for the corrosion inhibitor to reduce corrosion. Diluted solutions are more indicative of real-world conditions as the CaCl_2 brine will be mixed with snow and ice on the roads. Other than the sprayer truck and cars following close behind the sprayer truck, it is expected that vehicles on the road will be exposed to a diluted inhibited CaCl_2 brine mixture rather than the concentrated solution.

As well when comparing the diluted inhibited CaCl_2 brine solution (solution 10) to the diluted 3:97 mixture of NaCl salt and inhibited CaCl_2 brine (solution 6), solution 6 is significantly more corrosive to carbon steel coupons than solution 10. Solution 6 contained a much lower concentration of inhibitor compared to solution 10, while overall chloride concentration would have been similar. This indicates that there may be a minimum effective inhibitor concentration.

Additionally, it is unknown how the added inhibitor affects the CaCl_2 concentration in the brine. For the purposes of this study, the concentration of CaCl_2 between the brines was assumed to be approximately the same. Further testing of the CaCl_2 concentration in the brine products tested is recommended.

4.4.2.5 CORROSION OF CARBON STEEL COUPONS

The corrosion product formed on carbon steel exposed to oxygen and water is an iron oxide. The chemical reaction is shown in the equations below [22].



The carbon steel coupons were the most affected by the anti-icing/de-icing chemicals. 'Figure 47' shows the graphical representation of the mass change observed the carbon steel coupons.

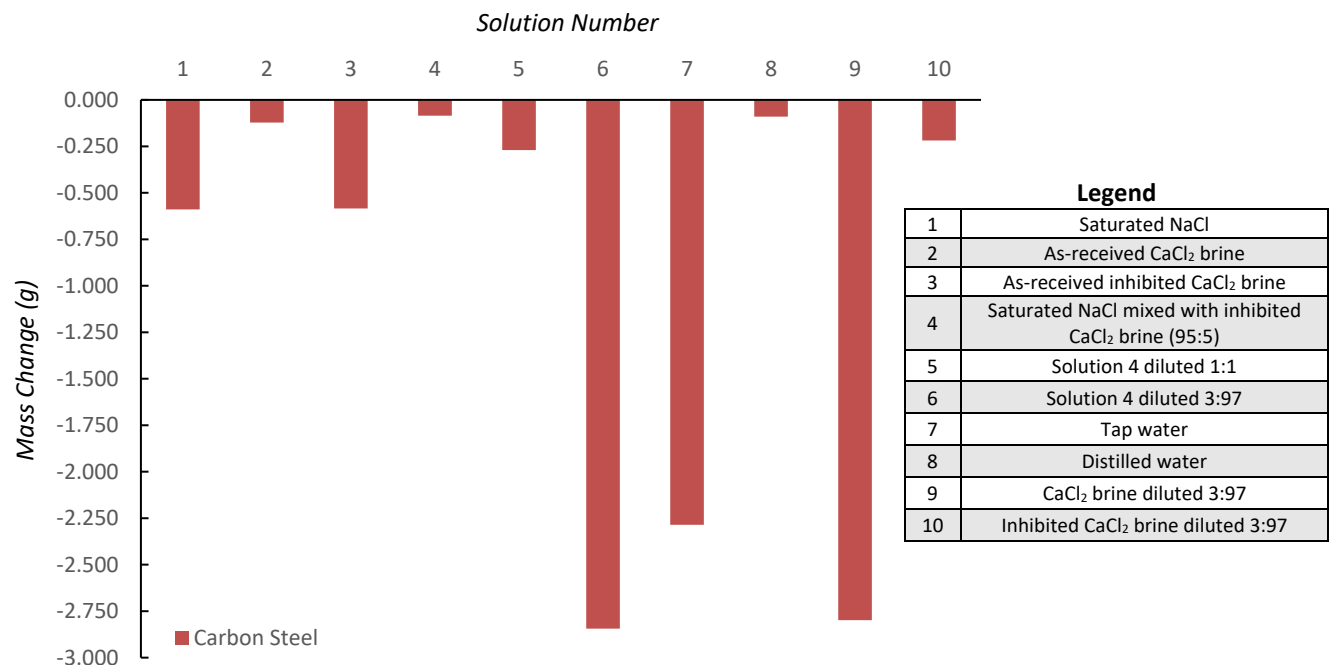


Figure 47 - Graphical Representation of Carbon Steel Coupon Mass Change

Most of the carbon steel coupons exposed to saturated NaCl, uninhibited CaCl₂ brine, and water formed orange corrosion products, assumed to be iron oxide [22]. The coupons exposed to inhibited CaCl₂ brine formed black corrosion products with slime-like consistency. The black corrosion products could also be black rust (Fe₃O₄),

which forms when there is limited oxygen present [24]. The limited oxygen content may have been caused by the formation of biological products in the solutions containing inhibited CaCl_2 brine.

The most corrosive solutions to carbon steel were solution 6, 7, and 9. These solutions had significant mass loss, approximately 3.00 g of metal loss compared to the next highest of approximately 0.6 g. From initial visual inspection of these coupons, all the coupons from these coupons formed a thick orange-black layer of iron oxide over the coupons. The formation of the thick layer of corrosion product likely resulted in concentration cells all over the coupon creating anodic regions where metal loss would favourably occur. 'Figure 48' shows the formation of iron oxide on the carbon steel coupons.



Figure 48 - Corroded Carbon Steel Coupons (From Left to Right: Solution 6, 7, and 9)

As discussed in "Section 4.4.2.1", the impurities in the tap water (solution 7) could have contributed greatly to the corrosion of the carbon steel. solutions 6 and 9 had small but critical amounts of CaCl_2 brine (and NaCl salt for solution 6) to speed up the corrosion reaction without decreasing any dissolved oxygen in the solution, as discussed in "Section 4.4.2.2". The decreasing quantity of inhibitor in these diluted solutions could also contribute to the increased amount of corrosion. There was significant mass loss

observed in these coupons, the cleaned corroded carbon steel coupons are shown in 'Figure 49'.

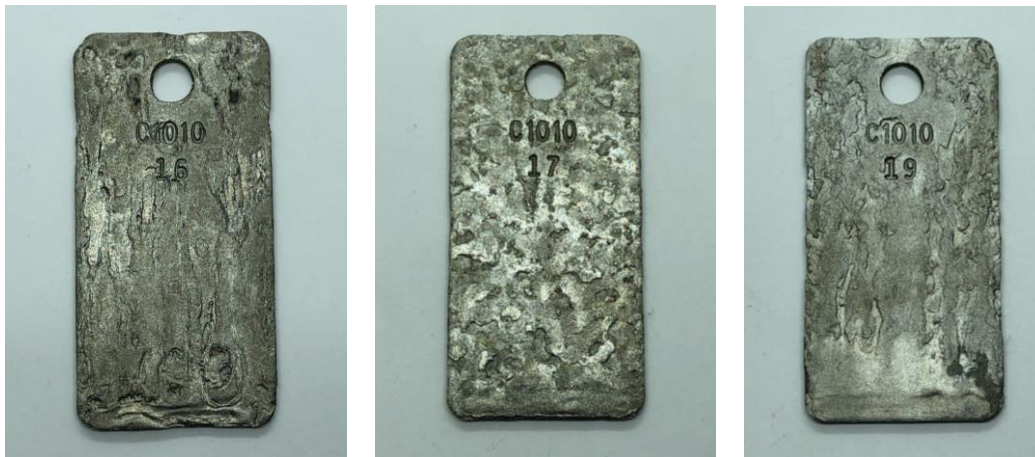


Figure 49 - Significant Mass Loss in Carbon Steel Coupons

The saturated NaCl and as-received brine solutions were still quite corrosive for carbon steel, but not as significantly as the solution discussed above. The mass change of the saturated NaCl (solution 1) and inhibited CaCl_2 brine (solution 3) is very similar so a definite conclusion on which one is more corrosive cannot be determined. The presence of biological products could have influenced the inhibited CaCl_2 brine solution as a black slime film was observed on the coupon. However, it is unclear if the biological products inhibited or encouraged the corrosion under these experimental conditions.

4.4.2.6 CORROSION OF STAINLESS STEEL COUPONS

The added chromium in stainless steel makes it more corrosion resistant than carbon steels [25]. The chromium will attach itself to oxygen more readily than iron. When the chromium attaches to the oxygen, it creates a chromium oxide layer which protects the rest of the material from degradation and corrosion. The break-down of this protective chromium layer will result in corrosion of the stainless steel. The presence of chloride ions and concentration cells induce localized corrosion (i.e. pitting) on stainless steel alloys [20].

‘Figure 50’ shows the graphical representation of the mass change observed the stainless steel coupons.

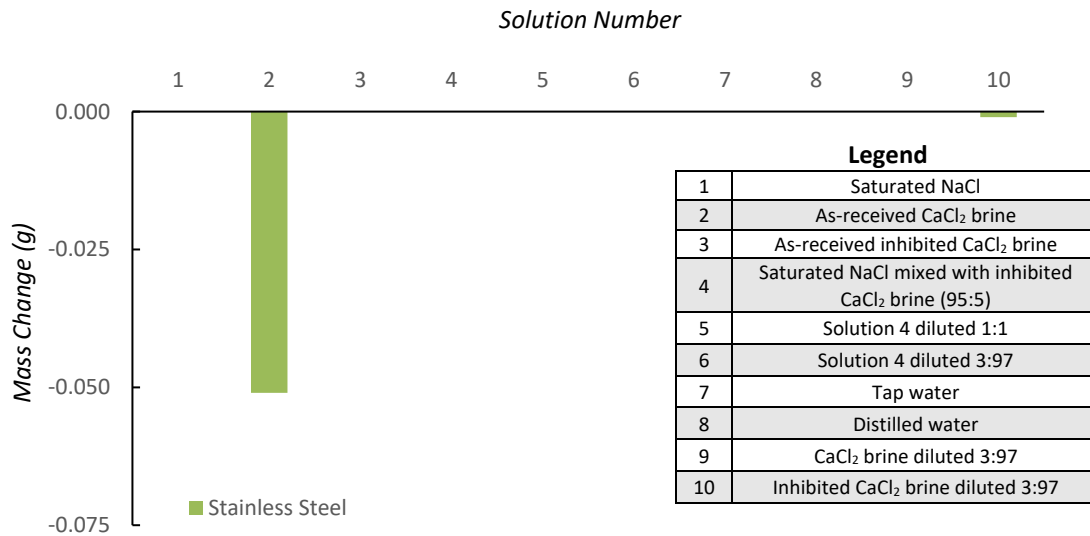


Figure 50 - Graphical Representation of Stainless Steel Coupons Mass Change

The stainless steel coupons did not seem to be affected by the anti-icing/de-icing chemicals at all, except for solution 2. The coupon exposed to the uninhibited as-received CaCl_2 brine had three severe pits near the bottom of the coupon and where the fishing line was secured to the mounting hole. Observations during testing showed that the solutions would pool at the bottom of the coupons while they were out of the solution. Solution would also get trapped in the crevice between the fishing line and the mounting hole. This would increase the exposure time of the coupons to their respective solutions. ‘Figure 51’ shows the pits observed on the stainless steel coupon exposed to uninhibited CaCl_2 brine.



Figure 51 - Stainless Steel Coupon Exposed to CaCl_2 Brine

A comparison between the NaCl salt and inhibited CaCl_2 brine cannot be determined as both coupons were not affected by their respective solutions. Based on the pitting corrosion caused by the uninhibited CaCl_2 brine (solution 2), it can be determined that the corrosion inhibitor in the inhibited CaCl_2 brine is effective at slowing down the corrosion of stainless steel.

4.4.2.7 CORROSION OF ALUMINUM COUPONS

The process of aluminum corrosion is called oxidation. The resulting aluminum oxide is a thin, hard layer that can passivate the metal and prevent further corrosion. Aluminum oxide appears as a powdery white or dull gray coating [26]. Metal loss of aluminum generally occurs as localized, pitting corrosion in areas where the aluminum oxide

protective layer is broken down [20]. The higher the ability of a solution to break down the aluminum oxide protective layer, the higher the rate of corrosion/metal loss on the aluminum.

'Figure 52' shows the graphical representation of the mass change observed in the aluminum coupons.

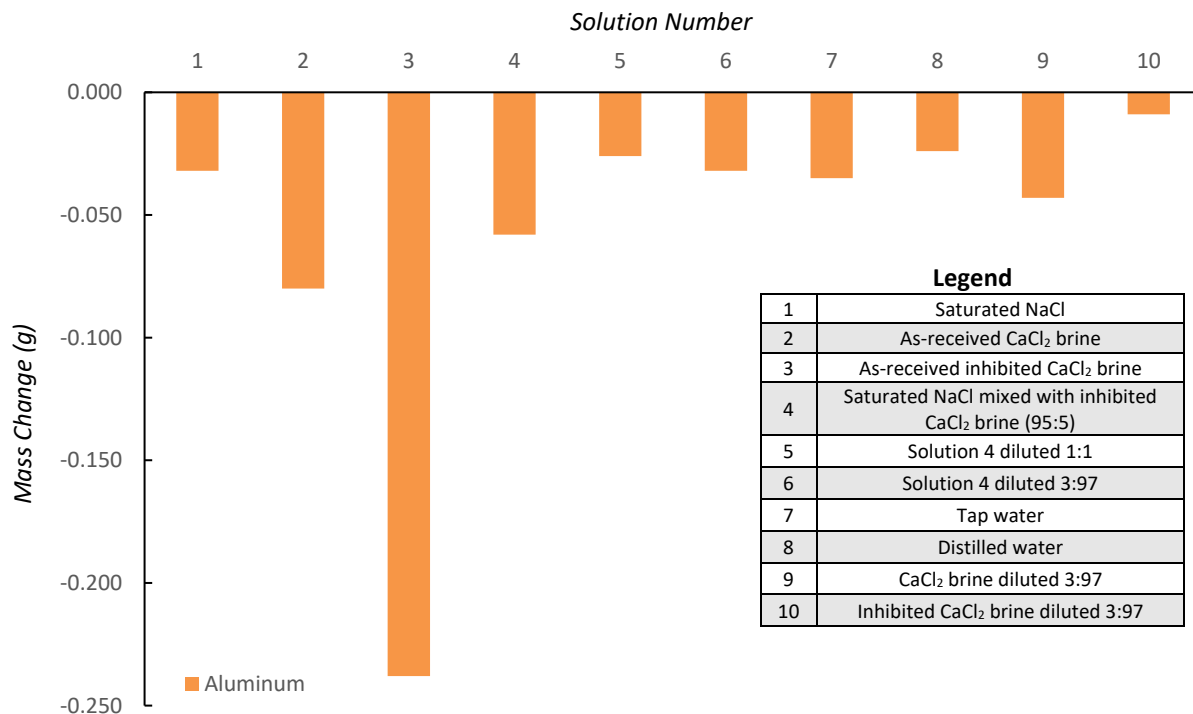


Figure 52 - Graphical Representation of Aluminum Coupon Mass Change

Corrosion was observed on all of the aluminum coupons; however, the amount of corrosion was relatively small when compared to the corrosion observed on the carbon steel and galvanized steel coupons. The only corrosion observed on the coupons was due to the expected pitting corrosion mechanism (shown in 'Figure 53').



Figure 53 - Pitting Corrosion on Aluminum Coupons

The concentrated CaCl_2 brine solutions (solutions 2 and 3) had the most observed corrosion on the aluminum coupons. Out of these, the inhibited CaCl_2 brine (solution 3) had the most significant pitting and the most overall mass loss due to corrosion. Comparatively less corrosion was observed in the diluted CaCl_2 brine solutions (solutions 9 and 10). Conversely, less corrosion was observed the inhibited solution (solution 10) versus the uninhibited solution (solution 9). Higher concentrations of CaCl_2 in solution appeared to increase the amount of corrosion observed; however, the addition of the inhibitor appeared to increase corrosion in a high concentration CaCl_2 brine but decrease corrosion in a more diluted solution of CaCl_2 . Further research could be conducted to better explain the differences in corrosion observed on the aluminum coupons when exposed to the different solutions in this study.

4.4.2.8 CORROSION OF GALVANIZED STEEL COUPONS

Galvanized steel is generally a plain carbon steel hot-dipped or otherwise coated in a protective layer of zinc. The zinc coating prevents corrosive substances from reaching

the underlying steel or iron. Additionally, the zinc protects the iron by corroding first, as it is the more active metal. Only after all the zinc is consumed will the carbon steel start to rust. 'Figure 54' shows a graphical representation of the mass change observed in the galvanized steel coupons.

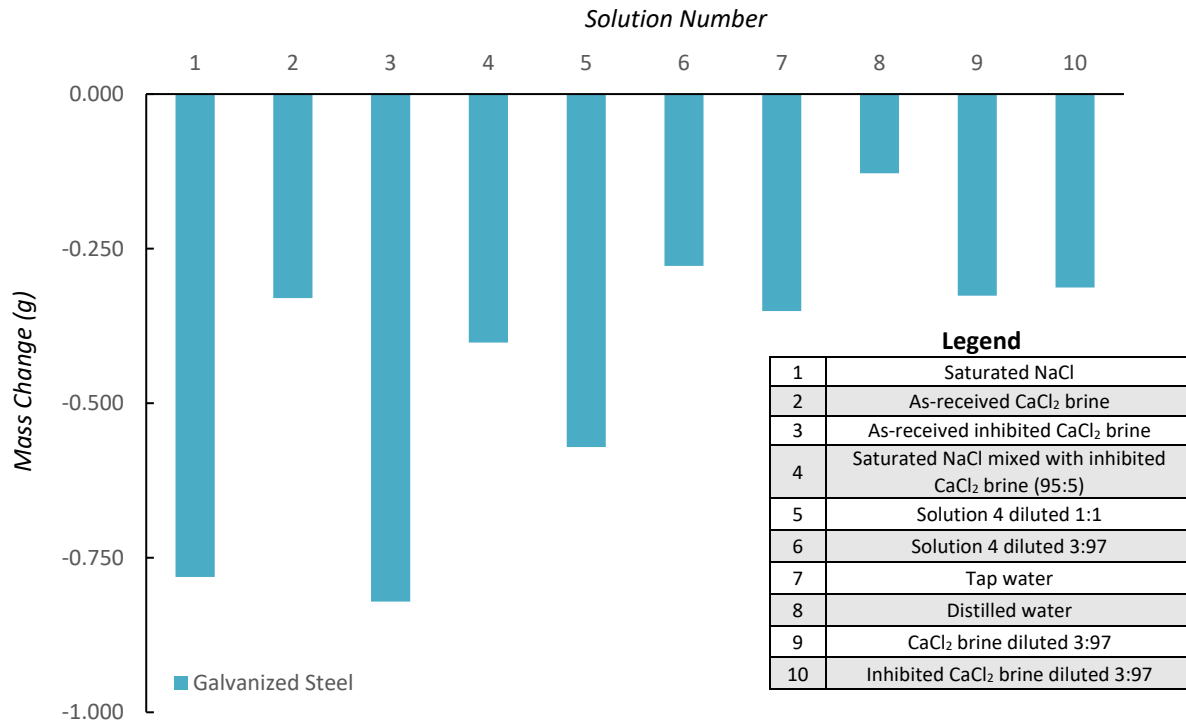


Figure 54 - Graphical Representation of Galvanized Steel Coupons Mass Loss

The corrosion of the galvanized steel coupons was varied, but generally it was much less than the corrosion seen on the carbon steel coupons. Therefore, the zinc coating was protecting the carbon steel base metal. The coupon exposed to saturated NaCl (solution 1) was the only galvanized steel coupon to form orange corrosion products. This indicates that the zinc coating was consumed from the coupon and the underlying steel below started to corrode. The zinc coating was also either completely or nearly completely consumed in the inhibited CaCl₂ brine solution (solution 3), which is known given that the mass change was close to that of solution 1. However, likely due to the biological products growing, the orange corrosion products were not observed.

Additionally, after the corrosion products were cleaned off degradation of the carbon steel base metal was seen, shown in 'Figure 55'.



Figure 55 - Zinc Coating Entirely Consumed from Inhibited CaCl_2 Brine (Solution 3)

On all other coupons, the zinc protective coating was still partially intact. In some of the coupons, the break-down of the zinc coating can visibly be seen (shown in 'Figure 56'). The zinc coating is still intact at the top of the coupon but the bottom the coating has broken down. This shows that applying a zinc coating on carbon steel can be an effective way a preventing corrosion of the base metal. However, the coating may need to be reapplied after a period of time.



Figure 56 - Zinc Coating Break-down on Galvanized Steel Coupons

Some of the coupons may have had a greater quantity of zinc applied when they were galvanized. A thicker coating of zinc would provide greater protection to the carbon steel base metal [20].

Based on the mass loss results, the corrosion effects of NaCl salt and inhibited CaCl₂ brine seem comparable. Both anti-icing/de-icing chemicals are quite corrosive to galvanized steel at higher concentrations. In solutions where NaCl salt and inhibited CaCl₂ brine were mixed, the corrosion effect was significantly decreased. As well, the chemicals seem to be less corrosive at lower concentration of salt or brine.

5.0 CONCLUSIONS

The corrosion effects of NaCl and CaCl₂ were analyzed by Corrpro for the City through a literature review, a field program, and a laboratory program. The main conclusions and recommendations are summarized below:

- Anti-icing and de-icing products, including CaCl₂, NaCl and other chloride salts, are used globally for winter road maintenance in areas that experience icy conditions.
- Research studies and pilot programs have been introduced worldwide to determine the impact of anti-icing and de-icing products on metal infrastructure and vehicles. However, the results of research programs found in literature review have been inconsistent. Both laboratory and field programs are highly dependent on several factors, such as metal type, temperature, humidity, amount of exposure, and many more. Literature review has shown significant variations between the corrosion effects of NaCl and CaCl₂.
- Literature review of various case studies has proven that laboratory and field testing results do not always correlate with each other. Unknown factors in real world results cannot be easily replicated in laboratory testing.
- Aqueous solutions containing chloride salts, such as NaCl, CaCl₂ and MgCl₂, are known to cause corrosion to metal infrastructure and vehicles. Regular cleaning and maintenance of protective coatings (i.e. paint) is recommended to minimize corrosion.
- The amount/length of exposure to corrosive solutions and environments was a major contributing factor to amount of corrosion observed on laboratory and field coupons. In general, more exposure to corrosive environments leads to more corrosion:
 - In the laboratory testing, increased corrosion was observed on coupons exposed to sample liquids/solutions for a longer period of time (for coupons where corrosion was observed). The standard NACE TM01669 test (72-hour test) was not a long enough time to observe measurable corrosion mass loss based on the measurement devices and coupons utilized for this study.

- In the field testing, increased corrosion was observed on coupons that were installed in areas expected to have higher relative exposure to corrosive solutions (and moisture in general):
 - Overall, more corrosion was observed on coupons installed on buses versus coupons installed on municipal infrastructure. This is likely due to the coupons on buses being exposed to a greater amount of moisture where they were installed on the buses (curbside by the wheels).
 - More corrosion was observed on coupons installed on bus mud flaps versus coupons installed further away from the road and wheel (on cabling behind the wheel well).
 - Slightly more corrosion was observed on buses that primarily traveled on routes that would have been part of the anti-icing pilot program (i.e. received applications of inhibited CaCl_2 brine) versus buses that primarily traveled on routes that would have been exposed to the City's existing program. This minor difference in mass change could be attributed to various factors, such as different exposure times, atypically few applications of inhibited CaCl_2 brine, and road conditions (speed, traffic, etc). It is recommended that field testing be continued in winter 2019/2020 to allow the coupons to be exposed to more typical amounts of inhibited CaCl_2 brine.
 - More corrosion was observed on coupons installed on municipal infrastructure near to major roadways (car traffic) versus coupons installed near bicycle lanes.
 - The least corrosion was observed on the coupons installed on municipal infrastructure located further away from roadways (less probability of splash exposure from vehicles).
- The amount of corrosion observed varied with coupon material type:

- In the field testing, the most corrosion was observed on the carbon steel coupons. A relatively much smaller amount of corrosion was observed on the aluminum and galvanized steel coupons, while a negligible amount of corrosion was observed on the stainless steel coupons.
- Compared with the field testing, a much larger amount of corrosion was observed in the lab testing:
 - The most severe corrosion was observed on carbon steel coupons.
 - The galvanized steel coupons were corroded by all solutions. The amount of corrosion observed varied but was either in the same order of magnitude or much less than the amount of corrosion observed on the carbon steel coupons. Based on the corrosion products observed, the zinc coating does sacrificially protect the underlying carbon steel, but only for a set period of time (depending on corrosion rate).
 - Relative to the carbon steel and galvanized steel coupons, much less corrosion was observed on the aluminum coupons. This is representative of the protective surface oxide layer of aluminum being, at minimum, partially effective in mitigating corrosion.
 - For the stainless steel coupons, corrosion was only observed in one solution. This is representative of the protective surface oxide being very effective in mitigating corrosion in nearly all experimental conditions.
- With regards to the comparison of anti-icing/de-icing programs, the field testing produced inconclusive results due to insufficient time in the field, varied/atypical application of inhibited CaCl_2 brine in winter 2018/2019, and due to the high correlation between exposure amount and amount of corrosion observed. Additional testing time in the field is recommended to further investigate the corrosion effects of the anti-icing pilot.
- In the lab program, the corrosion observed on the coupons varied with solution type:

- Tap water was one of the most corrosive liquids, while distilled water was one of the least corrosive liquids. These results display the large effect that impurities have on the corrosivity of water.
- Salt concentration had a large effect on corrosivity of the solutions:
 - Concentrated brine solutions (solutions 1, 2, 3 and 4) were much less corrosive to the carbon steel coupons than tap water and two of the diluted solutions (ones that contained little or no inhibitor concentration). Research has shown that increasing salt concentrations in a solution after a certain point can slow down the corrosion reaction.
 - For the stainless steel coupons, corrosion was only observed in the concentrated CaCl_2 brine solution (solution 2). The pitting corrosion observed was also only located in areas of the coupon expected to have been exposed to the solution for a near continuous period of time. Near continuous exposure to concentrated CaCl_2 brine is not expected to be a normal occurrence on the City of Edmonton's roadways. Therefore, additional corrosion due to the anti-icing program is not expected on stainless steel.
 - The most corrosion was observed on the aluminum coupons in the inhibited CaCl_2 brine solution (solution 2) followed by CaCl_2 brine solution (solution 3). While the addition of inhibitor appeared to have increased corrosion in these concentrated brine solutions, it appeared to have decreased corrosion in the 3:97 diluted variants of these solutions (solutions 9 and 10, respectively). More research is required to understand the variance in corrosion observed for the aluminum coupons due to salt concentrations.
 - The galvanized steel coupons were most heavily corroded in the NaCl brine and inhibited CaCl_2 brine solutions (solutions 1 and 2, respectively).

However, more research is required to understand the variance in corrosion observed due to salt concentrations.

- The addition of inhibitor had a varied effect on the corrosion observed, which appeared to depend on overall salt and inhibitor concentrations and potentially due to some observed biological activity:
 - Significantly less corrosion was observed for the carbon steel coupons exposed to the diluted and inhibited CaCl_2 brine solution (solution 10) versus the diluted CaCl_2 brine solution (solution 9). Solution 10 was also less corrosive to aluminum versus solution 9.
 - More corrosion was observed on the carbon steel, galvanized steel and aluminum coupons in the inhibited CaCl_2 brine (solution 3) versus the CaCl_2 brine (solution 2). The observation was reversed for the stainless steel coupons in that corrosion was only observed for the coupon exposed to the CaCl_2 brine solution (solution 2).
 - The amount of observed corrosion on the carbon steel increased significantly as the NaCl /inhibited CaCl_2 brine solution (solution 4) was diluted. It is unclear if this increase in corrosion is due to decreasing chloride content or due to increased effectiveness of the inhibitor.
 - Biological products were observed in solutions that contained diluted inhibited CaCl_2 brine. The effect of the formation of these biological products on the corrosion observed is unknown based on the research conducted to date. Further research is recommended.
 - Overall, the addition of inhibitor appears to reduce the corrosivity of *diluted* CaCl_2 brine but may only be effective over a range of inhibitor and chloride concentrations. A diluted state of the inhibited CaCl_2 brine may also be more typical of exposure conditions in Edmonton.
- The results indicate that carbon steel, zinc and aluminum can corrode when exposed to common environmental conditions found in Edmonton. It is recommended that

additional corrosion prevention methods be applied to metal surfaces exposed to corrosive environments. Examples methods include limitation of actual exposure to moisture (keeping surfaces dry), the application and maintenance of high-performance corrosion protection coatings (e.g. paint on a car) or lubrication (e.g. for bicycle chains/cassettes).

- There are many factors that can influence the corrosive effects of anti-icing/de-icing programs. Many of these factors could be investigated further for additional clarification.

REFERENCES

- [1] M. Fischel and The SeaCrest Group, "Evaluation of Selected Deicers Based on a Review of the Literature," Colorado Department of Transportation, Denver, 2001.
- [2] Pacific Northwest Snowfighters, "Snow and Ice Control Chemical Products Specifications and Test Protocols," PNS Association, 2010.
- [3] Y. Xi and Z. Xie, "Corrosion Effects of Magnesium Chloride and Sodium Chloride on Automobile Components," Colorado Department of Transportation, Denver, 2002.
- [4] E. V. Baroga, "2002-03 Salt Pilot Project," Washington State Department of Transportation, Olympia, 2003.
- [5] P. C. Casey, C. W. Alwan, C. F. Kline, G. K. Landgraf and K. R. Lisenmayer, "Impacts of Using Salt and Salt Brine for Roadway Deicing," Idaho Transportation Department Research Program, Boise, 2014.
- [6] W. A. Nixon, "Economic Effects of Using Calcium Chloride vs Sodium Chloride for Deicing/Anti-Icing," IHR Hydroscience and Engineering, University of Iowa, Iowa, 2008.
- [7] X. Shi, L. Fay, C. Gallaway, K. Volkening, M. M. Peterson, T. Pan, A. Creighton, C. Lawlor, S. Mumma, Y. Liu and T. A. Nguyen, "Evaluation of Alternative Anti-Icing and Deicing Compounds Using Sodium Chloride and Magnesium Chloride as Baseline Deicers - Phase 1," Colorado Department of Transportation, Denver, 2009.
- [8] X. Shi, L. Fay, C. Gallaway and K. Volkening, "Performance and Impacts of Current Deicing and Anti-icing Products: User Perspective versus Experimental Data," Washington Transportation Research Board, Bozeman, 2007.
- [9] X. Shi, L. Fray, Z. Yang, T. A. Nguyen and Y. Lui, "Corrosion of Deicers to Metal in Transportation Infrastructure: Introduction and Recent Developments," Walter de Gruyter GmbH & Co., 2009.
- [10] H. Marshall, "What Kinds of Metals Are Cars Made From?," It Still Runs, [Online]. Available: <https://itstillruns.com/kind-metals-cars-made-from-7331288.html>.
- [11] B. E. Brycki, I. H. Kowalczyk, M. Pakiet, O. Kaczerewska and A. Szulc, "Organic Corrosion Inhibitors," Dimensions, 2018.
- [12] Pacific NorthWest Snowfighters, "Qualified Products List," 2018.
- [13] NACE International, "NACE/ASTM TM0169 G0031 12A-2012-SG Standard Guide for Laboratory Immersion Corrosion Testing of Metals," 21200-SG, 2012.
- [14] ASTM International, "ASTM B117-18 Standard Practice for Operating Salt Spray (Fog) Apparatus," G01.05, 2018.
- [15] SAE International, "SAE J2334 Laboratory Cyclic Corrosion Test," 2003.
- [16] W. A. Nixon and J. Xiong, "Investigation of Materials for the Reduction and Prevention of Corrosion on Highway Maintenance Equipment," Iowa Highway Research Board, University of Iowa - Hydroscience & Engineering, 2009.

-
- [17] W. Goulden, "Anti-icing Brine Pilot Project; Environmental Monitoring and Metrics Report," City of Edmonton - Intergrated Infrastructure Services, Edmonton, 2017-2018.
 - [18] C. Gillespie, "How Does Salt Water Rust Metals?," Sciecing, 2018.
 - [19] S. Wang, D. Liu, N. Du, Q. Zhao, S. Liu and J. Xiao, "Relationship between Dissolved Oxygen and Corrosion Characterization of X80 Steel in Acidic Soil Simulated Solution," International Journal of Electrochemical Science, Volume 10, 2015.
 - [20] P. R. Roberge, Corrosion Basics: An Introduction, vol. Third Edition, Houston, Texas: NACE International, 2018, p. 209.
 - [21] G. Mahura, Interviewee, *VP Sales and Business Development at Tiger Calcium*. [Interview]. 16 07 2019.
 - [22] S. A. Bradford, Corrosion Control, New York: Van Nostrand Reinhold, 1993, p. 253.
 - [23] R. S. Potter and R. S. Snyder, "Abstracts of Bacteriology, Volume 2 - The Production of Carbon Dioxide by Molds Inoculated into Sterile Soil," Soil Science, 1918.
 - [24] Armour Protective Packaging, "Corrosion: Types of Rust," 2019.
 - [25] Aalco Metals Limited, "Stainless Steel - General Information - Alloying Elements in Stainless Steel," Aalco Metals Limited, England & Wales, 2018.
 - [26] Total Materia, "Corrosion of Aluminum and its Alloys: Forms of Corrosion," 2008.
 - [27] M. A. Salman, G. Al-Nuwaibit, M. Safar and A. Al-Mesri, "Solubility Limit of Major Salts in Sodium Chloride Solutions," International Journal of Emerging Technology and Advanced Engineering, Kuwait Institute for Scientific Research, 2015.
 - [28] NACE, "Standard Practice SP0169 Control of External Corrosion on Underground or Submerged Metallic Piping Systems," NACE International, Houston, TX, (latest version).
 - [29] ASTM International, "ASTM G1 Standard Practice for Preparing, Cleaning, and Evaluation Corrosion Test Specimens," 2017.
 - [30] O. Seri, D. Murakami, R. Shimomura and M. Kimura, "Polarization Curve and its Analysis of Aluminum in Conditions of Deareated and Open-to-air in NaCl Solution," Zairyo-to-Kankyo, 2014.