Developing Locally Sourced Brine Additive for Anti-Icing

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The objective of this project was to develop a series of anti-icers tailored to meet the varying requirements of highway anti-icing performance, cost-effectiveness, and minimized corrosion and environmental impact for typical road weather scenarios and user priorities in the three ADOT&PF regions. Development and evaluation of potential deicing chemicals, additives, and mixtures made from local agricultural products or the by-products of local distilleries/breweries or other manufacturing processes for use on roadways and other transportation facilities were included as the project's research. The use of sustainable resources offers a cost-effective alternative to high-cost proprietary products that enhance the performance characteristics of salt brine for anti-icing on Alaska roads. This research was accomplished through literature review, agency surveys, and laboratory investigation followed by field operational tests. Specifically, locally sourced salt brine additives suitable for anti-icing during winter maintenance in Alaska were developed and tested.

Several test methods, such as differential scanning calorimetry, electrochemical impedance spectroscopy, and SHRP H205.2 Test Method for Ice Melting of Liquid Deicing Chemicals, were used to determine the performance of various anti-icing formulations relative to traditional sodium chloride (NaCl) and magnesium chloride (MgCl2) liquids. The negative effect of anti-icing formulations on bare steel and concrete were investigated to identify the most infrastructure-friendly anti-icing formulation.

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SI* (MODERN METRIC) CONVERSION FACTORS

APPROXIMATE CONVERSIONS TO SI UNITS

Symbol	When You Know	Multiply By	To Find	Symbol
LENGTH				
in	inches	25.4	millimeters	mm
ft	feet	0.305	meters	m
yd	yards	0.914	meters	m
mi	miles	1.61	kilometers	km
AREA				
in^2	square inches	645.2	square millimeters	mm^2
ft^2	square feet	0.093	square meters	m^2
yd^2	square yard	0.836	square meters	m^2
ac	acres	0.405	hectares	ha
mi^2	square miles	2.59	square kilometers	km^2
VOLUME				
fl oz	fluid ounces	29.57	milliliters	mL
gal	gallons	3.785	liters	L
ft^3	cubic feet	0.028	cubic meters	m^3
yd^3	cubic yards	0.765	cubic meters	m^3
NOTE: volumes greater than 1000 L shall be shown in m^3				
MASS				
oz	ounces	28.35	grams	g
lb	pounds	0.454	kilograms	kg
T	short tons (2000 lb)	0.907	megagrams (or "metric ton")	Mg (or "t")
TEMPERATURE (exact degrees)				
^{o}F	Fahrenheit	5 (F-32)/9 or (F-32)/1.8	Celsius	^{o}C
ILLUMINATION				
fc	foot-candles	10.76	lux	lx
fl	foot-Lamberts	3.426	candela/m^2	cd/m^2
FORCE and PRESSURE or STRESS				
lbf	poundforce	4.45	newtons	N
lbf/in^2	poundforce per square inch	6.89	kilopascals	kPa

APPROXIMATE CONVERSIONS FROM SI UNITS

Symbol	When You Know	Multiply By	To Find	Symbol
LENGTH				
mm	millimeters	0.039	inches	in
m	meters	3.28	feet	ft
m	meters	1.09	yards	yd
km	kilometers	0.621	miles	mi
AREA				
mm^2	square millimeters	0.0016	square inches	in^2
m^2	square meters	10.764	square feet	ft^2
m^2	square meters	1.195	square yards	yd^2
ha	hectares	2.47	acres	ac
km^2	square kilometers	0.386	square miles	mi^2
VOLUME				
mL	milliliters	0.034	fluid ounces	fl oz
L	liters	0.264	gallons	gal
m^3	cubic meters	35.314	cubic feet	ft^3
m^3	cubic meters	1.307	cubic yards	yd^3
MASS				
g	grams	0.035	ounces	oz
kg	kilograms	2.202	pounds	lb
Mg (or "t")	megagrams (or "metric ton")	1.103	short tons (2000 lb)	T
TEMPERATURE (exact degrees)				
^{o}C	Celsius	1.8C+32	Fahrenheit	^{o}F
ILLUMINATION				
lx	lux	0.0929	foot-candles	fc
cd/m^2	candela/m^2	0.2919	foot-Lamberts	fl
FORCE and PRESSURE or STRESS				
N	newtons	0.225	poundforce	lbf
kPa	kilopascals	0.145	poundforce per square inch	lbf/in^2

*SI is the symbol for the International System of Units. Appropriate rounding should be made to comply with Section 4 of ASTM E380.
(Revised March 2003)

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Acknowledgments

Abstract

The objective of this project was to develop a series of anti-icers tailored to meet the varying requirements of highway anti-icing performance, cost-effectiveness, and minimized corrosion and environmental impact for typical road weather scenarios and user priorities in the three ADOT&PF regions. Development and evaluation of potential deicing chemicals, additives, and mixtures made from local agricultural products or the by-products of local distilleries/breweries or other manufacturing processes for use on roadways and other transportation facilities were included as the project's research. The use of sustainable resources offers a cost-effective alternative to high-cost proprietary products that enhance the performance characteristics of salt brine for anti-icing on Alaska roads. This research was accomplished through literature review, agency surveys, and laboratory investigation followed by field operational tests. Specifically, locally sourced salt brine additives suitable for anti-icing during winter maintenance in Alaska were developed and tested. A literature review and agency surveys were conducted to define the scope and direction for laboratory tests.

Several test methods, such as differential scanning calorimetry, electrochemical impedance spectroscopy, and SHRP H205.2 Test Method for Ice Melting of Liquid Deicing Chemicals, were used to determine the performance of various anti-icing formulations relative to traditional sodium chloride (NaCl) and magnesium chloride ($MgCl_2$) liquids. The negative effect of anti-icing formulations on bare steel and concrete were investigated to identify the most infrastructure-friendly anti-icing formulation.

Executive Summary

The goal of this project was to develop and evaluate potential deicing chemicals, additives, and mixtures made from local by-products of local distilleries/breweries for use on roadways and other transportation facilities. The use of sustainable resources offers a cost-effective alternative to high-cost proprietary products that enhance the performance characteristics of salt brine for anti-icing on Alaska roads. Anti-icing is the application of material prior to a storm system to prevent the bonding of ice to the pavement, whereas deicing is the application of material after a storm system to break the ice-pavement bond. This research was accomplished through literature review, agency surveys, and laboratory investigation. Specifically, locally sourced salt brine additives suitable for anti-icing during winter maintenance in Alaska were developed and tested.

Chloride-based chemicals, known as road salts, play a key role in ensuring safe winter-driving conditions, especially on highways during cold and snowy weather. However, there are growing concerns about the impact of road salts on transportation infrastructure, motor vehicles, and the environment. Development of alternative anti-icing products serves the public interest, as this research is expected to generate significant cost savings for Departments of Transportation and other maintenance agencies, provide traveler benefits in terms of improved safety and mobility, and increase societal benefits by reducing corrosion and environmental impacts. The U.S. currently spends approximately \$2.3 billion annually to keep highways free of snow and ice, and the associated corrosion and environmental impacts add at least \$5 billion (FHWA 2005). This research will provide AKDOT&PF with more options for snow and ice control and promote sustainable winter road service.

Laboratory analysis revealed favorable ice-melting properties for two distillery by-products, labeled Sample 1 and Sample 2 and sodium metasilicate and potassium gluconate were identified to contain optimal corrosion-inhibition properties. The top ten highest performance mixes determined by SHRP H205.2 Test Method for Ice Melting of Liquid Deicing Chemicals were Mixes 3, 4, 6, 12, 13, 16, 19, 20, 22, and 27, which had significantly higher ice-melting capacities than the 23% NaCl control. Furthermore, Mix 35 and 36 were determined to be the most effective mixture since the ice melting capacity increased with time whereas, the ice melting capacities of the other mixtures decreased due to evaporation as shown in Figure 6. Mix 35 and 36 also contained significantly lower amounts of Boost, therefore, decreasing overall costs. The NACE TM0169-95 PNS Modified Dip Test was performed using Mix 3, Mix 22, Mix 3A, Mix 22A, and the controls, which were 23% NaCl and 30% $MgCl_2$. The 72-hour corrosion test revealed very similar weight loss values for Mix 3 and Mix 22, which were significantly lower than weight loss values for 23% NaCl and 30% $MgCl_2$. Corrosion rate data presented in **Error! Reference source not found.** show significantly reduced corrosion rates for anti-icer formulations containing Sample 1 and Sample 2 compared to the controls, which were 23% NaCl and 30% $MgCl_2$.

Table **1** shows the results of the ice melting tests at 30°F, 15°F, and 20°F and the corrosion rates of various deicer formulations containing the by-products.

Table **2** also shows various mix designs and the results of the freeze/thaw cycling and corrosion tests to carbon steel. The negative effects of evaporation were minimized in Mix 35 and 36, which showed the highest ice melting capacity 60 minutes after initial application at 20°F.

Table 1: Ice melting capacity and corrosion rates of various formulations

Mix	Corrosion Inhibitors	Sample 1	Sample 2	Additive	Ice Melting Capacity, 60 min @ 30°F (ml brine/g deicer)	Ice Melting Capacity, 60 min @ 15°F (ml brine/g deicer)	Ice Melting Capacity, 60 min @ 20°F (ml brine/g deicer)	Corrosion Rate (MPY)
3	1% KGluc 0.2%NaMetaSil	7%	5%	2% KAc	4.880	1.562	1.70	16.85
4	1% KGluc 0.2%NaMetaSil	5%	5%	2% urea	4.578	1.436	-	-
6	1% KGluc 0.2%NaMetaSil	3%	3%	2% KSuc	4.577	1.476	-	-
12	1% KGluc 0.2%NaMetaSil	7%	5%	2% KSuc	-	1.380	-	-
13	1% KGluc 0.2%NaMetaSil	5%	3%	2% urea	4.782	1.444	1.88	-
16	1% KGluc 0.2%NaMetaSil	7%	3%	2% KAc	4.646	1.460	-	-
19	1% KGluc 0.2%NaMetaSil	5%	4%	2% KAc	4.587	1.499	-	-
20	1% KGluc 0.2%NaMetaSil	7%	4%	2% KSuc	4.996	1.436	-	-
22	1% KGluc 0.2%NaMetaSil	7%	4%	2% KAc	5.134	1.483	1.71	18.85
27	1% KGluc 0.2%NaMetaSil	7%	5%	2% urea	4.593	1.499	-	-
35	0.5% KGluc 0.1%NaMetaSil	2.5%	0.5%	3% Boost 1.0% urea	-	-	1.93	-
36	0.5% KGluc 0.1%NaMetaSil	2.5%	0.5%	5% Boost 1.0% urea	-	-	2.00	-

Note: KGluc = potassium gluconate; NaMetaSil = sodium metasilicate; KAc = potassium acetate; MgSil = magnesium silicate; CaSil = calcium silicate; KSil = potassium silicate

Table 2: Corrosion rate to carbon steel and weight loss of Portland cement concrete specimens exposed to various deicer formulations.

Mix	Corrosion Inhibitors	Sample 1	Sample 2	Additive	Amount of NaCl and MgCl$_2$	PCC Weight Loss (%)	Corrosion Rate (MPY)
3A	1% KGluc 0.2%NaMetaSil	7%	5%	2% KAc	7% MgCl$_2$ 8.1% NaCl	12.76	25.08
3B	1% KGluc 0.2%NaMetaSil	7%	5%	2% KAc 3% MgSil	7% MgCl$_2$ 8.1% NaCl	2.77	25.30
3C	1% KGluc 0.2%NaMetaSil	7%	5%	2% KAc 3% CaSil	7% MgCl$_2$ 8.1% NaCl	2.61	23.47
22A	1% KGluc 0.2%NaMetaSil	7%	4%	2% KAc	7% MgCl$_2$ 8.1% NaCl	8.77	23.91
22B	1% KGluc 0.2%NaMetaSil	7%	4%	2% KAc 3% KSil	7% MgCl$_2$ 8.1% NaCl	1.27	25.75
13X	1% KGluc 0.2%NaMetaSil	5%	0%	2% urea	23% NaCl	7.27	-
13Y	1% KGluc 0.2%NaMetaSil	0%	1%	2% urea	23% NaCl	6.95	-
13Z	1% KGluc 0.2%NaMetaSil	5%	1%	2% urea	23% NaCl	6.20	-

Note: KGluc = potassium gluconate; NaMetaSil = sodium metasilicate; KAc = potassium acetate; MgSil = magnesium silicate; CaSil = calcium silicate; KSil = potassium silicate

Commercially available by-products were successfully used in the development of high performance anti-icer formulations, resulting in lower corrosion impacts, lower costs, and decreased environmental impact through the application of sustainable resources. The anti-icer formulations were observed to contain desirable characteristics such as high ice-melting capacities and low corrosion rates as compared with the traditional deicers, sodium chloride and magnesium chloride.

There is a need to better utilize locally available by-products, the addition of two Barley distillery by-products from Alaska and sodium metasilicate and potassium gluconate to salt brine have been demonstrated to greatly enhance the ice melting capacity of salt brine at relatively cold temperatures to the level of MgCl$_2$ at reasonable costs. The additives have also displayed significant benefits to reduce the corrosiveness of salt brine to carbon steel. Some additives have also been identified and tested for their benefits in reducing the deterioration of Portland cement concrete in the presence of diluted anti-icer solutions and freeze/thaw cycling. At 20°F, the 60-min ice melting capacity of the WTI formulations (Mix 3, Mix 22, Mix 13, Mix 13Z, Mix 35, Mix 36) are significantly higher than the products currently used by AKDOT&PF.

Additionally, the process in which the two Barley distillery by-products were identified as effective salt brine additives proved to be an efficient method for determining the value of the use of by-products in highway maintenance applications. The process is outlined in Figure **1**. The first step is to identify acceptable waste materials or by-products (e.g., without heavy metal contaminants) and then define various concentrations to determine the most efficient using laboratory methods. Ice melting performance, corrosion to carbon steel, and impacts to concrete

can be determined following test methods SHRP H205.2, NACE TM0169-95, and SHRP H205.8, respectively. Finally, field operational tests need to be performed before implementation to highway maintenance agencies.

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┌─────────────────────┐      ┌─────────────────────┐      ┌─────────────────────┐
│ Identify Potential  │  →   │ Design of           │  →   │ Determine Ice       │
│ Waste Material or   │      │ Experiments to      │      │ Melting Performance,│
│ By-Products         │      │ Determine           │      │ Corrosion to Steel, │
│                     │      │ Concentrations      │      │ and Impacts to      │
│                     │      │                     │      │ Concrete            │
└─────────────────────┘      └─────────────────────┘      └─────────────────────┘

┌─────────────────────┐      ┌─────────────────────┐      ┌─────────────────────┐
│ Laboratory          │  →   │ Field Operational   │  →   │ Implementation to   │
│ Investigation       │      │ Testing of Highest  │      │ Maintenance Agencies│
│ Following SHRP      │      │ Performers          │      │                     │
│ H205.2 NACE         │      │                     │      │                     │
│ TM0169-95, and      │      │                     │      │                     │
│ SHRP H205.8         │      │                     │      │                     │
└─────────────────────┘      └─────────────────────┘      └─────────────────────┘
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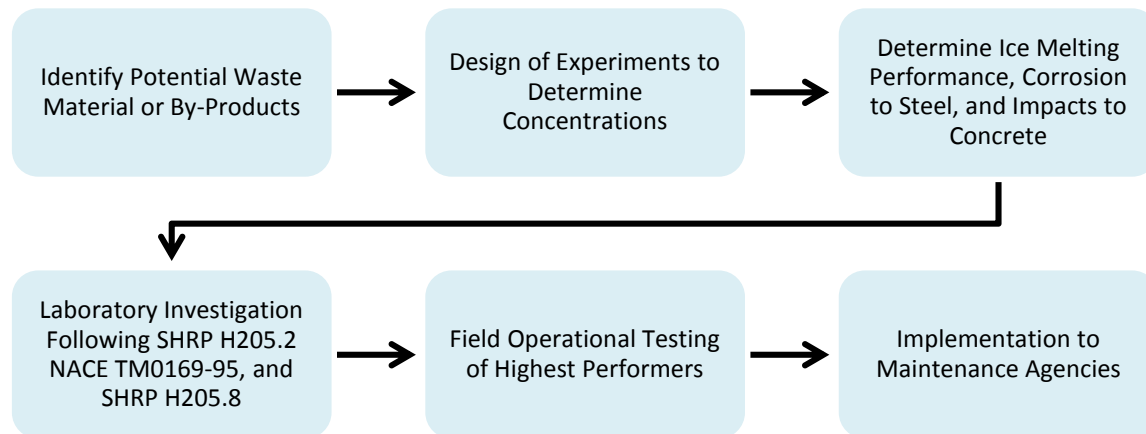
Figure 1: Process for developing alternative deicers.

1. CHAPTER 1 – INTRODUCTION AND RESEARCH APPROACH

1.1. Problem Statement and Research Objective

Currently the U.S. spends approximately $2.3 billion annually to keep highways free of snow and ice; the associated corrosion and environmental impacts add at least $5 billion (FHWA 2005). Departments of Transportation (DOTs) are continually challenged to provide safe, reliable winter highways in a cost-effective and eco-friendly manner, while dealing with increased traffic demands, higher customer expectations, and unprecedented staffing and funding constraints. Anti-icing has been gradually accepted and adopted by North American maintenance agencies as a proactive approach to winter highway safety and mobility. Taylor et al. (2010) evaluated the brines made of glycerol, sodium chloride (NaCl), magnesium chloride ($MgCl_2$), and commercial deicers individually or in combination and concluded that the blend of 80% glycerol with 20% NaCl showed the greatest promise in good performance and low negative impacts. This blend, however, has very high viscosity, and its dilution allows anti-icing application but reduces effectiveness. Furthermore, since the chemical oxygen demand of waste glycerol was reported at a high level of 1.986g O_2/g glycerol, the use of glycerol may cause negative impacts to water quality, which has to be mitigated by limiting the dosage of glycerol in the formulation and controlling the contaminants in it (Mackay et al. 2008).

The ADOT&PF has a number of pilot programs in Southeast Alaska and the Northern Region currently making salt brine for roadway anti-icing. The process is replacing $MgCl_2$ as the primary anti-icing chemical. Raw salt can be purchased at much lower costs than $MgCl_2$. Shipping costs for salt in a solid form are more economical, as $MgCl_2$ can only be shipped as a liquid solution, and much of the transportation costs are to ship water, which is in cheap, abundant supply locally. The main issue is that salt brine has a much higher eutectic temperature and thus effective temperature than $MgCl_2$. Additives such as Boost® are proprietary formulas based on organics like sugar or alcohol to suppress the freeze points of salt brine. Such products are costly but necessary in cold climates to produce a solution with a lower melt point (similar to $MgCl_2$). There are growing concerns about the anti-icers available on the market due to their corrosion to metals (chlorides), impact on concrete and asphalt (acetates), and toxicity to aquatic resources (agro-based products). Agencies are constantly seeking alternatives that maximize the benefits of acetates and agro-based products while minimizing their drawbacks. Also, there is a need to better utilize industrial by-products such as glycerol, a biodiesel by-product, or distillery by-products. The addition of glycerol and other additives to salt brine may enhance anti-icing performance at cold temperatures to the level of $MgCl_2$ at reasonable costs.

The objective of this project was to determine if local agricultural products or by-products of local distilleries/breweries or other manufacturing processes could be a cost-effective replacement for high-cost proprietary products to enhance the performance characteristics of salt brine for anti-icing on Alaska roads. The research was accomplished through literature review, agency surveys, and laboratory investigation. Specifically, locally sourced salt brine additives suitable for anti-icing during winter maintenance in Alaska were developed and tested.

Development of alternative anti-icing products serves the public interest since this research is expected to generate significant cost savings for DOTs and other maintenance agencies, provide traveler benefits in terms of improved safety and mobility, and increase public benefits by reducing corrosion and environmental impacts. This research will provide ADOT&PF with more

options for snow and ice control and promote sustainable winter road service; it will also likely reduce the costs of winter road maintenance for the State of Alaska and boost local economic growth. Furthermore, this research will allow the department's budget to cover more winter road maintenance or more frequent anti-icing, thus increasing safety in winter driving. This research will help the value-added utilization of industrial by-products. Local bio-based materials may also be useful for dust suppression and soil stabilization, adding to their potential benefits.

1.2. Research Approach

Task 1. Literature Review, Survey of User Requirements and Availability of Local Materials

Task 1 involved a comprehensive literature review and a survey of ADOT&PF and other stakeholders about anti-icers currently available on the market and identification of user requirements for successful anti-icers in the three ADOT&PF regions. Available literature was examined to understand the state of the practice related to commercial anti-icers in the U.S. and other countries, particularly physio-chemical properties including freezing point depression, application rate, environmental impacts, corrosion, handling, cost, and availability. Research conducted in European countries and China and by other international sources was reviewed wherever available, along with ongoing research and existing documents published by the Department of Defense (DOD), DOTs, university transportation centers (UTCs), and the Transportation Research Board (TRB). Patents were examined to understand the state of the art and identify active ingredients and additives for eco-friendly anti-icing formulations.

Concurrent with the literature review, a survey was designed and distributed to gather input from winter maintenance professionals in the three ADOT&PF regions, in an effort to capture the experience of these practitioners in managing winter roads and to identify requirements for successful use of anti-icers in each region. The alternative deicer evaluation project that the Western Transportation Institute (WTI) conducted for the Colorado DOT (Shi et al. 2009a) identified some desirable attributes of anti-icers and deicers (i.e., low cost-per-lane mile, low effective temperature, high ice-melting capacity, ease of application) and some key negative concerns over their use (i.e., corrosion to metal, impacts on concrete and asphalt pavements, and impacts on water quality, soil, vegetation, wildlife, and human health). For different agencies, the priorities may change depending on meteorological, environmental, and financial considerations, and area-specific or segment-specific emphases placed on traveler safety, environmental conservation, and infrastructure preservation. The ultimate goal was to strike the right balance and identify the most appropriate anti-icing formulation for a given maintenance agency or district or for a given highway segment (e.g., where sensitive species or aging highway bridges are exposed to the negative impacts of snow and ice control materials). To this end, research is needed to develop anti-icing liquids tailored to address the specific user requirements. This goal can be achieved through better understanding of the complex interactions and potential synergism between locally sourced additives, rock salt, and other additives, as they define the anti-icing performance, cost-effectiveness, corrosion, and environmental impacts of a given anti-icer.

An ad was designed and placed in local newspapers to engage producers of local low-cost materials and establish contacts with Alaska businesses that produce target materials. These materials could include biodiesel by-products and other renewable, bio-based chemicals, including by-products from agriculture or distilleries/breweries or from other manufacturing

processes (e.g., fishery and forestry residues) that may contain active ingredients for freezing-point suppression or corrosion inhibition.

Task 2. Experimental Design, Laboratory Testing and Optimization of Anti-icing Formulations

In light of findings from Task 1, Task 2 involved preliminarily performance testing of the identified freezing-point depressants, corrosion inhibitors, and other ingredients/additives at the WTI Corrosion and Sustainable Infrastructure laboratory (CSIL). This step is an essential part of a mass customization strategy that requires modular product design. For instance, ionic strength is one of the key factors defining the ice-melting capacity of an anti-icing solution, and the monovalent metal hydroxides (e.g., NaOH, KOH) are more efficient in producing anti-icers than the divalent metal hydroxides (Yang and Montgomery 2003). The constituent materials selected should pose minimal toxicity to the environment (e.g., with low nitrogen-N, P, and heavy metal contents), and those that come from eco-friendly processes and/or reduce the final anti-icer cost are preferred. Mixed with 20% salt brine, several types of locally sourced bio-based materials and at least three commercial additives with little toxicity were tested for their potential in freezing-point suppression or corrosion inhibition. For instance, preliminary testing has found that 50 wt.% potassium succinate (KSc) solution featured similar ice-melting capacity and outstanding ice-penetration and ice-undercutting performance at 5°F (-15°C), relative to other airport runway anti-icers, such as potassium acetate (KAc), potassium formate (KFm), and blends of glycols with urea or KAc. Furthermore, a 3-week immersion test demonstrated that 50 wt.% KSc solution is non-corrosive to both uncoated and galvanized steel specimens, whereas the galvanized steel exposed to KAc or KFm showed significant corrosion pitting. The scaling of non-air-entrained concrete exposed to the 50 wt.% solution of KSc, KAc, and KFm was measured at 0.05, 2.83, and 7.47 kg/m^2 respectively, per AMS 1435A. Adding KSc to NaCl at 2:98 reduced the corrosion of steel in 3 wt.% salt solution from 17.9 to 7.7 milli-inches per year (per SHRP H205.7), or by 57%.

Once preliminary experiments at the WTI CSIL identified the appropriate type and dosage range of each constituent to use in the anti-icer formulations, a comprehensive study was initiated. For all the tests, commercial anti-icers used by ADOT&PF (based on 23 wt.% NaCl or 30 wt.% $MgCl_2$) were used as controls for benchmarking.

Following the established experimental design, several measures were used for screening tests of promising anti-icing formulations. Specifically, a recently completed project for the Clear Roads pooled fund established a rapid and reliable method to assess the characteristic temperature of anti-icers and predict their ice-melting capacity at 30°F and 15°F, respectively, based on differential scanning calorimetry (DSC) thermograms (Akin and Shi 2010). This method was used to differentiate the performance of anti-icer blends. Additionally, the PNS-NACE *corrosion test* and the EIS (electrochemical impedance spectroscopy) test were employed to assess the corrosiveness of these anti-icer blends to carbon steel.

2. CHAPTER 2 – RESULTS AND DISCUSSION

The literature search and synthesis were conducted to document the state of the practice and the state of the art related to this project. A literature synthesis is included in the Appendix (1. Literature Review), and the key findings are presented in this section.

2.1. Formulation Development

Formulation development was performed by following a specific set of procedures. The first step involved screening to determine properties of potential constituents selected as a result of the literature review. The second step was the initial formulation, which consisted of selecting the best materials based on data gathered from the initial screening. Following initial formulation, optimization was performed through a process of testing, formulation, and evaluation. Final selection consisted of selecting the best performing formulations for further investigation.

Differential scanning calorimetry (DSC) data analysis revealed favorable ice-melting properties for both distillery by-products, which are labeled Sample 1 and Sample 2. Furthermore, potassium acetate, urea, and potassium succinate demonstrated effective ice-melting characteristics. Subsequently, potassium gluconate and sodium metasilicate exhibited optimal corrosion-inhibition properties as evaluated through electrochemical impedance spectroscopy (EIS) testing. Therefore, these compounds were selected to be the main components in the deicer formulations generated by the design of experiments. The mix formulations contained three components consisting of Sample 1 and 2 that varied with percent concentration and one of the following additives, potassium acetate, urea or potassium succinate In addition, performance, cost, toxicity, and availability were taken into consideration when selecting the most valuable anti-icer formulations. All 27 mixes were subjected to further DSC and EIS testing to determine the mix designs with the highest performance.

To evaluate specific components of anti-icing formulations more efficiently, a design of experiments consisting of three variable components was introduced after initial DSC and EIS analysis. This approach enabled optimization techniques of desired chemical properties and the minimization of detrimental characteristics. For example, higher concentrations of the winery by-products generally yield higher ice-melting capacities with minimal negative impacts.

2.2. Key Findings from Laboratory Investigation

The most effective additives were selected to be included in a mix design of experiments, which was generated in order to maximize efficiency. It was determined that the two by-products along with potassium acetate, urea, potassium succinate, potassium gluconate and sodium metasilicate were the most effective additives; therefore, these components were included in the mix design. The mix design contained three components: two of which varied with percent concentration and the third was one of three different additives with the same percent concentration. In addition, performance, cost, toxicity, and availability were taken into consideration when selecting the most valuable anti-icer formulations. The best performing mixes were chosen for further testing, which consisted of the ice-melting procedure described in SHRP H205.2 Test Method for Ice Melting of Liquid Deicing Chemicals and NACE TM0169-95 PNS Modified Dip Test.

DSC Thermogram Test Protocol

The purpose of the DSC thermogram test is to rapidly and consistently characterize and quantify the thermal properties of deicer compounds using a DSC thermogram. Differential scanning calorimetry is a laboratory technique that measures the heat flow to provide insight into their freeze/thaw behavior, effective temperatures, and ice-melting capacity. The DSC machine used for test method development was a TA Instruments Q200.

Interpretation

DSC measures the energy necessary to maintain a near-zero temperature difference between the test substance (deicer) and an inert reference material, with the two subjected to an identical temperature program. The heat-flow measurements over the temperature range of interest indicate phase transitions, energy changes, and kinetics. The average peak temperature determined from the analysis, which is the characteristic temperature of the deicer. This is compared with the characteristic temperature of a 23% NaCl salt brine, which was found to be 21.8°F. If the characteristic temperature of the test deicer is lower than 21.8°F, the relative performance of the tested deicer is greater than 23% NaCl and it is most likely more effective in the field at lower temperatures than 23% NaCl.

If the tested deicer is a chloride-based liquid deicer, the integrated heat flow (enthalpy of fusion) and characteristic temperature can be used to estimate the performance of the tested deicer under the modified SHRP ice-melting test using the empirical equations shown below:

$$IMC_{30°F} \ (mL \ brine) = -4.476 - 0.0288T + 3.83 \log(\Delta H)$$

$$IMC_{15°F} \ (mL \ brine) = 9.027 - 0.1009T - 2.54 \log(\Delta H)$$

IMC = expected volume of brine that will be collected in Modified SHRP Ice Melting Test after 60 minutes (mL)
ΔH = 334 J/g – average enthalpy of fusion (H_{avg} in J/g)
T = average peak temperature (T_{avg} in °F)

Equation 1: Ice-melting capacity (IMC) equations.

Various deicers develop unique characteristic peaks along both the warming cycle and the cooling cycle; however, the warming cycle is preferred for data analysis, since the cooling cycle data can contain interference due to the supercooling effect. Most deicers produce one peak during the warming cycle; however, sodium chloride solutions show two peaks. The characteristic temperature and enthalpy of fusion for the warmer peak provide information relevant to deicing on roads. The warmer temperature peak corresponds to the field scenario when the temperature drops and the pavement gets icy. Figure 2 provides a comparison of 23% NaCl, Mix 3, and Mix 22. The DSC test provides the characteristic temperature (T) and enthalpy of fusion (H) associated with the peaks. The characteristic temperature corresponds to the peak on the right side as labeled by the three vertical lines. The enthalpy of fusion can be determined

by calculating the area corresponding to the characteristic temperature peak. These values are used in Equation 1 to calculate a predicting ice melting capacity at 30°F and 15°F.

Differential scanning calorimetry provides two opportunities for data interpretation and application that DOTs can use. Primarily, the first peak temperature at the high temperature end of the warming cycle is defined as the characteristic temperature of the deicer. The characteristic temperature for a deicer can be compared to that of sodium chloride; it thus indicates its effective temperature range relative to sodium chloride. Furthermore, a strong correlation between the DSC data, specifically the characteristic temperature and the enthalpy of fusion, and the modified SHRP ice-melting test data can be developed. This provides another opportunity to use the DSC test results to predict the performance of a chloride-based deicer in the ice-melting test
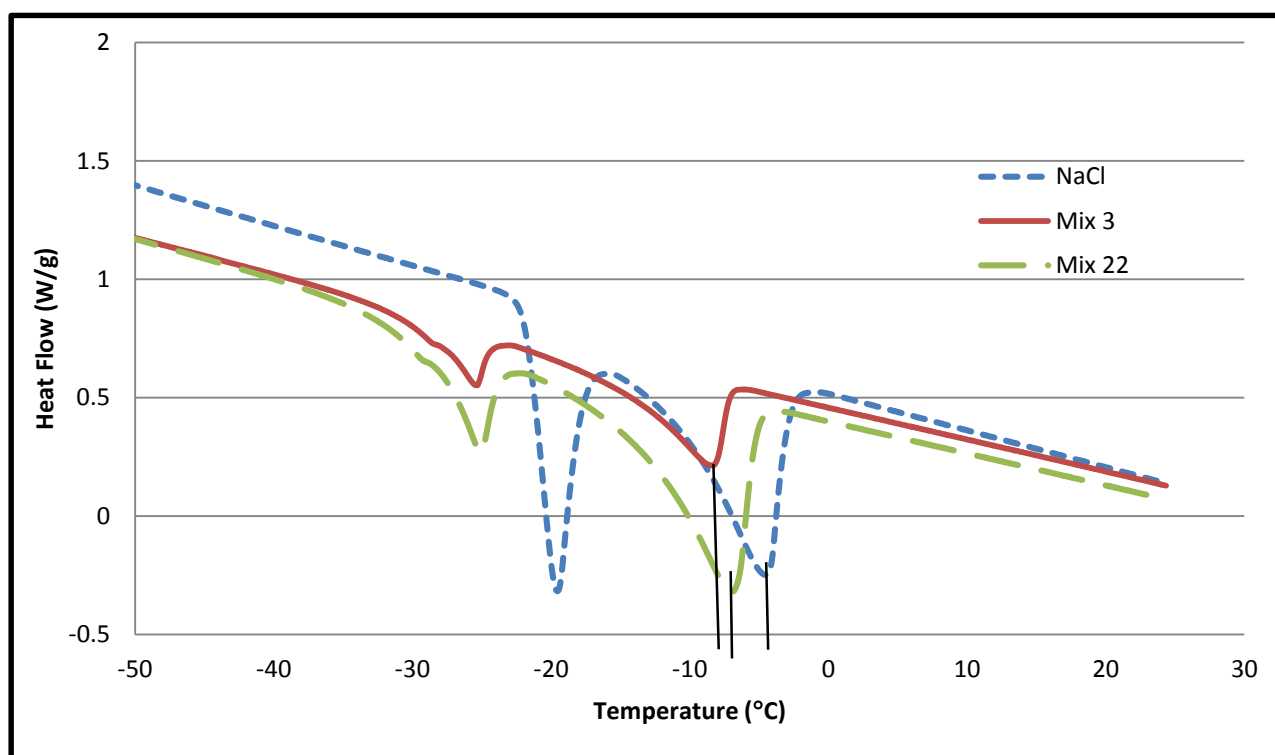
(Akin and Shi 2010).

Figure 2: DSC thermograms for 23% NaCl, Mix 3, and Mix 22.

Preliminary DSC data of various additives was analyzed to determine which additives demonstrated the most potential as an effective deicer additive. This method isolated each additive to assist in the formulation development. The top performers were selected for inclusion in the mix design to further refine overall mix compositions.

2.2.1. Ice Melting Performance

Ice melting performance of the liquid deicers was evaluated following the SHRP H205.2 test method. This test method quantifies the amount of ice melted by the liquid deicer at a specified temperature. First, 130 mL of distilled water is frozen in a 9 in diameter acrylic dish and then the ice surface is melted and re-frozen using a flat metal disk to ensure a smooth surface. A volume of 3.8 mL of liquid deicer is applied to the ice surface and at 10, 20, 30, 45, and 60 min after application the dish is titled and the melted brine is collected with a syringe and the volume is recorded. The brine is returned to the ice sample after each measurement.

The ten mixes with the highest performance, as determined by both DSC and EIS testing, were selected for further investigation to evaluate ice-melting capacity following procedures described in SHRP H205.2 Test Method for Ice Melting of Liquid Deicing Chemicals. These top ten mixes as determined by DSC and EIS were Mixes 3, 4, 6, 12, 13, 16, 19, 20, 22, and 27, which had significantly higher ice-melting capacities at 15°F than the 23% NaCl control as shown in **Error! Reference source not found.**. Since three replicates were tested, the average ice melting capacity is reported with the error bars shown as the black lines. Subsequently, Mixes 22 and 3 have significantly higher ice-melting capacities than sodium chloride and other formulations at 30°F and 15°F, respectively, as shown in **Error! Reference source not found.** and **Error! Reference source not found.**. Therefore, Mixes 3 and 22 were selected to be further evaluated for corrosiveness as described by NACE TM0169-95 PNS Modified Dip Test.

It was determined that the predicted ice melting capacities based on the DSC data exaggerated the difference in performance of the selected deicers. The ice melting performance of the anti-icer formulations was found to have significantly lower variation than the DSC data analysis predicted.
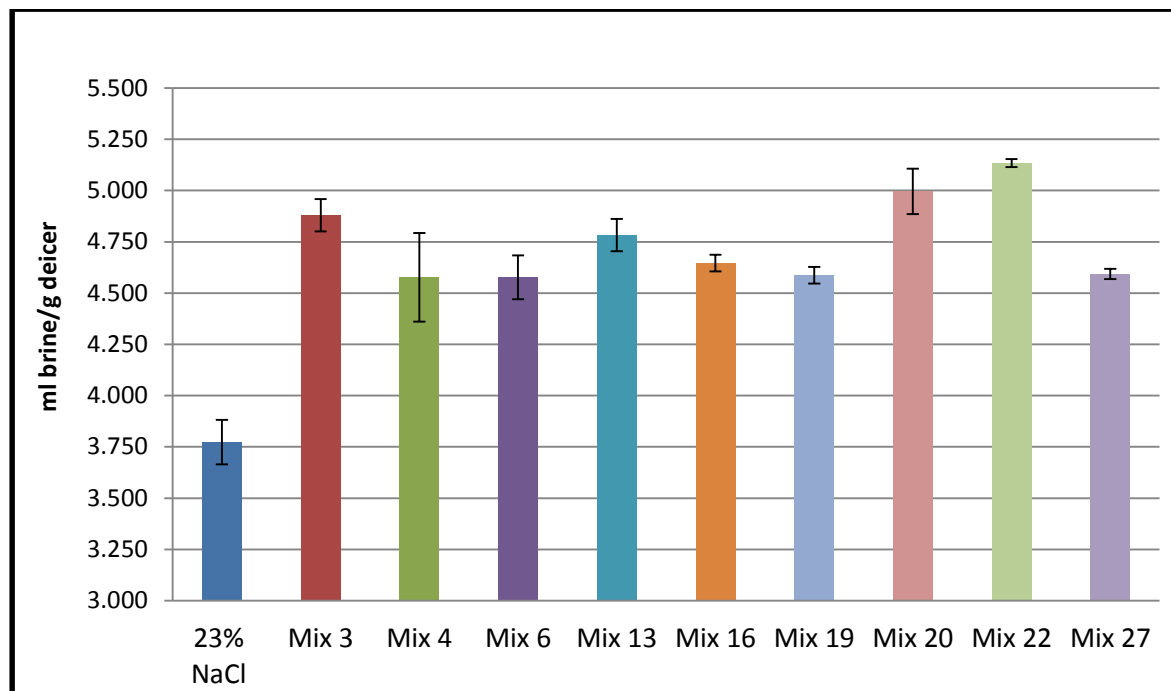
Figure 3: Ice Melting Performance at 60 min at a temperature of 30°F.
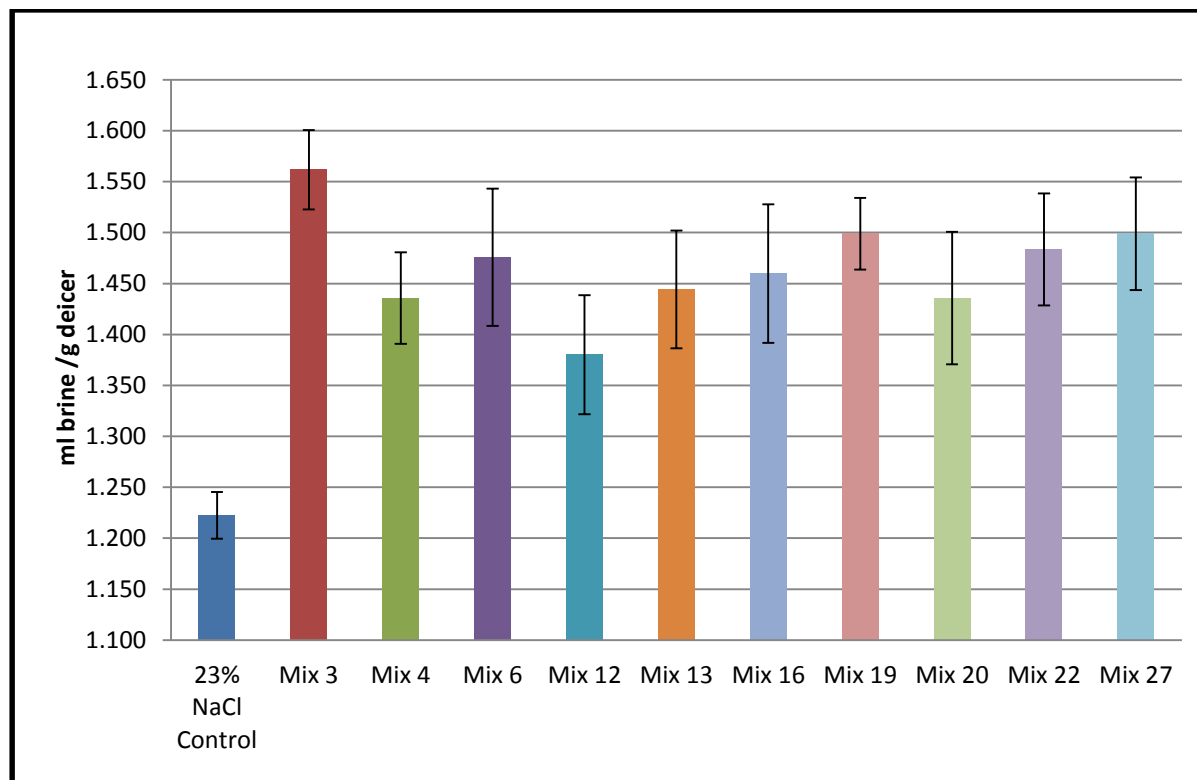
Figure 4: Ice Melting Performance at 60 min at a temperature of 15°F.

Additional investigation at a temperature of 20°F of formulations containing various amounts of Sample 1, Sample 2, and Boost were performed following procedures outlined in SHRP H205.2. Laboratory measurements revealed performance characteristics as compared to the control, which was a blend of salt brine and Boost at a ratio of 80:20. The ice melting performance for Mix 28 and Mix 29 was shown to be relatively similar to the ice melting performance of the control. However, the cost of Mix 28 and Mix 29 is significantly lower than the control since a lower concentration of Boost, an expensive additive, was used. The average ice melting capacities and the corresponding error bars are shown in **Error! Reference source not found.**. The ice melting behavior with respect to time at 20°F is displayed in **Error! Reference source not found.**. It can be noted that the ice melting capacity of the top performers increases with time whereas, other formulations decrease as time increases. This decrease in ice melt is most likely due to the effects of evaporation on the deicer additives.

Figure 5: Ice Melting Performance at 60 min at a temperature of 20°F.

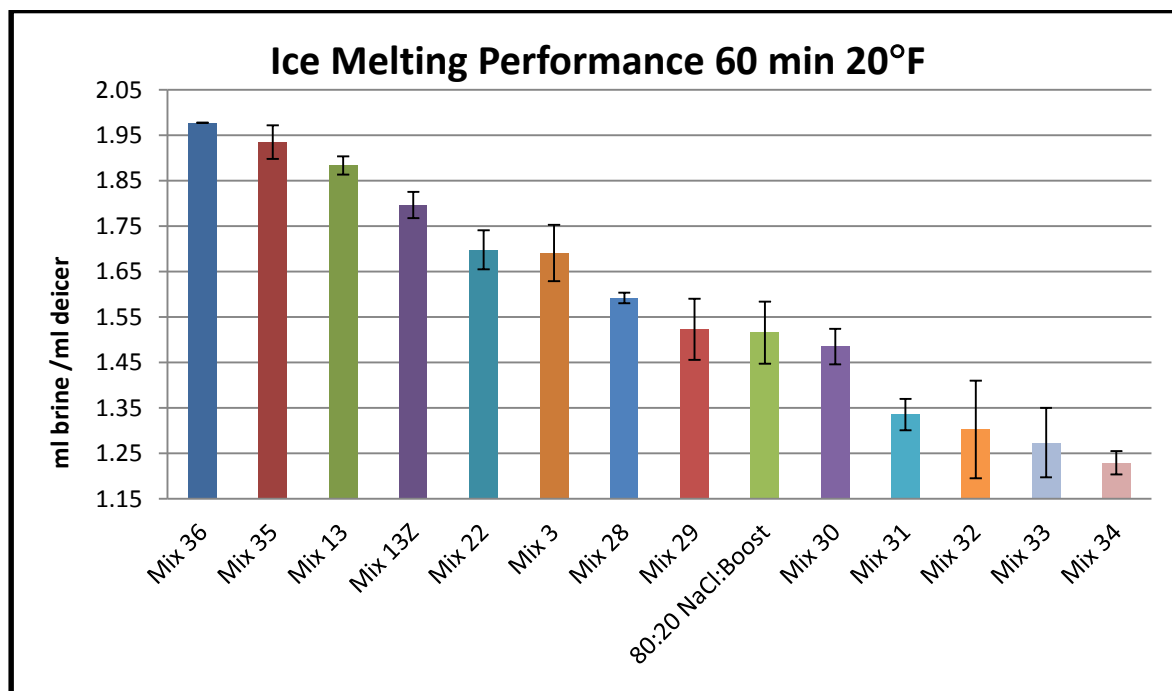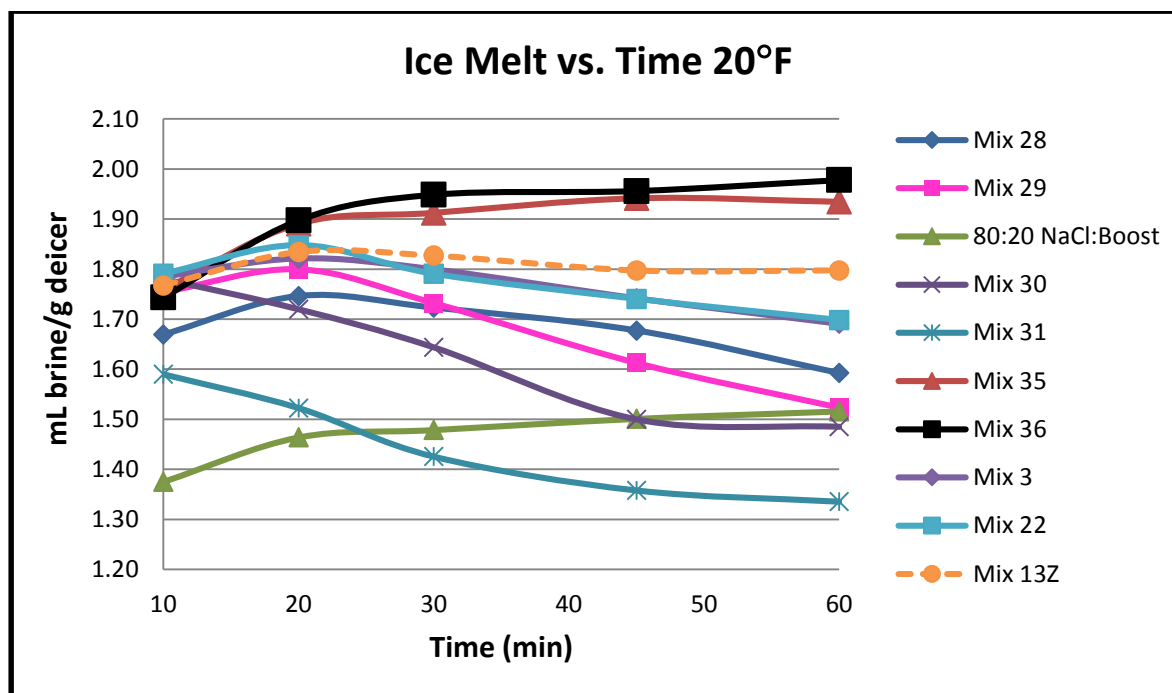**Figure 6: Results of ice melting test showing Ice melt vs. time at 20°F.**

Based on the testing data thus far, it has been observed that reducing the percentage of total by-products to a total of no more than 8% would not significantly sacrifice the ice melting capacity but effectively minimize any evaporation of anti-icers. This is shown in Figure 6 with Mix 35 and Mix 36, where the effects of evaporation are no longer observed. Furthermore, evaluation of results and formulations reveals that synergistic effects become a major contributor in performance mechanisms. The combination of additives in Mix 35 and 36 reduced the effects of evaporation, thus increasing the ice melting performance.

Error! Reference source not found. displays results from the initial screening tests from the DSC thermogram calculations for predicting ice-melting capacity and the actual ice-melting capacity data collected in the Subzero Science and Engineering Facility at Montana State University at 30°F and 15°F. The DSC thermogram test protocol was used to determine theoretical ice-melting capacities, and the SHRP H205.2 Test Method for Ice Melting of Liquid Deicing Chemicals was used to determine actual ice-melting capacities at 30°F and 15°F. As **Error! Reference source not found.** shows, the predicted ice-melting capacities at both 30°F and 15°F generally underestimated the actual ice-melting capacities. A number of variables such as dilution rates, evaporation, and humidity are potential causes for the variations in predicted ice-melting capacity and the actual ice-melting capacity. Additionally, the mixing action and fate/transport of deicers in the field are complicated by factors of traffic, UV absorption, gradation and angularity of deicer particles, moisture content and density of snow, pavement type and condition, wind, relative humidity, and possibly other factors. In general however, higher predicted ice-melting capacities showed a strong correlation with high actual ice-melting

capacities; therefore DSC screening tests offer effective initial assessments of anti-icing characteristics.

Table 3: Ice melting capacity of customized locally sourced anti-icing formulations

	Ice Melting Capacity, 60 min @ 30°F (ml brine/g deicer)	Predicted Ice Melting Capacity, 60 min @ 30°F (ml brine/g deicer)	Ice Melting Capacity, 60 min @ 15°F (ml brine/g deicer)	Predicted Ice Melting Capacity, 60 min @ 15°F (ml brine/g deicer)
Mix 3	4.88	4.260	1.56	1.139
Mix 4	4.58	3.842	1.44	1.184
Mix 6	4.58	3.570	1.48	0.534
Mix 13	4.78	3.659	1.44	1.335
Mix 16	4.65	3.306	1.46	1.431
Mix 19	4.59	3.591	1.50	1.366
Mix 20	5.00	3.736	1.44	1.207
Mix 22	5.13	3.527	1.48	1.407
Mix 27	4.59	3.300	1.50	1.413
23% NaCl anti-icer	3.50	3.664	1.15	0.872
32% CaCl$_2$ anti-icer	4.00		1.55	
32% MgCl$_2$ anti-icer	4.25		1.75	

2.2.2. Corrosion Evaluation

It is well known that deicer products cause significant damage to bare metals on winter maintenance equipment and transportation infrastructure. Therefore, the corrosive effects of various deicer formulations were tested according to the National Association of Corrosion Engineers (NACE) Standard TM0169-95 as modified by the Pacific Northwest Snowfighters (PNS). This test method determines the weight loss of carbon steel coupon samples due to the corrosive effects of the deicer solution. The samples are exposed to the deicer solution and the results are reported as Percent Corrosion Rate (PCR) relative to solid salt and deionized water. The metal coupons were purchased from Ad-Tek, Inc., and were 0.5 in flat steel washers with dimensions of 0.38 in × 0.56 in × 0.11 in and an average density of 7.85 g/cm^3. The metal coupons were cleaned using hydrochloric acid and then rinsed in tap water, then de-ionized water, then wiped dry and placed in chloroform. The coupons were then placed in the fume hood and allowed to dry for 15 minutes. The coupons were then weighed and placed in the corrosion testing machine (Corrosion Testing Machine CTM10-10/50, AD-TEK). The corrosion testing machine lowered the three metal coupons into the diluted deicer solutions for 10 minutes and then raised the metal coupons into ambient air for 50 minutes. This cycle continued every hour for 72 hours. The liquid deicers were diluted 3% volume-to-volume with deionized water (3 parts liquid deicer to 97 parts deionized water). The two controls used were a 3% weight-to-volume solution of reagent grade NaCl and deionized water. The final weight of the coupons was

recorded after 72 hours of cyclic testing and cleaning.

The corrosion test provides corrosion rate evaluation in terms of MPY (mils per year or milli-inches per year). Based on the corrosion measure from the deionized water control, corrections are applied and comparisons are made between the corrosion measured from the NaCl control in terms of Percent Corrosion Rate (PCR) where NaCl is designated a value of 100% and deionized water is 0%. Therefore, deicers with a PCR >100% are more corrosive than 3% NaCl and deicers with a PCR < 0% are less corrosive than water. PNS considers a PCR value of less than 30% to be an acceptable corrosion inhibitor.

The NACE TM0169-95 PNS Modified Dip Test was carried out using Mix 3, Mix 22, Mix 3A, Mix 22A, Mix 3B, Mix 3C, and Mix 22B to compare to traditional deicers 23% NaCl and 30% $MgCl_2$. The 72-hour corrosion test revealed very similar weight loss values for Mix 3 and Mix 22, which were significantly lower than the weight loss values for 23% NaCl and 30% $MgCl_2$. **Error! Reference source not found.** shows the calculated corrosion rates and the corresponding error bars . The corrosion rates for the new formulations containing the by-products were significantly lower than 23% NaCl and 30% $MgCl_2$. These corrosion rates correspond to a percent corrosion rate of approximately 12% and 17% for Mix 3 and Mix 22, respectively, as compared with percent corrosion rates of 86% and 165% for 23% NaCl and 30% $MgCl_2$, respectively. Mix 3 and Mix 22 contain effective corrosion inhibitors that successfully minimize corrosion to steel. However, more investigation is needed to identify the mechanisms involved. Since the percent corrosion rates for Mix 3, Mix 22, and Mix 3A have a percent corrosion rate of less than 30% Mix 3, Mix 22, and Mix 3A are considered to be acceptable corrosion-inhibited chemicals according to the guidelines outlined in NACE TM0169-95. It was determined that Sample 1 and Sample 2 have significant corrosion inhibition properties to carbon steel, which can significantly reduce long term costs due to corrosion impacts to equipment and various components.
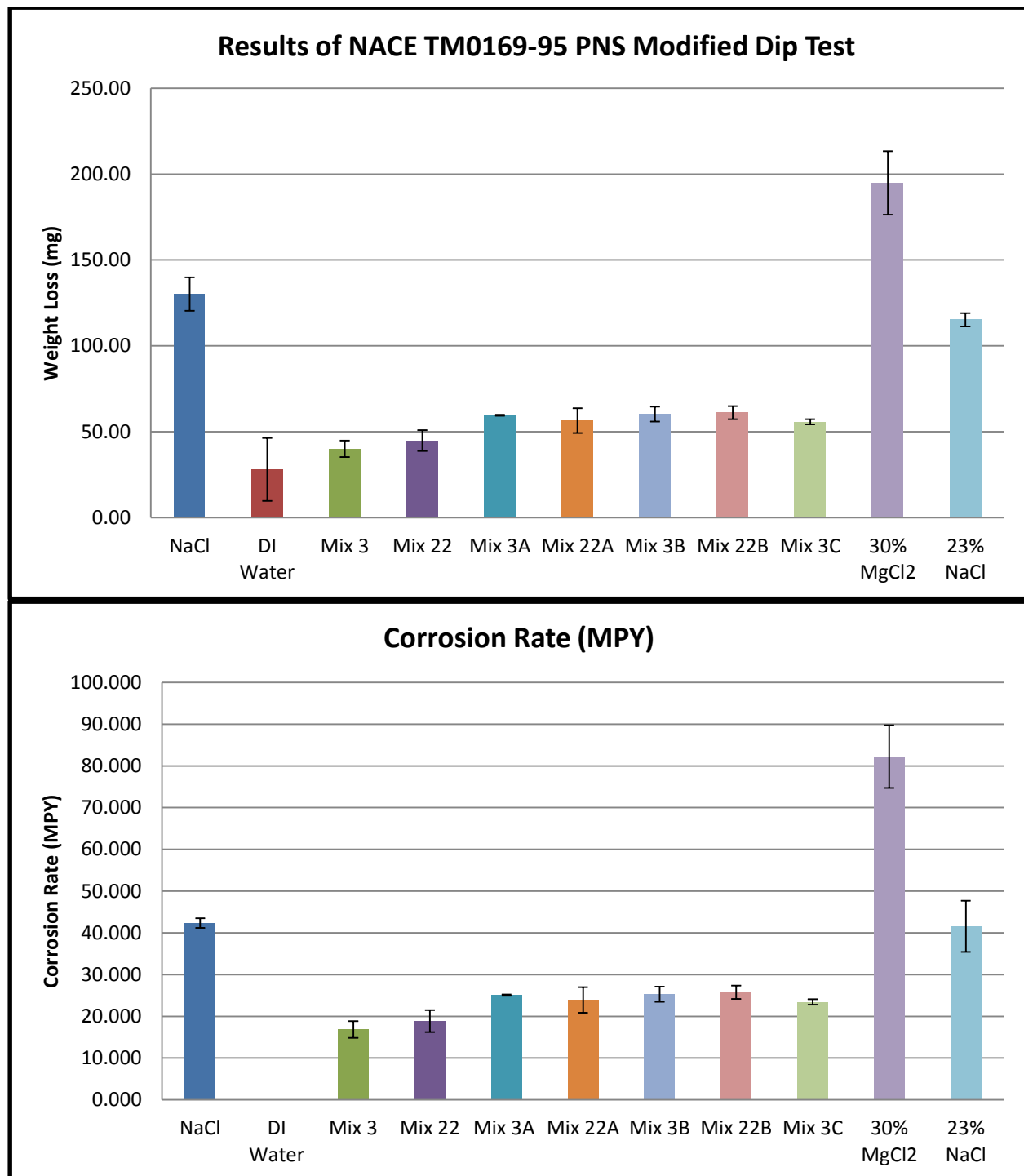
Figure 7: Results of NACE TM0169-95 PNS Modified Dip Test.

2.2.3. Deicer Impact on Concrete

In addition, conventional deicer products have been reported to cause significant impact to Portland cement concrete (PCC) commonly used in transportation infrastructure (Shi, 2008; Sutter et. al 2008; Cody et al. 1996). The effects of diluted liquid deicers on PCC samples were evaluated by performing freeze-thaw tests according to the SHRP H205.8 test method. This test method evaluates the combined effects of liquid chemicals and freeze-thaw cycling on concrete specimens. The concrete samples were made in 2 in. diameter × 4 in. length poly (vinyl chloride) tubing. The concrete mix design had a water-to-cement ratio of 0.55, a slump of 1 in. and air content of 2.9 percent with a commercial air entraining agent admixed at 0.006% by the mass of cement, which is half dose of typical concrete. The samples were cured in the mold for 24 hours then taken out of the mold and cured in open air for 27 days with a relative humidity of 25±5%. The average 28-day compressive strength of three test cylinders was 4,933 psi. The concrete samples were then cut to a final length of 3 in and the dry weight of each sample was recorded.

The SHRP H205.8 test method uses four concrete specimens, which are placed in a container with a sponge and 310 mL of diluted anti-icer solution (3%). The container is covered and then placed in the freezer for 16 to 18 hours at 0 ± 5°F and then taken out and allowed to thaw in the laboratory environment with a temperature of 73.4 ± 3°F for 6 to 8 hours. This cycle was repeated for a total of 10 freeze-thaw cycles. The concrete specimens were then removed from the container, rinsed to remove any loose material, and then air-dried overnight. Then the final weight of each sample was recorded. The two controls used for comparison are 3% NaCl and de-ionized water. The SHRP H205.8 test method reports the effects of deicers and freeze-thaw cycling to PCC in terms of weight loss by comparing the final weight to the initial weight of each sample.

The selected mixes were further evaluated to assess the impact of deicer on PCC following SHRP H205.8 Test Method for Rapid Evaluation of Effects of Deicing Chemicals on Concrete. The results, shown in **Error! Reference source not found.**, illustrate the significant differences among various anti-icer formulations. Since four concrete specimens were tested, the corresponding error bars are also shown in

Figure 8: Weight loss results of half-air-entrained Portland cement concrete following the SHRP H205.8 freeze/thaw test.

. Deionized water and 30% $MgCl_2$ had the lowest percent weight loss, whereas Mix 3 and Mix 22 had the highest percent weight loss. Mix 3 and Mix 22 had a more negative effect on the PCC specimens than the 23% NaCl control. However, Mix 3A and Mix 22A had significantly lower impacts on the PCC specimens.
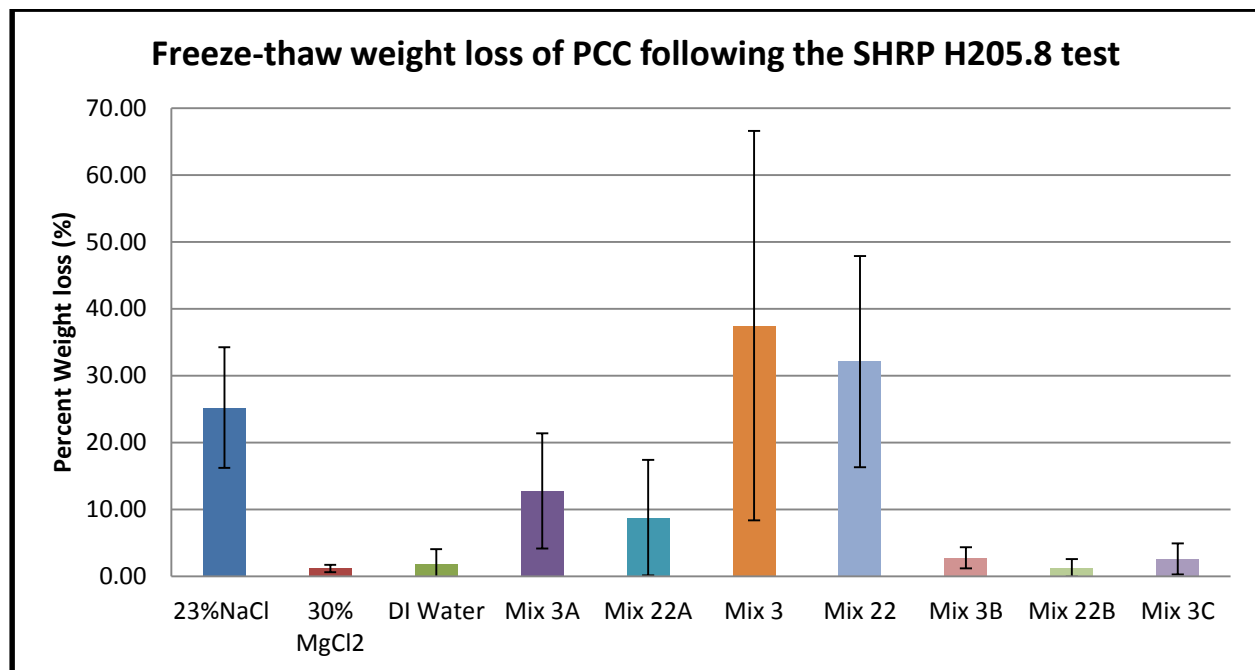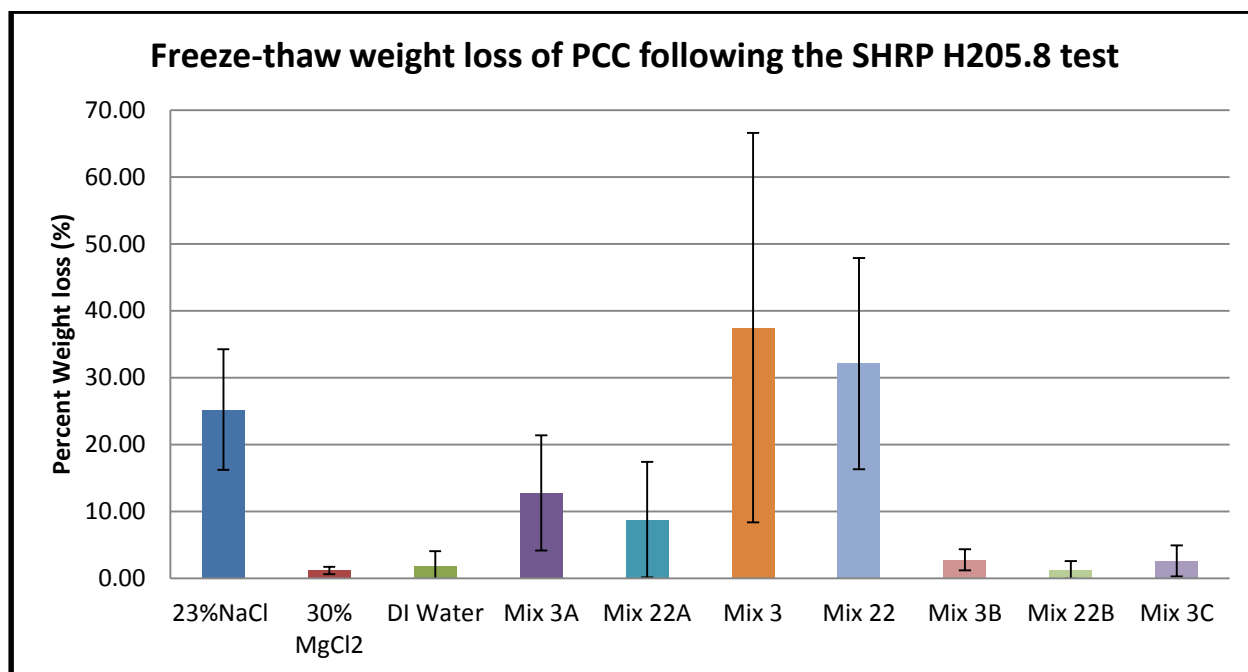
Figure 8: Weight loss results of half-air-entrained Portland cement concrete following the SHRP H205.8 freeze/thaw test.

Significant damage of PCC in the presence of NaCl or NaCl-based deicers can be explained by the role of NaCl in increasing the number of freeze/thaw cycles inside the concrete and aggravating the freeze/thaw damage to its microstructure. Magnesium chloride did not have as much impact on the freeze/thaw resistance of PCC. However, multiple studies have suggested that $MgCl_2$-based deicers are more destructive to PCC than NaCl-based deicers (Cody et al. 1996; Mussato et al. 2004). The difference in the findings can be attributed to the differences in the deicer concentrations such as concentrated versus diluted, the PCC samples used such as old cored concrete versus new concrete that features different cement hydration products and concrete microstructure, the test procedures including wet/dry cycles and freeze/thaw cycles, and the test duration. Although previous studies used mostly concentrated deicer solutions, this study tested diluted deicers diluted to a 3% concentration for all liquid and solid deicers, since the deicer concentrations experienced by the PCC structures and pavements in the field are generally low over long durations. Laboratory findings from the SHRP H205.8 and other test methods do not necessarily accurately predict the deicer/concrete interactions in the field, and research is still needed to establish the correlation between the laboratory data and the field data. Additional examination of the chemical changes in the cement paste after the SHRP freeze/thaw test found that $MgCl_2$ did react with the cement hydrates to form fibrous or needlelike crystals characteristic of magnesium chloride hydroxide hydrate (Shi et al. 2009c), which is consistent with the findings of Sutter et al. (2008), Cody et al. (1994, 1996), Deja et al. (1999), and Lee et al. (2000).

In addition to mass loss, splitting tensile strength evaluation determined that the concrete specimens exposed to various formulations had comparable strength thus a similar reduction in

strength after 10 freeze\thaw cycles as shown in Figure 9. The reduction in strength can be attributed to the chemical degradation of the cementitious phases in the concrete. The concrete specimens exposed to NaCl and Mix 13Y showed the lowest splitting tensile strength and thus the highest reduction in strength after ten freeze/thaw cycles. The concrete specimens exposed to the NaCl also showed the highest weight loss due to scaling. The specimens exposed to Mix 13Y showed minimal scaling; however, the splitting tensile strength was similar to that of the specimens exposed to NaCl. Therefore, the scaling effects from chemical deicers to Portland cement concrete are not representative of strength degradation.
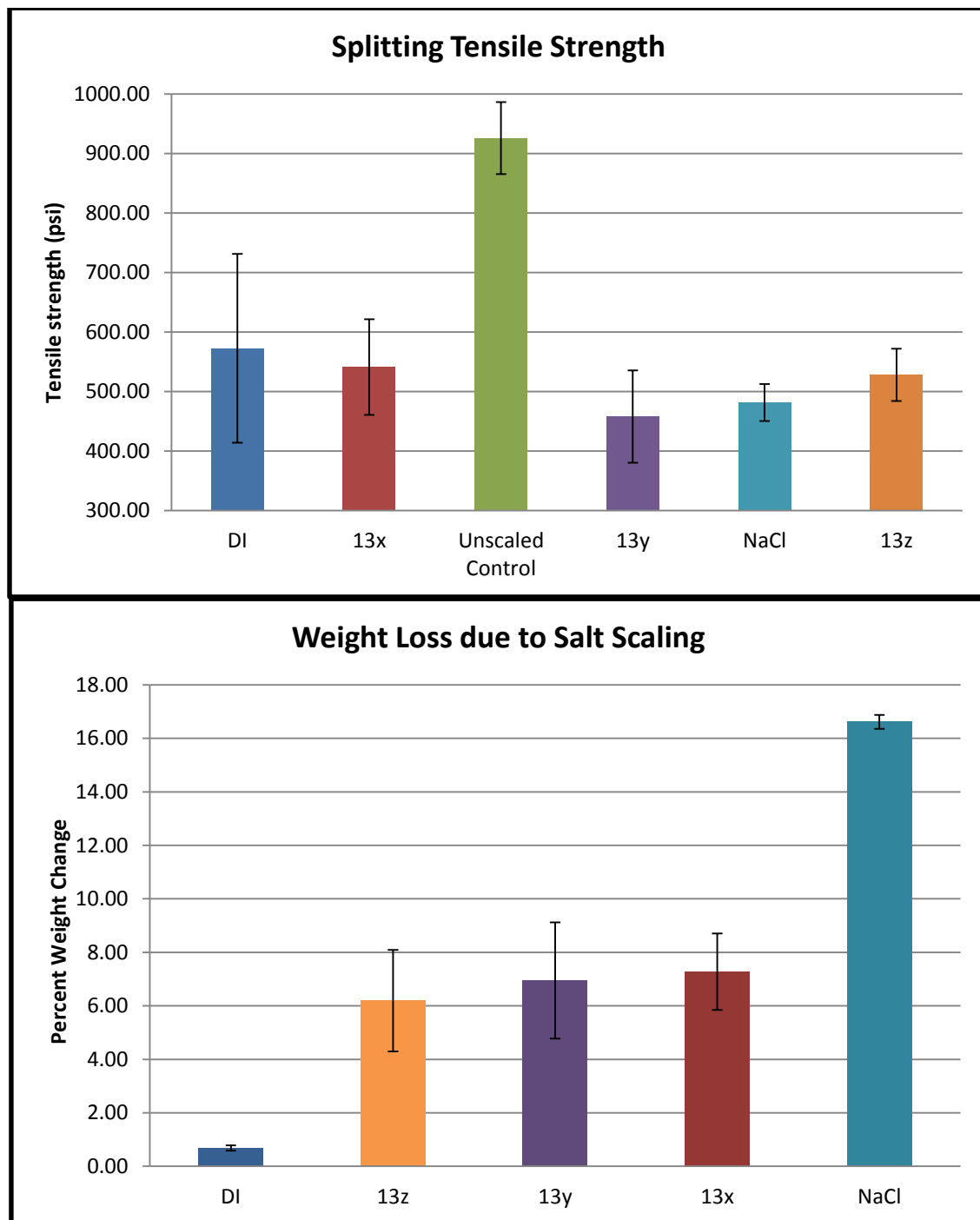
Figure 9: Splitting tensile strength and weight loss due to salt scaling following SHRP H205.8 freeze/thaw test.

3. CHAPTER 3 – INTERPRETATION, APPRAISAL, AND APPLICATIONS

The number of deicer formulations was refined by selecting the formulations that exhibited the highest performance as determined through data analysis from data collected using DSC thermogram evaluations and EIS techniques. The selected deicer formulations representing the lowest corrosion rates determined by EIS were further evaluated for ice-melting capacity following SHRP H205.2 Test Method for Ice Melting of Liquid Deicing Chemical. In addition, components were selected based on various factors such as cost, availability, corrosiveness, toxicity, and performance. A flow chart of the process of developing deicers from by-products is shown in Figure 10.
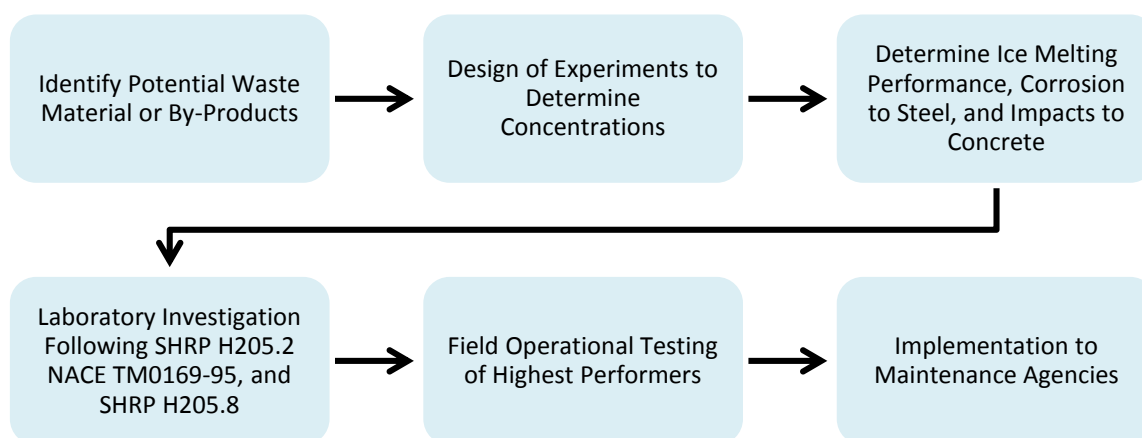
Figure 10: Flow chart of the process of developing deicers from by-products.

3.1. General Recommendations

As discussed in the previous section, the results of the laboratory investigation demonstrate the effectiveness of using industrial by-products to enhance performance and decrease the negative impacts of anti-icers used on roadways. The performance of the anti-icers integrated with agro by-products surpassed the performance of traditional NaCl with respect to ice-melting capacity and corrosiveness, both of which ranked among the top priorities according to survey results. In addition, these formulations reduce costs and use sustainable resources.

The DSC thermogram test proved to provide the thermal properties of deicers in an aqueous state. The DSC-based test is highly reproducible and suitable for quality assurance of deicers. Furthermore, DSC data can provide an estimate of characteristic temperature and ice-melting capacity for liquid deicers. The SHRP ice-melting test provided further performance assessment by determining ice-melting capacity of potential anti-icer formulations, which is a representation of anti-icer effectiveness when used on roadways.

An assessment of metal corrosion was determined by initial EIS testing, and further investigations were provided using the NACE TM0169-95 PNS Modified Dip Test. Weight loss due to corrosion was determined, and corrosion rates of promising anti-icer formulations were calculated. In addition, deicer impact on concrete was analyzed to assess potential damaging effects of selected anti-icer formulations to PCC specimens.

The results of this research will provide guidance in the use of locally sourced additives for anti-icing in the State of Alaska. To facilitate the technology transition into practice and to realize the substantial benefits inherent in the technology, we sought feedback from AKDOT&PF end users and other stakeholders in producing formulations that meet user needs, are environmentally safe, and can be readily implemented. The selected anti-icers will be preliminarily validated through field operational tests. Subsequently, collaboration with AKDOT&PF will be encouraged for conducting additional research, field demonstration, or long-term studies, to promote the use of such eco-friendly anti-icers and advance the knowledge base relevant to anti-icing tactics (e.g., appropriate application rate under various road weather scenarios). To produce usable products and identify areas for improvements, the research team will work closely with stakeholders at every stage of research deployment. The developed anti-icer formulations can be used as anti-icers as well as pre-wetting agents for solid salts/abrasives to be applied on highways or local roads.

It is generally beyond the DOT's interest to produce enhanced salt brine with multiple additives. Therefore, it is anticipated that the private sector can use the research findings from this project and manufacture the best-performing anti-icing formulations. These formulations would be competing with anti-icers currently available in the State of Alaska, such as the 80:20 (by volume) blend of salt brine with BOOST™. The estimated market size in the State of Alaska: 360,000 gallons per typical winter season by the AKDOT&PF as well as usage by other maintenance agencies (e.g., military, counties and cities, and commercial parking lots). The "green" anti-icing formulations would need to be further validated through field operational tests before they can be accepted by the maintenance agencies. The following provides an example for a reasonable cost range: currently solid rock salt is sold at approximately $148/ton delivered and the BOOST additive is sold at approximately $2.50/gallon. So the 80:20 blend is estimated to cost $0.90/gallon whereas the non-modified salt brine costs about $0.30-$0.35/gallon.

Ultimately, it would be even more desirable if all or most of the additives for the salt brine could be produced into one single solid additive, since shipping costs would decrease significantly compared to that of liquid additives.

3.2. Applications

Agencies are continually challenged to provide safe, reliable winter highways in a cost-effective and eco-friendly manner, while dealing with increased traffic demands, higher customer expectations, and unprecedented staffing and funding constraints. There are growing concerns over the use of deicers and anti-icers during winter and their impact on transportation infrastructure, motor vehicles, and the environment (Buckler and Granato 1999; FHWA 2002; Levelton 2007; Shi et al. 2009a, 2009b, 2009c). When using road salts for snow and ice control, the average costs due to corrosion and environmental effects are estimated to be at least three times as high as the nominal cost (Shi 2005). However, such hidden costs are often ignored in formulating highway winter-maintenance strategies.

Deicers or anti-icers may have detrimental effects on PCC infrastructure and thus reduce concrete integrity as indicated by expansion, mass change, and loss in the dynamic modulus of elasticity, and strength (Shi et al. 2009c). Such effects of deicers on the durability of PCC structures and pavements occur through three main pathways: (1) physical deterioration of the concrete through salt scaling; (2) chemical reactions between deicers and cement paste particularly when Mg_{2+} and Ca_{2+} ions are present; and (3) aggravation of aggregate-cement reactions, including an anion-oriented process in the case of chlorides and acetates/formates, which affects alkali-silica reaction, and a cation-oriented process in the case of calcium chloride ($CaCl_2$) and magnesium chloride ($MgCl_2$), which affects alkali-carbonate reaction.

Deicers or anti-icers may have detrimental effects on asphalt pavement (Pan et al. 2008; Shi et al. 2009c), affecting pavement structure and causing loss of strength and elasticity of asphalt concrete. Exposure to freeze/thaw cycles and deicers was found to affect the viscosity of the recovered asphalt binder and the gradation of recovered aggregates. Formate/acetate-based deicers were found to significantly damage asphalt pavements through a combination of chemical reactions, emulsifications and distillations, as well as generation of additional stress inside the asphalt concrete.

Deicers or anti-icers may cause corrosion damage to motor vehicles and to transportation infrastructure such as reinforced or pre-stressed concrete structures and steel bridges (Shi et al. 2009b). One study estimates that road salt imposes infrastructure corrosion costs of at least $615/ton, vehicular corrosion costs of at least $113/ton, and aesthetic costs of $75/ton if applied near environmentally sensitive areas, plus uncertain human health costs (Vitaliano 1992). Johnson (2002) estimated that the annual cost of deicer corrosion on motor vehicles was $32 per vehicle, totaling more than $2 billion (Shi 2005). The cost of installing corrosion protection measures in new bridges and repairing old bridges in the snowbelt states is estimated to be between $250 million and $650 million annually (Yunovich et al. 2002).

Finally, deicers and anti-icers can have significant impacts on the environment, and the impacts depend on a wide range of factors unique to each formulation and the location of application (Shi et al. 2009a; Fay and Shi 2010). Despite the potential damaging effects, chemicals used for snow

and ice control can reduce the need for applying abrasives, and they pose less threat to surrounding vegetation, water bodies, aquatic biota, air quality, and wildlife.

It is necessary to use the most recent advances in the application of materials, winter maintenance equipment and sensor technologies, road weather information systems, as well as other decision support systems to apply the right type and amount of materials in the right place at the right time for snow and ice control. Such best practices are expected to improve the effectiveness and efficiency of winter operations, to optimize material usage, and to reduce associated annual spending, corrosion, and environmental impacts. Within this context, maintenance agencies have increasingly adopted proactive practices (e.g., anti-icing) over reactive practices (e.g., deicing and sanding) for snow and ice control.

4. CHAPTER 4 – CONCLUSIONS AND SUGGESTED RESEARCH

Initial laboratory investigations assisted in the determination of high-performance anti-icer formulations that use by-products from wine processing and select corrosion inhibitors to decrease the impact of deicers and anti-icers on metal and concrete. It was determined that Mix 3 and Mix 22 had higher ice-melting capacities than 23% NaCl and comparable corrosion rates to steel, which were significantly lower than corrosion rates observed for NaCl and $MgCl_2$.

4.1. Conclusions

Understanding the performance characteristics and negative impacts of anti-icers is essential when making effective decisions during winter maintenance operations. Five test methods were used to analyze anti-icers integrated with industrial by-products that enhance their performance and reduce costs. Differential scanning calorimetry and EIS proved successful as evaluation techniques for performance analysis of various components to assist in the decision-making process of selecting high-performance, low-cost additives. The SHRP ice-melting test identified two formulations—Mix 3 and Mix 22—that have significantly higher ice-melting capacities than 23% NaCl. The NACE TM0169-95 PNS Modified Dip Test determined four formulations—Mix 3, Mix 22, modified Mix 3, and modified Mix 22— that have significant corrosion impacts on steel. In addition, the SHRP H205.8 Test Method for Rapid Evaluation of Effects of Deicing Chemicals on Concrete revealed substantial anti-icer impacts on PCC for Mix 3 and Mix 22. However, modified Mix 3 and modified Mix 22 had lower percent weight losses than the NaCl control, and the $MgCl_2$ solution had little effect on the PCC specimens.

Laboratory test results do not take into account the mixing action and fate/transport of anti-icers in the field caused by variables such as traffic, UV absorption, moisture content and density of snow, pavement type and condition, and wind. Continued research is needed to accurately represent anti-icer behavior in a laboratory setting.

Commercially available by-products were successfully used in the development of a high-performance anti-icer formulation, which resulted in lower corrosion impacts, lower costs, and decreased environmental impact through the application of sustainable resources. The anti-icer formulations were observed to contain desirable characteristics such as high ice-melting capacities and low corrosion rates as compared with traditional deicers, sodium chloride and magnesium chloride. A trend in high ice-melting capacities is observed in which higher concentrations of by-products Sample 1 and Sample 2 correlate with high ice-melting capacities. This correlation suggests that the by-products contain performance enhancement properties, therefore, surpassing the performance of traditional sodium chloride deicers. A summary of the laboratory testing results and the formulations of various deicers are presented in Table 4 and Table 5

Table 4: Results of ice melting tests at 30°F, 20°F, and 15°F and corrosion tests of various deicers.

Mix	Corrosion Inhibitors	Sample 1	Sample 2	Additive	Ice Melting Capacity, 60 min @ 30°F (ml brine/g deicer)	Ice Melting Capacity, 60 min @ 15°F (ml brine/g deicer)	Ice Melting Capacity, 60 min @ 20°F (ml brine/g deicer)	Corrosion Rate (MPY)
3	1% KGluc 0.2%NaMetaSil	7%	5%	2% KAc	4.880	1.562	1.70	16.85
4	1% KGluc 0.2%NaMetaSil	5%	5%	2% urea	4.578	1.436	-	-
6	1% KGluc 0.2%NaMetaSil	3%	3%	2% KSuc	4.577	1.476	-	-
12	1% KGluc 0.2%NaMetaSil	7%	5%	2% KSuc	-	1.380	-	-
13	1% KGluc 0.2%NaMetaSil	5%	3%	2% urea	4.782	1.444	1.88	-
16	1% KGluc 0.2%NaMetaSil	7%	3%	2% KAc	4.646	1.460	-	-
19	1% KGluc 0.2%NaMetaSil	5%	4%	2% KAc	4.587	1.499	-	-
20	1% KGluc 0.2%NaMetaSil	7%	4%	2% KSuc	4.996	1.436	-	-
22	1% KGluc 0.2%NaMetaSil	7%	4%	2% KAc	5.134	1.483	1.71	18.85
27	1% KGluc 0.2%NaMetaSil	7%	5%	2% urea	4.593	1.499	-	-
35	0.5% KGluc 0.1%NaMetaSil	2.5%	0.5%	3% Boost 1.0% urea	-	-	1.93	-
36	0.5% KGluc 0.1%NaMetaSil	2.5%	0.5%	5% Boost 1.0% urea	-	-	2.00	-

Note: KGluc = potassium gluconate; NaMetaSil = sodium metasilicate; KAc = potassium acetate; MgSil = magnesium silicate; CaSil = calcium silicate; KSil = potassium silicate

Table 5: Results of corrosion testing to carbon steel and freeze/thaw cycling of various deicers.

Mix	Corrosion Inhibitors	Sample 1	Sample 2	Additive	Amount of NaCl and $MgCl_2$	PCC Weight Loss (%)	Corrosion Rate (MPY)
3A	1% KGluc 0.2%NaMetaSil	7%	5%	2% KAc	7% $MgCl_2$ 8.1% NaCl	12.76	25.08
3B	1% KGluc 0.2%NaMetaSil	7%	5%	2% KAc 3% MgSil	7% $MgCl_2$ 8.1% NaCl	2.77	25.30
3C	1% KGluc 0.2%NaMetaSil	7%	5%	2% KAc 3% CaSil	7% $MgCl_2$ 8.1% NaCl	2.61	23.47
22A	1% KGluc 0.2%NaMetaSil	7%	4%	2% KAc	7% $MgCl_2$ 8.1% NaCl	8.77	23.91
22B	1% KGluc 0.2%NaMetaSil	7%	4%	2% KAc 3% KSil	7% $MgCl_2$ 8.1% NaCl	1.27	25.75
13X	1% KGluc 0.2%NaMetaSil	5%	0%	2% urea	23% NaCl	7.27	-
13Y	1% KGluc 0.2%NaMetaSil	0%	1%	2% urea	23% NaCl	6.95	-
13Z	1% KGluc 0.2%NaMetaSil	5%	1%	2% urea	23% NaCl	6.20	-

Note: KGluc = potassium gluconate; NaMetaSil = sodium metasilicate; KAc = potassium acetate; MgSil = magnesium silicate; CaSil = calcium silicate; KSil = potassium silicate

4.2. Suggested Research

Additional research such as pavement friction analysis and field operational testing is needed to determine performance in a field environment and establish application rate guidelines. Environmental effects such as BOD and COD need to be evaluated to ensure minimal impacts to aquatic habitats are achieved. Moreover, corrosion rates of the formulations containing BOOST need to be evaluated, which will provide valuable information on the long term effects and the associated costs of corrosion control. Further research will also help the value-added utilization of glycerol, which is the principal by-product of biodiesel production. Glycerol can offer potential benefits and requires evaluation as a possible component of an anti-icer formulation. Extensive research and development in the utilization of glycerol is needed to effectively advance the production of bio-based anti-icer formulations in a cost-effective and environmentally conscious approach. The bio-based local materials may also be useful for dust suppression and soil stabilization, adding to the potential benefits.

APPENDIX

1.   Chemical Analysis

Chemical analysis was performed on the two by-products using Fourier Transform Infrared (FTIR) spectroscopy and gas chromatography (GC) in order to determine the composition of these by-products. FTIR spectroscopy measures the infrared intensity versus wavelength of light to detect the vibrational characteristics of specific chemical functional groups. Gas chromatography (GC) is a process in which the components of a sample mixture are separated based on vapor pressures. GC identifies the compounds and the relative amount of each compound within a sample. The FTIR results shown in Figure 11 revealed a strong broad peak near wavenumber 3100-3600 cm^{-1} for both Sample 1 and Sample 2, indicating the presence of an alcohol functional group. Additionally, GC analysis determined that both Sample 1 and Sample 2 contain a high amount of ethanol, which corresponds with the FTIR results. Sample 1 also contains a small amount of acetaldehyde and ethyl acetate, which corresponds to the peaks at wavenumbers 2970 cm^{-1} and 1044 cm^{-1}, respectively.
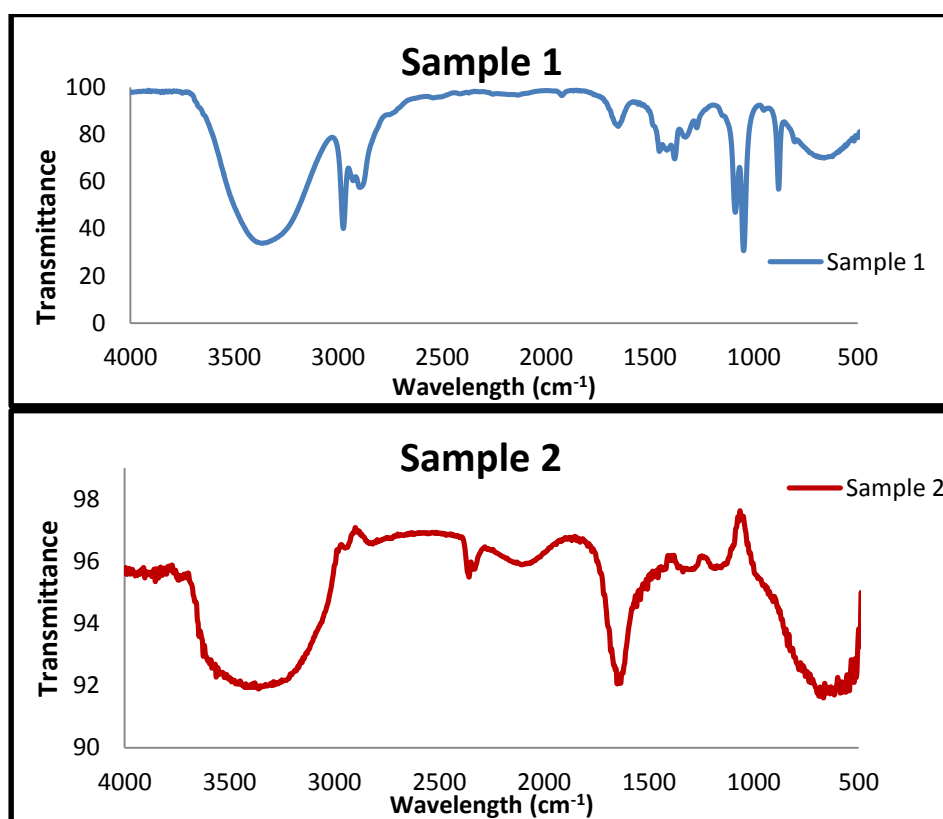
Figure 11: Fourier Transform Infrared spectroscopy results for Sample 1 and Sample 2.

Time	Compound	Score	CAS
5.139	Acetaldehyde, C_2H_4O	95.12	75-07-0
5.709	Ethyl Acetate, $C_4H_8O_2$	91.83	141-78-6
6.438	Acetonitrile, C_2H_3N	98.99	75-05-8 (solvent used to rinse syringe)
7.160	Ethanol, C_2H_6O	95.44	64-17-5

Time	Compound	Score	CAS
6.438	Acetonitrile, C_2H_3N	98.97	75-05-8 (solvent used to rinse syringe)
7.545	Ethanol, C_2H_6O	97.1	64-17-5
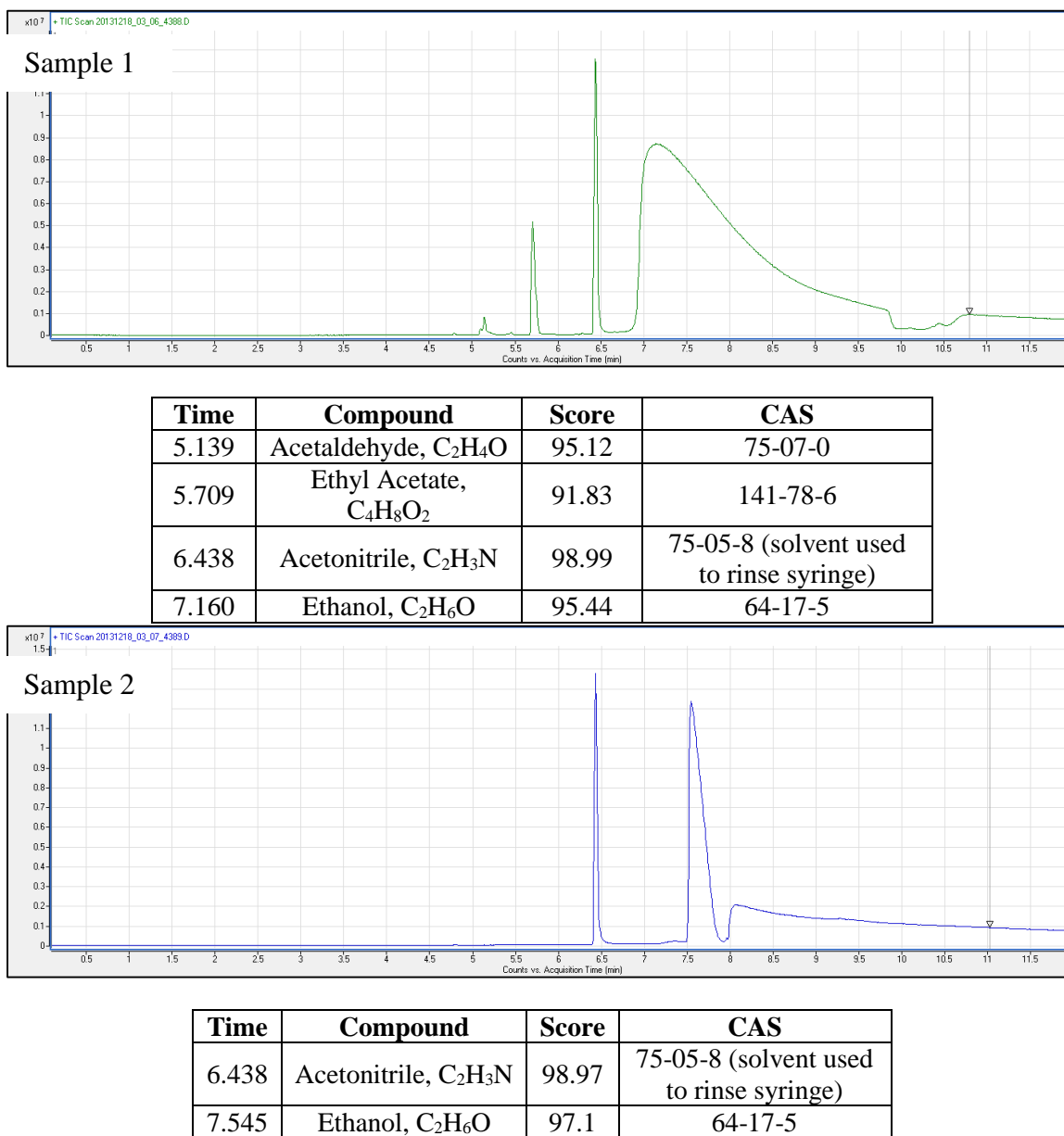
Figure 12: Gas chromatography results of sample 1 and 2.

2. Literature Review

Recently, bio-derived freezing point depressants are being developed for airport runway applications. For each gallon of biodiesel produced, approximately 0.35 kg (0.76 lb) of crude glycerol is also produced; there is an urgent need to better utilize this by-product with added value (Thompson and He 2006; Pachauri and He 2006). Crude glycerol is also very cost-effective, as it is available at $0.02 per gallon. The addition of succinate salts and glycerol to salt brine will enhance anti-icing performance at cold temperatures to the level comparable to

magnesium chloride or potassium acetate at reasonable costs, while producing substantial savings through reduced application rates, reduced corrosion to metals, and reduced impact on concrete or asphalt materials.

While the fermentation-derived succinate salts have shown great potential for airport runway applications, they have never been used in commercial anti-icers or deicers. For highway applications, a different set of priorities exist for anti-icing products. New research efforts are needed to develop commercially viable formulations consisting of agro-based succinate salts, rock salt, and other additives to develop cost-effective formulations addressing the needs of winter highway operations. Deicer formulations may involve blending the bio-derived 50 wt.% potassium succinate (KSc) with a 20 wt.% aqueous solution of rock salt at the ratio of 2:98 and 18:82 to produce low-end and high-end formulations, respectively, while other additives such as glycerol can be used for additional flexibility in performance enhancement and corrosion inhibition. For each identified anti-icing formulation, performance at different temperatures, corrosion, and other negative impacts need to be assessed. Subsequently, field operational tests need to be conducted to validate their effectiveness at the given application rate under the given road weather scenario.

Many commercial airports have transitioned from using urea and propylene glycol, which contain high levels of BOD and COD, to using organic salts such as potassium acetate and sodium or potassium formate as deicers and anti-icers. It is common practice to use solid deicers in combination with liquid deicers. Solid deicers cut through snow and ice allowing liquid deicers to disrupt the bond at the surface. However, acetate and formate deicers are highly corrosive; thus, advancement is needed to develop less corrosive, highly effective, and environmentally safe deicers. Battelle has been able to successfully modify the transesterification process in the production of biodiesel. The original process creates a by-product containing glycerin, NaCl salt, methanol, and free fatty acids, which requires further expensive treatment. The modification presented by Battelle uses an organic acid instead of HCl to neutralize the NaOH, which creates an acetate or formate salt and glycerin. In addition, glycerin naturally behaves as a corrosion inhibitor. Table A-1 shows the formulations of various deicing fluids made from pure components, and Table A-2 shows formulations of various deicing fluids made from biodiesel by-products. Test procedures including ice melting, ice penetration, and ice undercutting were performed on the deicing fluids at various temperatures. Figure A-1–Figure A-6 display the results of testing at 25°F. The results reveal that the proposed new deicing fluids have comparable performance to that of commercially available potassium acetate. Figure A-7 displays the freezing points of various deicers. No significant differences were observed between purified materials and raw biodiesel by-product materials. Furthermore, these new deicing fluids are cost-effective with lower corrosion rates and perform as effectively as commercially available deicers (Chauhan et al. 2009).

Table A-1: Deicing fluid composition from pure components (Chauhan et al.2009).

RDF # (RDF Name) / Additives	9136	9146	9156	10256	110606-3 (RDF 6-3)	110606-4 (RDF 6-4) (RDF G)	110606-5	60707 (RDF 6-2) (RDF B)	61407	121207A (RDF D)	042108A (RDF A)
Bio-based FPD Mixture	54.7%	58.4%	62.1%	65.3%	58.4%	62.1%	65.9%	54.6%	54.6%	54.6%	54.9%
Additives	2.1%	3.0%	3.8%	5.3%	3.0%	3.8%	4.6%	2.4%	2.4%	2.5%	1.9%
Water	43.2%	38.6%	34.1%	29.4%	38.6%	34.1%	29.5%	43.0%	43.0%	42.9%	43.2%
pH	9.4	9.4	9.3	10.9	11.1	11.0	10.8	10.9	10.5	10.9	10.8

Table A-2: Deicing fluid composition from biodiesel by-product (Chauhan et al. 2009).

RDF# (RDF Name) / Additives	30307	32207	32107	32607	111907 (RDF 6-12)	31708A (RDF J)
Bio-based FPD Mixture	60.9%	69.5%	58.0%	61.2%	55.4%	58.0%
Additives	0.5%	0.6%	0.6%	0.6%	0.8%	0.9%
Water	38.6%	29.9%	41.4%	38.2	43.8%	41.1%
pH	10.01	8.99	10.9	11.0	10.9	10.9
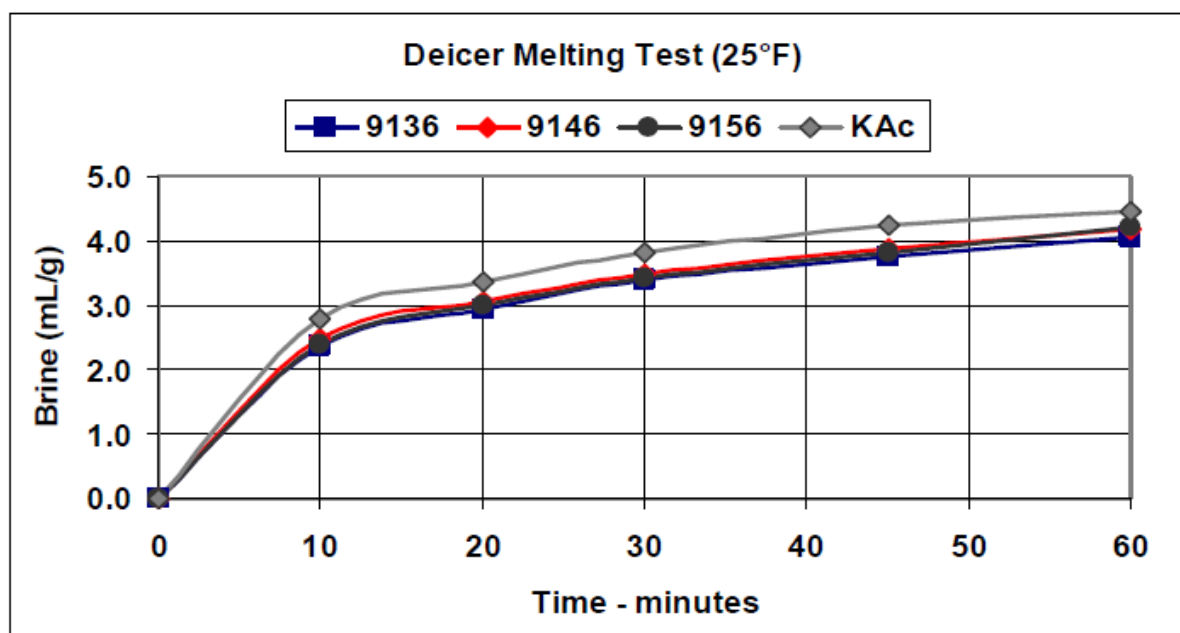
Figure A-1: Ice-melting comparison test results at 25°F (Chauhan et al. 2009).
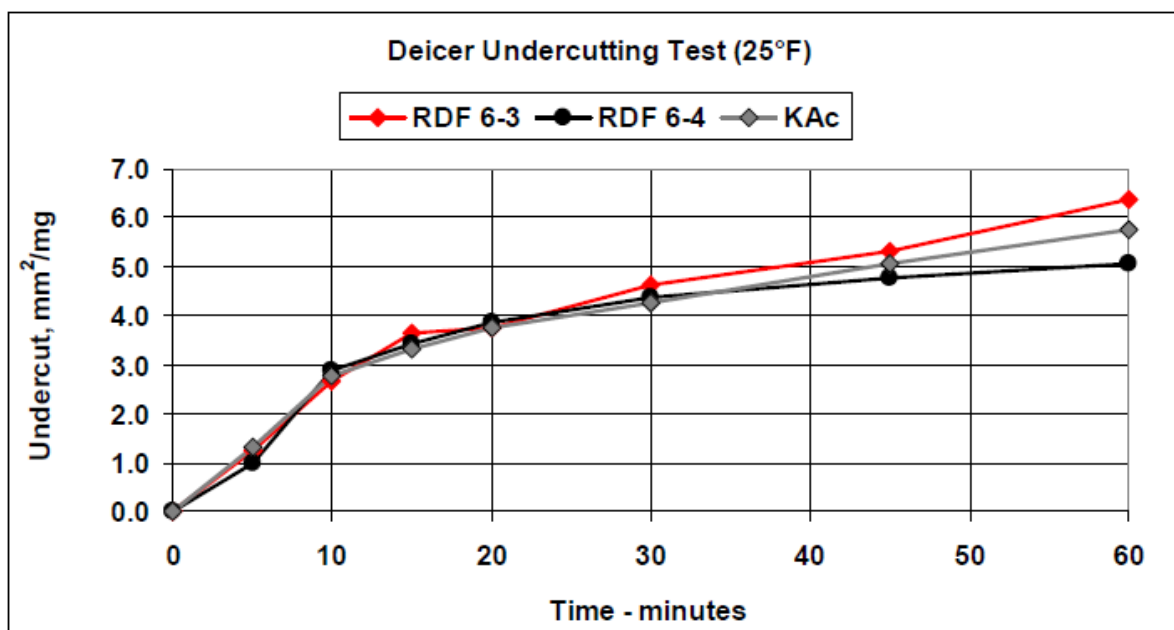
Figure A-2: Ice-undercutting comparison test results at 25°F (Chauhan et al. 2009).
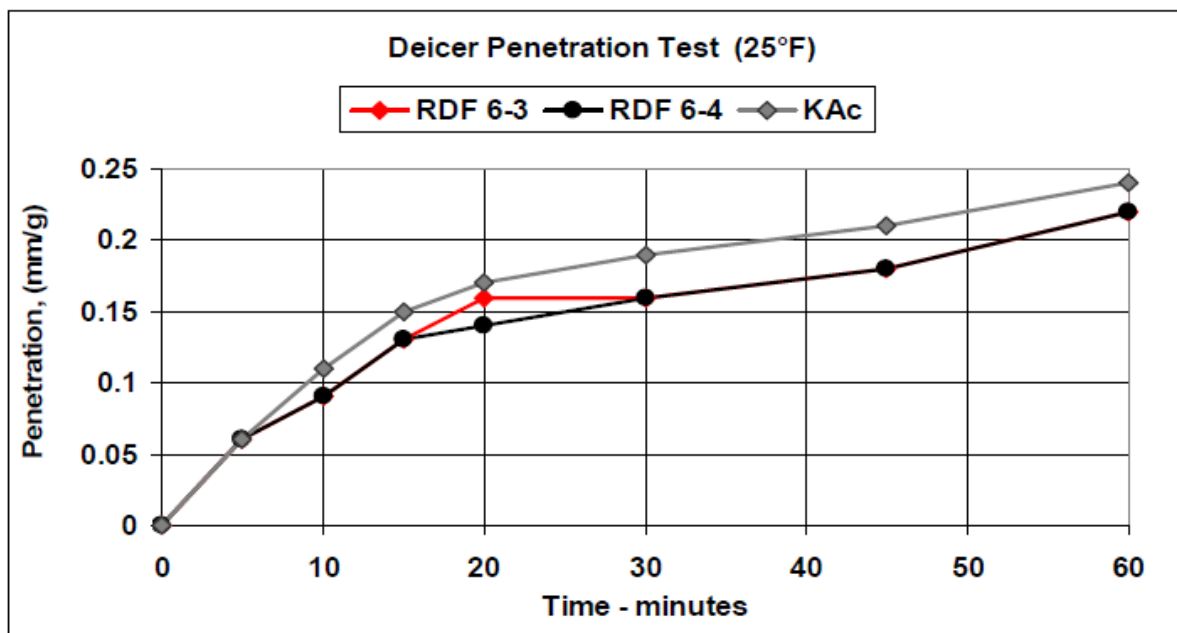
Figure A-3: Ice-penetration comparison test results at 25°F (Chauhan et al. 2009).
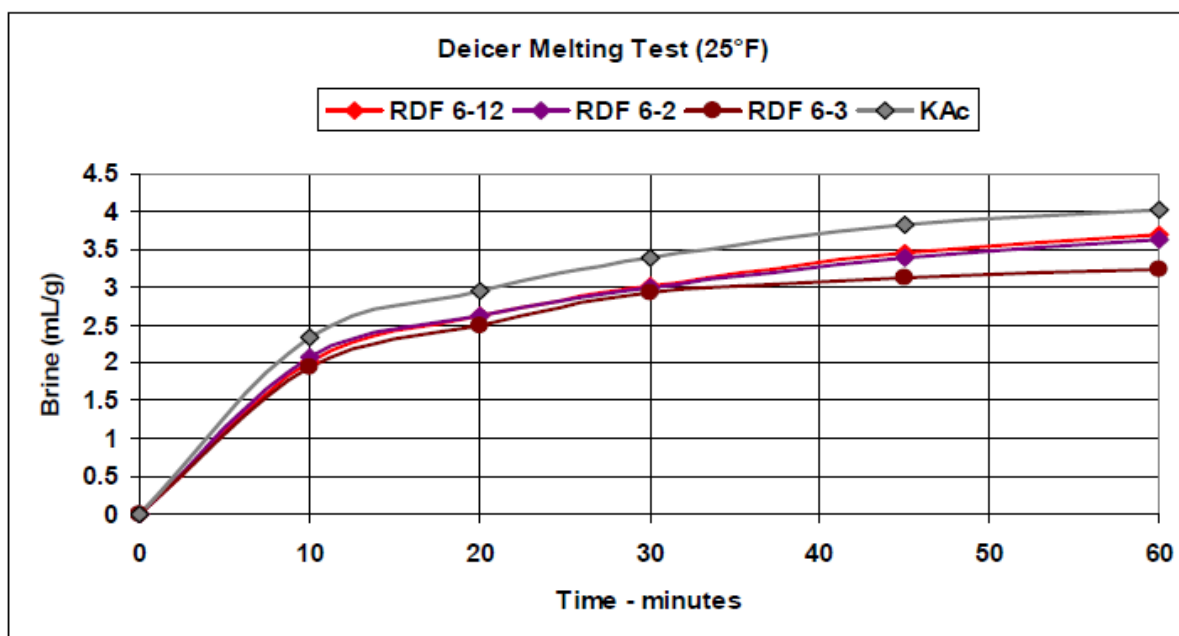
Figure A-4: Ice-melting comparison test results at 25°F (Chauhan et al. 2009).
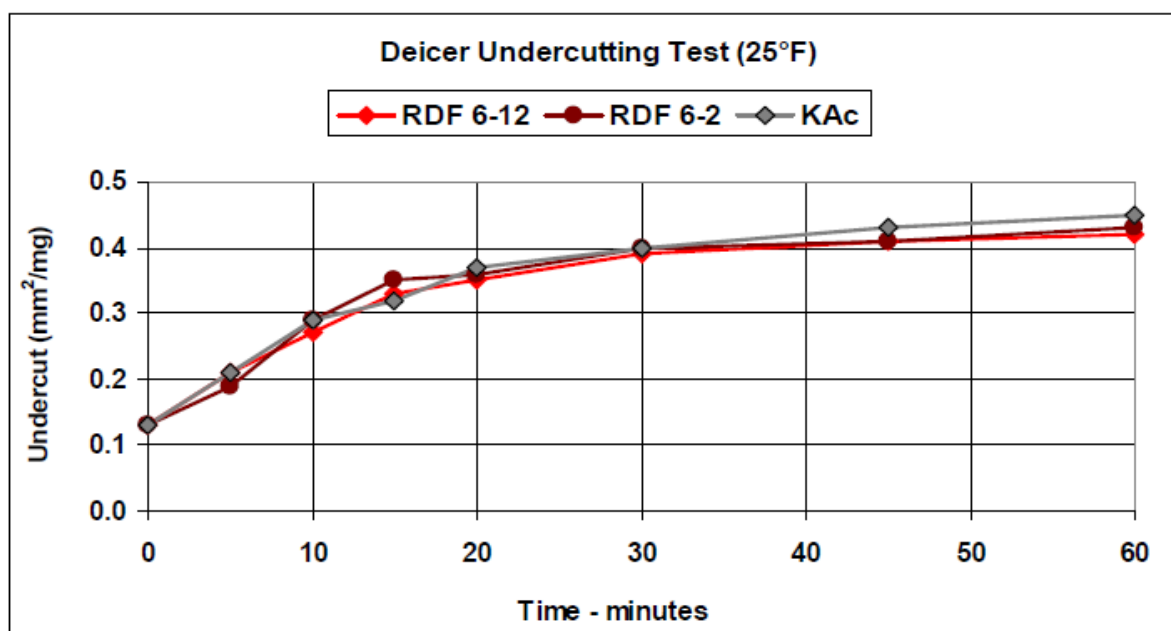
Figure A-5: Ice-undercutting comparison test results at 25°F (Chauhan et al. 2009).
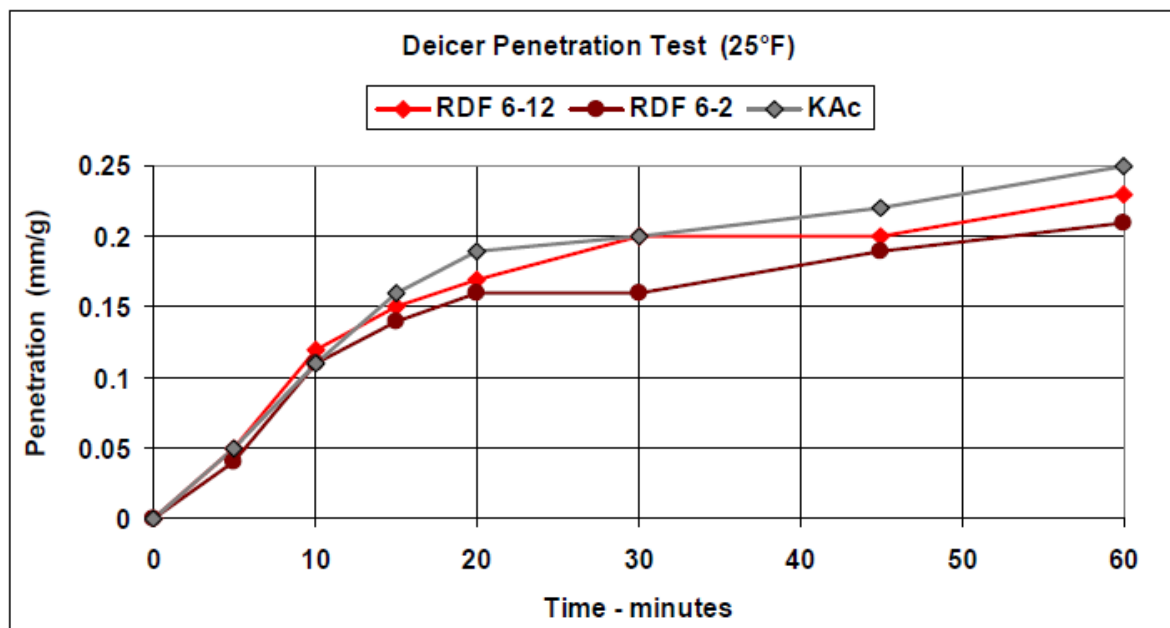
Figure A-6: Ice-penetration comparison test results at 25°F (Chauhan et al. 2009).
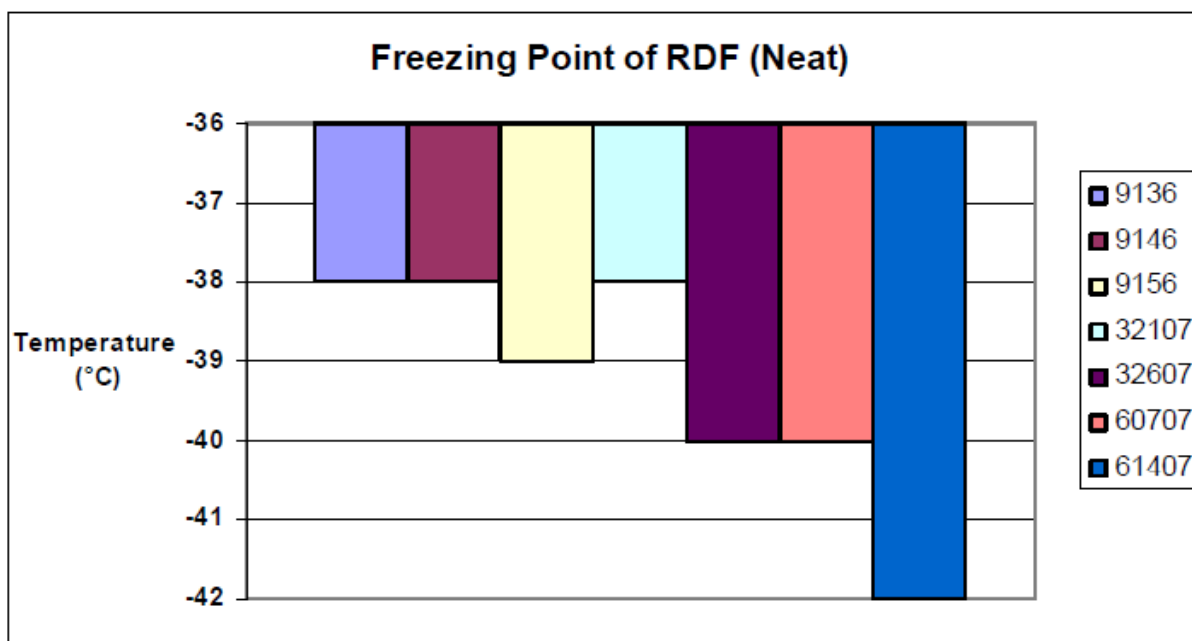
Figure A-7: Freezing points of various deicers (Chauhan et al. 2009).

A recent study investigated performance properties of selected commonly used deicers. Figure A-8 displays the results from the SHRP H205.1 and H205.2 ice-melting capacity test methods, corresponding to 60 minutes after application of deicers. This demonstrates the variations in ice-melting capacity with deicer and temperature. Solid deicers show increased ice-melting performance at temperatures around 0°C, whereas liquid deicers show improved performance at

colder temperatures. Sodium chloride rock salt has the best overall performance. In addition, data were collected for ice penetration of selected deicers using SHPR H205.3 and H205.4 test methods. The results of these methods (see Figure A-9) show that the liquid deicers outperformed the solid deicers (Fay and Shi 2011). This study was able to demonstrate the wide range of performance attributes among commonly used deicers and show some of the challenges required in the development of new deicers.
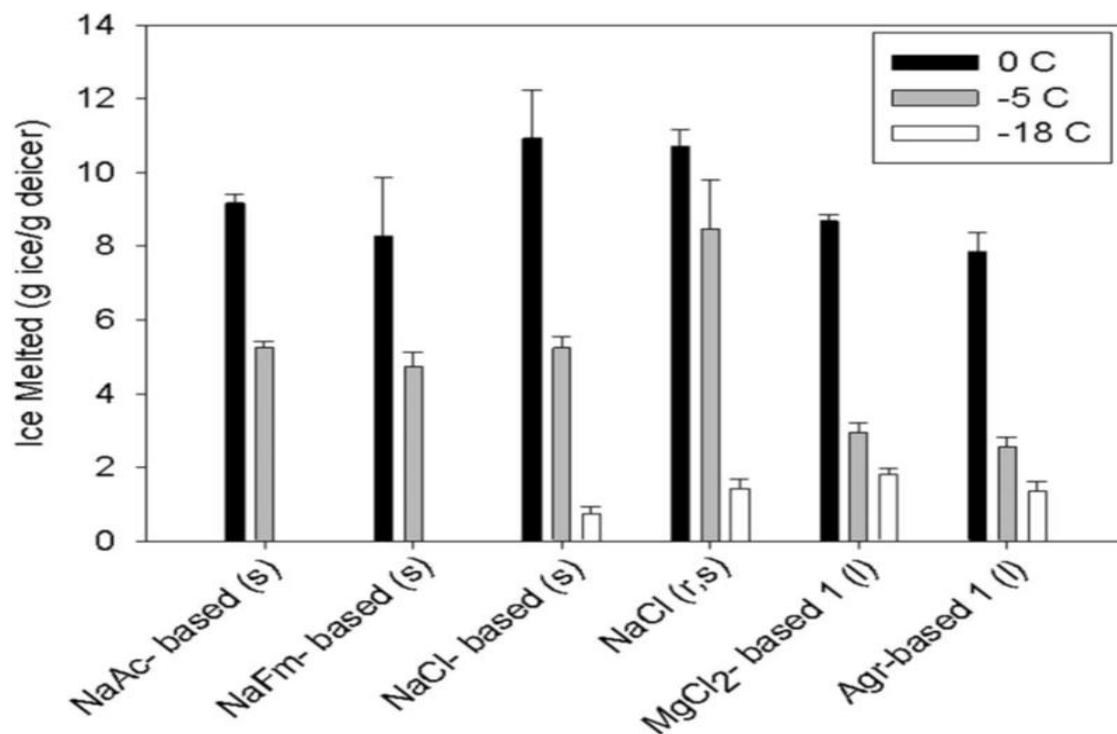
Figure A-8: Data from SHRP ice-melting capacity test after 60-minute exposure to deicers (Fay and Shi 2011).
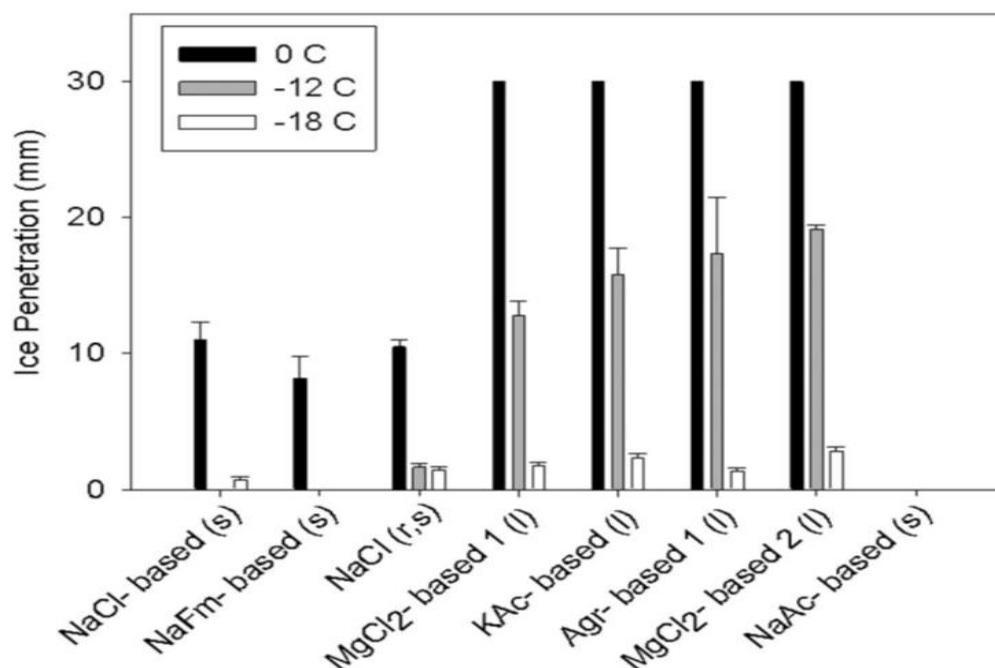
Figure A-9: Results from SHRP ice-penetration test after 60-minute exposure to deicers (Fay and Shi 2011).

Deicing chemicals melt snow and ice by lowering the freezing point of water, thus causing ice to melt. Several similarities can be observed among typical chemical deicer properties and characteristics. Chemical deicers can be referred to as freezing point depressants. Freezing point depressants usually have low molecular weight and contain strong hydrogen bonding, which improves performance. Freezing point depressants often consist of several oxygen atoms and only single bonds, which contribute to low chemical reactivity. Freezing point depressants containing nitrogen are considered harmful to the environment since they contribute to eutrophication. To achieve the desired shear-thinning behavior of anti-icing fluids, thickeners are added to formulations. Commonly used thickeners include polysaccharides. These thickeners are usually long-chain, water-soluble polymers that become entangled and create high viscosities. Deicing and anti-icing fluids with high viscosities tend to remain on surfaces for longer periods of time effectively maximizing exposure to snow and ice. In addition, the possibility of deicing fluids caking causes concern. The process of caking can occur when temperatures increase, causing adsorbed water to evaporate and recrystallization of salt, which prevents sufficient flowability. Consequently, an anti-caking additive, potassium carbonate, is usually added (ACRP 2010).

Chemical deicing fluids usually consist of a freezing point depressant, water, and additives. These additives can include wetting agents, pH buffers, antioxidants, dyes, anti-precipitation agents, corrosion inhibitors, and foam suppressors. Common wetting agents are composed of nonylphenol ethoxylates, which reduce surface tension. However, the constituent nonylphenol can cause adverse health risks if introduced into streams from runoff. A proposed deicing solution contains polyols as the freezing point depressant. Polyols are defined as an alcohol containing several hydroxyl groups and can be produced from renewable resources such as corn or other agricultural sources. The wetting agent used in this formulation consists of nontoxic,

biodegradable organophosphates. These wetting agents are effective by displacing bonded water and creating a hydrophobic surface, making ice crystal formation difficult. The main component in this proposed deicing fluid is glycerol supplemented with a small amount of a deicing salt. Samuels et al. (2006) demonstrated that this deicing fluid is nontoxic with a LD$_{50}$ of 58,000 mg/L for fathead minnow. Glycerol is becoming a popular freezing point depressant in new agro-based deicer formulations, mostly due to low cost, low environmental impact, and abundant quantity.

DNP-sponsored laboratory testing has demonstrated that AMS 1435A certified potassium succinate (KSc) anti-icing liquids for airport runway applications (1) significantly reduce the corrosion of alloys and concrete scaling, relative to KAc solution; and (2) feature low biological oxygen demand, BOD of 0.15 g O$_2$/g fluid, and outstanding deicing performance such as ice-melting, penetration, and undercutting comparable to KAc. Furthermore, the production of KSc via fermentation uses large quantities of carbon dioxide in the process and is thus a green technology characteristic of zero carbon footprint. The DNP fermentation-based biotechnology has enabled significant cost reduction in the production of succinate salts. While the fermentation-derived succinate salts have shown great potential for airport runway applications, they have never been used in commercial anti-icers or deicers. For highway applications, a different set of priorities exist for anti-icing products, and new research efforts are needed to develop commercially viable formulations consisting of agro-based succinate salts, rock salt, and other additives in order to develop cost-effective formulations that address the needs of winter highway operations.

In addition, the fermentation process of sugars produces a mixture of organic acids, which can be reacted with a source of calcium and magnesium to yield calcium magnesium propionate. Calcium magnesium propionate is a less expensive alternative to calcium magnesium acetate, which can also be produced from products of the fermentation process. Mathews (1994) has proposed a procedure for the practice of utilizing fermentation products to create road deicer products, having determined that calcium magnesium propionate is equally as effective as calcium magnesium acetate as a freezing point depressant. Furthermore, Klyosov et al. (2000) determined that deicer compositions formed from organic acids such as lactic, succinate, acetic, and formic acids, obtained from the fermentation of commercially available glucose, possess effective ice-melting and anti-corrosive properties.

Recent deicer developments focus on cost, performance, corrosiveness, and environmental impact when designing new and improved deicer formulations. In addition, sustainable resources such as by-products from agricultural processes are becoming potential constituents in deicer formulations. A recent development by Natural Solutions, ICEBAN, is made from the natural, organic by-products produced in the processing of alcohol, cheese, or corn. ICEBAN is a liquid deicer with good deicing and anti-icing properties and is non-corrosive. However, since ICEBAN is a liquid deicer, it would not be suitable for agencies equipped with solid deicer application equipment, and its viscosity at low temperatures may cause complications. Various deicer formulations take advantage of exothermic reactions that release heat when in contact with water and combining the freezing point depressant effect to the solution. Unfortunately, these compounds commonly contain chlorides, which are highly corrosive. Berglund et al. (2003) developed a deicer formulation that contains a succinic acid and/or succinic anhydride and a neutralizing base, which produces succinate salts and creates heat when in contact with

water, allowing the succinate salts to act as freezing point depressants. Some formulations contain glycol, which impedes reformation of ice. Several heat reactions occur when this composition is exposed to water. The hydration of succinic anhydride, the dissolution of the base, and the neutralization of the acid produce heat and effectively melt ice. This dual action composition demonstrates effective ice-melting characteristics (Berglund et al. 2003).

Developing deicer compositions using sustainable resources such as by-products of agricultural processes offers many advantages. This approach is beneficial to the environment by reducing waste, decreasing impact, and creating environmentally safe deicers. Janke et al. (1997) developed an environmentally friendly deicer or anti-icing agent from a by-product of a wet milling process of corn called *steep water*. The deicer formulation is noncorrosive, inexpensive, water-soluble, and readily available in large quantities. This formulation has been proposed for use as an anti-icing agent and for integration into abrasives or other chemical deicers as an additive to improve performance or inhibit corrosion. Tests have shown that successful inhibition is achieved with the addition of steep water solubles to chloride salts (Janke et al. 1997). Similarly, Kharshan et al. (2012) demonstrated the successful increased corrosion protection of carbon steel using corn extracts. Table A-3 displays the typical composition of steep water. It is suggested that 20 to 60 gallons per lane mile of steep water deicer be applied to effectively clear snow and ice from roadways. When applied to roadways, steep water deicer is not easily removed by passing vehicles or wind, and remains in contact with the road, which provides continued snow and ice removal with decreased application rates. Ice-melting tests compared steep water concentrated at 50% by weight of dry substance to an industrial salt/sand mixture. Each deicer was applied to a 3.5-inch-thick sheet of snow and approximately 20 square yards. The steep water demonstrated higher melting performance than the salt/sand mixture with respect to both duration and strength. In addition, the steep water deicer showed active ice-melting temperatures as low as 7.5°F, whereas ice melting with the salt/sand mixture stops around 20°F (Janke et al. 1997). Additionally, Montgomery and Yang proposed a deicer formulation, derived from corn steep water, in which glucose and corn steep water is combined with sodium hydroxide to form a biodegradable deicer solution with a low freezing point of around -26°C (Montgomery and Yang 2003). Furthermore, corrosion testing resulted in little effect on mild steel, as shown in Table A-4. Mild steel bolts immersed in various concentrations of steep water showed no oxidation after four months. Moreover, mild steel bolts sprayed with various concentrations of steep water showed no signs of oxidation after four months; rather the mild steel bolts appeared to be sealed with a protective coating (Janke et al. 1997).

Table A-3: Typical composition of steep water (Janke et al. 1997).

MATERIAL	CORROSION (mils per year - MPY)
Mild Steel	0.50
Stainless Steel	None detectable
Aluminum	None detectable

Table A-4: Corrosion results (Janke et al. 1997).

ITEM	DRY BASIS (No Moisture)	CONDENSED (48% solids/52% Moisture)
Crude Protein	33.0%	16.0
Crude Fat	0.2%	0.1%
Acid Degergent Fiber	0.66%	0.32%
Phosphorus	2.31%	1.12%
Calcium	0.02%	0.01%
Sulfur	0.56%	0.27%
Potassium	2.74%	1.32%
Magnesium	1.08%	0.52%
Sodium	0.13%	0.06%
Iron	145 ppm	70 ppm
Aluminum	22 ppm	10 ppm
Manganese	34 ppm	17 ppm
Copper	8 ppm	4 ppm
Zinc	140 ppm	68 ppm
Total Ash	27%	5.4–21.68%

Similarly, another proposed deicing composition made from a fermentation by-product is presented by Janke et al. The proposed deicing composition is made from a by-product of processing cheese known as whey. Whey has many desired deicer properties including good water solubility, low freezing point in solution, low cost, and availability; also, it is non-corrosive and environmentally acceptable. During the cheese-making process, milk coagulates and is strained, leaving a liquid behind known as whey. The composition of whey is shown in Table A-5. This liquid is condensed to 50% solubles and used as an additive in livestock feed (Table A-6). It is suggested that this whey deicer composition can be used as an additive with sand or other chemical deicers. When mixed with chloride salts, the whey product becomes an effective corrosion inhibitor. Tests have shown significant reductions in corrosion when using the whey product with 5% by weight chloride salts compared with a solution of 5% salts. Also, the whey composition can be used as an anti-icer, applied to a roadway prior to the accumulation of snow and ice. Tests have shown that the whey composition deicer is effective at melting snow and ice and has a freezing temperature just below 0°F. In addition, corrosion tests have shown that a minimal amount of oxidation occurs when mild steel bolts are immersed in various concentrations of whey (Janke et al. 1998a). In addition, Janke et al. proposed an additional noncorrosive, environmentally safe deicer composition made from vinters condensed solubles acquired from the processing of wine. This wine by-product deicer has a low freezing point of -20°F and Table A-7 shows its composition (Janke et al. 1998b).

Table A-5: Composition of whey (Janke et al. 1998a).

ITEM	DRY BASIS (No Moisture)	CONDENSED (50% solids/50% Moisture)
Protein	12.80%	6.20%
Crude Fat	0.2%	0.1%
Carbohydrates	74.13%	37.07%
Calcium	4.20%	2.10%
Iron	1.10%	0.55%
Magnesium	1.30%	0.65%
Phosphorus	2.11%	1.06%
Potassium	4.64%	2.32%
Sodium	0.58%	0.29%
Zinc	0.20%	0.10%
Amino Acids	1.01%	0.51%
Lipids	0.24%	0.12%

Table A-6: Properties of steep water solution with 50% solubles (Janke et al. 1997).

SOLUTION CONCENTRATION		FREEZING TEMPERATURE	VISCOSITY (SSU)		BOD	pH
(°Brix)	(°Baumé)	(°F.)	(@20° F.)	(@70° F.)		
50	30	0	475	195	.235	4.2

"Brix" is the measurement on a hydrometer scale that indicates the relative percentage by weight of a substance in solution. "Baumé" is a measurement on a hydrometer scale that indicates the specific gravity of a substance.

Table A-7: Composition of vintners condensed solubles (Janke et al. 1998b).

ITEM	DRY BASIS (No Moisture)	CONDENSED (48% solids/52% Moisture)
Crude Protein	33.0%	16.0%
Crude Fat	0.2%	0.1%
Crude Fiber	5.2%	2.51%
Total Carbo-hydrates	50.0%	25.0%
Unfermented Sugars	3.6%	1.8%
Phosphorus	2.31%	1.12%
Sulfur	0.56%	0.27%
Potassium	2.74%	1.32%
Magnesium	1.08%	0.52%
Sodium	0.13%	0.06%
Iron	145 ppm	70 ppm
Aluminum	22 ppm	10 ppm
Manganese	34 ppm	17 ppm
Copper	8 ppm	4 ppm
Zinc	140 ppm	68 ppm
Tartaric Acid	trace	trace
Malic Acid	trace	trace
Acetic Acid	trace	trace
Ascorbic Acid	trace	trace
Cream of Tarter	1.20%	0.60%
Yeast	2.20%	1.10%

Although the deicer compositions presented by Janke et al. offer viable alternative deicers to chloride salts, some negative characteristics are present. By-products from fermentation or cheese processing are biologically reactive, which can result in continued growth of organisms after application, producing undesirable strong odors and causing foam. Furthermore, the strong odor of distillation and fermentation by-products may not be suitable in residential areas. Thus, a deicer formulation made from a waste product of processing sugar beet molasses is proposed. Sugar beets are processed to remove sugar and produce commercial grade sugar. A syrup is formed and then heated to separate crystals that become commercial grade sugar from a liquor that is the desugared sugar beet molasses. Currently, this waste product, called *desugared sugar beet molasses*, is used as animal feed. The composition of desugared sugar beet molasses is shown in Table A-8.

Table A-8: Composition of desugared sugar beet molasses (Bloomer 2000).

Item	Content
Moisture	40%
Fructose Polymers	15%
Amino Acid Protein Polymers	12%
Other Carbohydrates, Starches, and Polymers	17%
Potassium	9%
Sodium	3%
Chlorine	1%
Other Ash/Calcium Oxide	3%

It was discovered that this waste product is an effective freezing point depressant and can be used directly from the manufacturer without further processing. It does not contain alcohols or microorganisms, and thus is biologically inactive. It can be integrated as an additive with other chemical deicers to improve deicing performance and inhibit corrosion. Results from ice and snow melting tests, where four different solutions were applied to ice and snow of between ¼ and 1 inch thick are shown in Table A-9. Corrosion tests of desugared sugar beet solution on mild steel showed no corrosion. Corrosion inhibition testing of mild steel with two solutions—one made of 30% by volume of 60% solids by weight desugared sugar beet solution plus 70% by volume of a 30% solids by weight magnesium chloride, and another made of 30% by volume of a 65% solids by weight desugared sugar beet solution plus 70% by volume of a 32% solids by weight calcium chloride—showed no corrosion after three months (Bloomer 2000). A study of a similar molasses-based product performed by Petkuviene and Paliuslis (2009) showed comparable results. The corrosion inhibition of Safecote, an organic substance based on molasses, was tested and found effective as a corrosion inhibitor. Immersion and spray testing coupled with mass loss measurements were performed on a variety of metals. Safecote exhibits good performance test results after 100 days as shown in Figure A-10–Figure A-13.

Table A-9: Ice and snow melting results (Bloomer 2000).

Application Rate	Composition	Observations
1–2 oz./ sq. yd.	Desugared sugar beet molasses alone 60–65% solids	Performed very well; melted snow and ice and continued to move laterally; moved underneath surface of snow.
1–2 oz./ sq. yd.	70% desugared sugar beet molasses (60–65% solids by weight) mixed with 30% magnesium chloride (30% solids by weight)	Very good results; Improved flow and melted more from the top of the ice downward to underneath the surface.
3 oz./5 lbs (8 gal./ ton)	Desugared sugar beet molasses (60–65% solids by weight) mixed with rock salt	Very good results; spread at a fast rate.
1–2 oz./ sq. yd.	40% desugared sugar beet molasses (60–65% solids by weight) mixed with 50% of a 30% solids by weight magnesium chloride and 10% water by volume	Excellent results; no solids formed in solution, which avoided clogging the spray nozzles.
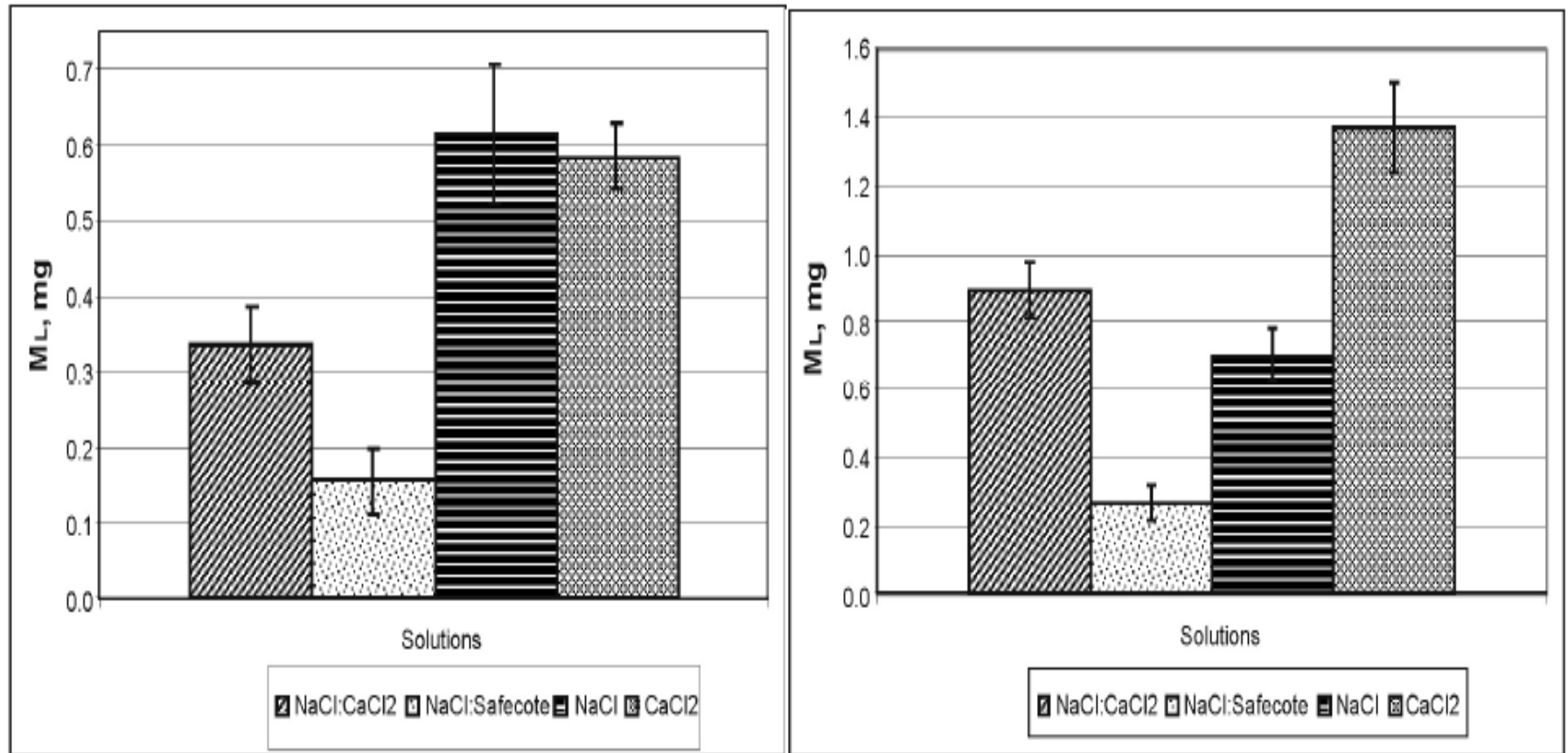
Figure A-10: Aluminum mass loss by immersion method on left and spray on right (Petkuviene and Paliuslis 2009).

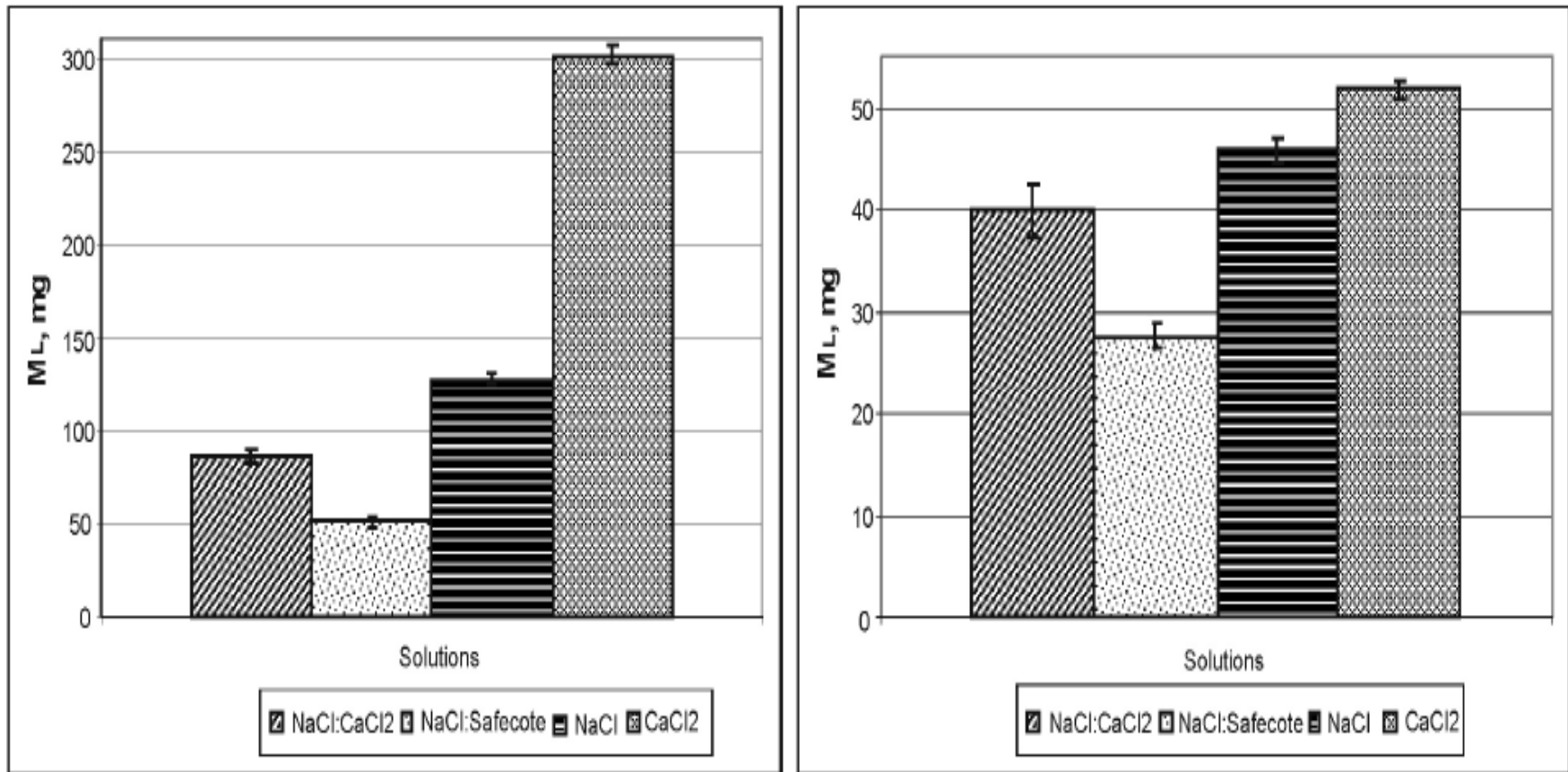**Figure A-11: Galvanized steel mass loss by immersion method on left and spray on right (Petkuviene and Paliuslis 2009).**
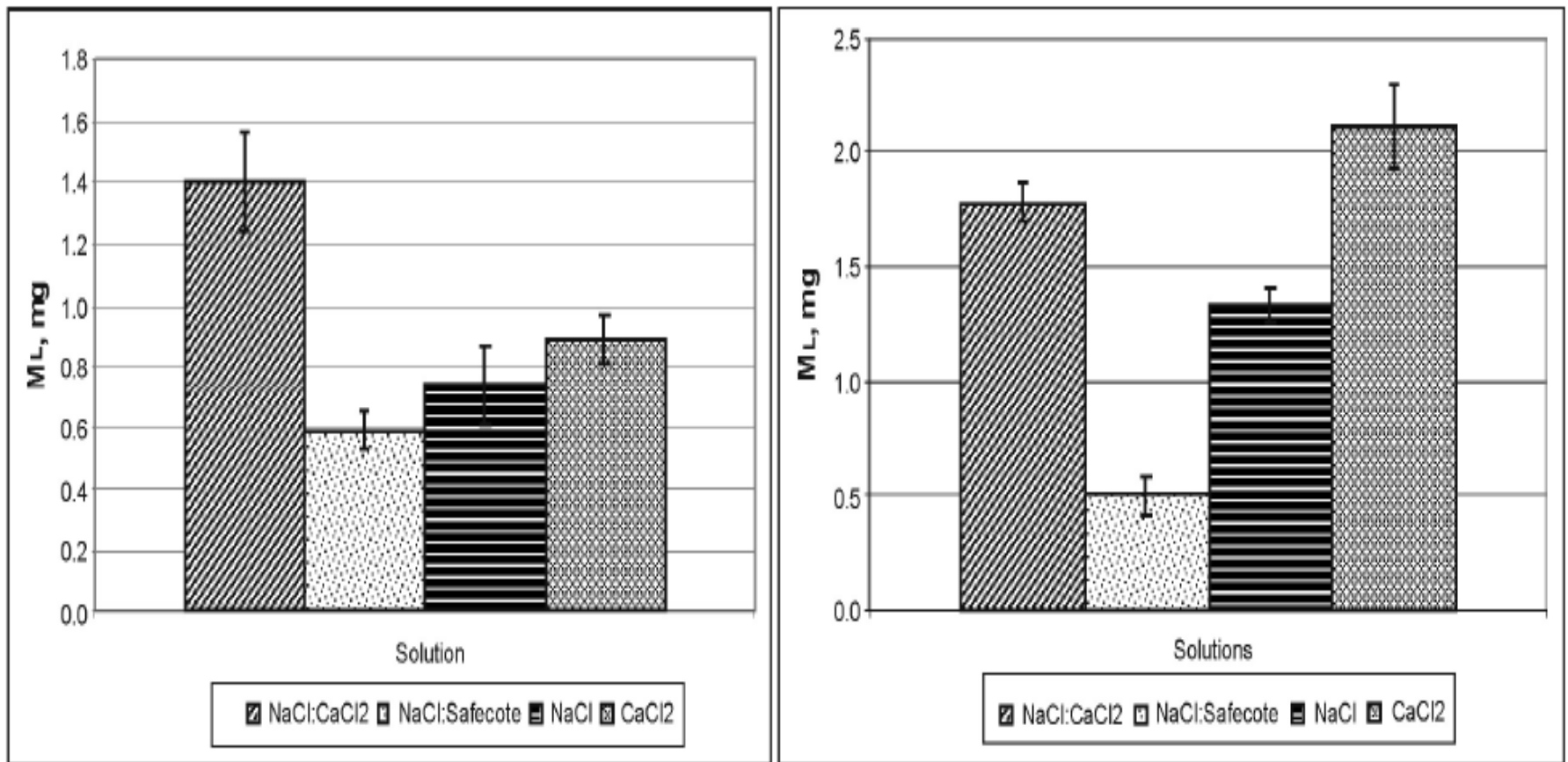
Figure A-12: Stainless steel mass loss by immersion method on left and spray on right (Petkuviene and Paliuslis 2009).
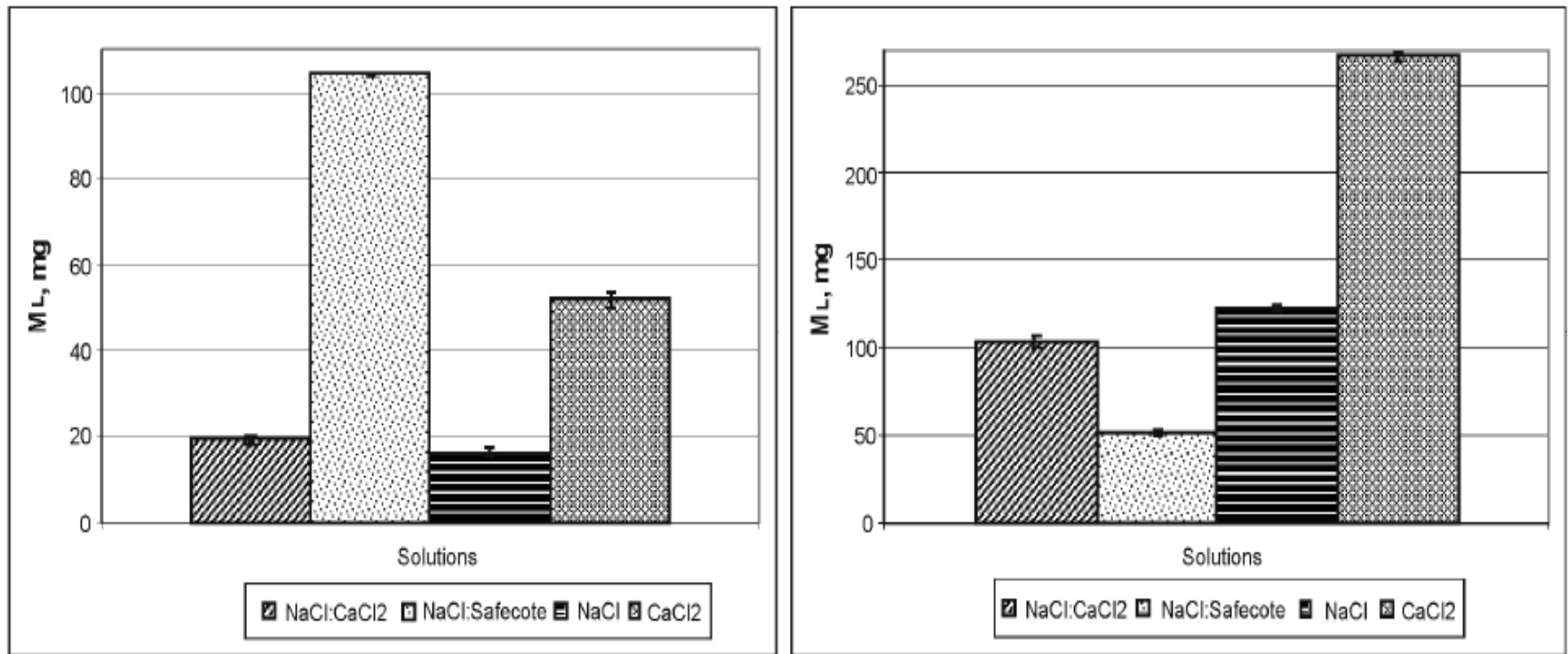
Figure A-13: Carbon steel mass loss by immersion method on left and spray on right (Petkuviene and Paliuslis 2009).

Although Janke et al. and Bloomer used materials that are naturally occurring and are considered renewable resources, it is believed that they contain hundreds of components and are inconsistent with variable properties depending on source and batch. In addition, these materials have undesirable ingredients with high organic content, which causes biological degradation and high biological oxygen demand. Therefore, Hartley et al. (2001) have proposed a new synergistic approach for developing an effective deicer, in which a low molecular weight carbohydrate is integrated with an inorganic freezing point depressant. Specifically, polysaccharides derived from agricultural-based products such as corn, wheat, barley, oats, sugar cane, or sugar beets are added to chloride salts. A series of filtration mechanisms is used to isolate the active components in brewers' condensed solubles such that low molecular carbohydrates can be utilized. Carbohydrate composition greatly varies; therefore, an evaluation was needed of simple sugars, disaccharides, and polysaccharides to determine a relationship between freezing point and molecular weight. The results are shown in Table A-10 and Table A-11. In addition, the effect of chloride salt content on freezing point in the deicing solution was evaluated and the results are shown in Table A-12. Corrosion results shown in Table A-13 were obtained following SHRP H205.7 Test Method for Evaluation of Corrosive Effects of Deicing Chemical on Metals, and suggest that corrosion inhibition was observed due to the carbohydrate additive (Hartley et al. 2001). A very similar deicer composition made from sugars, referred to as Caliber 1000, was proposed by Bytnar (2009). Performance and corrosion test results presented by Bytnar are shown in Figure A-14, Figure A-15, and Figure A-16. Additionally, Hartley et al. proposed a deicer composition, with improved viscosity characteristics, derived from brewers' condensed solubles. This composition contains a mixture of carbohydrates and chloride salts to maintain a high level of performance (Hartley et al. 2006).

Table A-10: Freezing point test results for simple carbohydrates (Hartley et al. 2001).

SIMPLE CARBOHYDRATES

Carbohydrate		% Concentration	Freezing Point	
Type	Name	of Carbohydrate	° F.	° C.
Control	MgCl$_2$ (15%)	Nil	−4.7	−20.4
Sugar	Fructose	25.0	−8.9	−22.7
Sugar	Fructose	50.0	−18.2	−27.9
Sugar	Fructose	75.0	−31.9	−35.5
Sugar	Glucose	30.0	−11.4	−24.1
Sugar	Glucose	65.0	−37.3	−38.5
Disaccharide	Maltose	25.0	−8.3	−22.4
Disaccharide	Lactose	25.0	−11.7	−24.3

Table A-11: Freezing point test results for complex carbohydrates (Hartley et al. 2001).

COMPLEX CARBOHYDRATES

Carbohydrate	% Concentration of Carbohydrate	Freezing Point ° F.	° C.	Comments
Control MgCl$_2$ (15%)	Nil	−4.7	−20.4	
Corn syrup-high maltose	30	−5.6	−20.9	Contains glucose, maltose and maltotrisoe
Corn syrup-high maltose	65	−19.1	−28.4	
Corn syrup solids DE20	25.0	−9.9	−23.3	Average Mol. Wt. 3746
Corn syrup solids DE44	25.0	−11.6	−24.2	Average Mol. Wt. 1120
Corn syrup solids DE44	50.0	−21.3	−29.6	
Corn syrup solids DE44	65.0	−27.0	−32.8	

Table A-12: Freezing point test results (Hartley et al. 2001).

Chloride Salt	% salt by weight	% Carbohydrate by weight	Freezing Point ° F.	° C.
MgCl$_2$	22.7	18.0	Less than −47	Less than −43.9
MgCl$_2$	15.0	25.5	−22	−30
CaCl$_2$	29.6	18.6	Less than −47	Less than −43.9
CaCl$_2$	17.5	4.1	−5.4	−20.8
CaCl$_2$	15.0	4.1	−0.6	−18.1

Table A-13: Corrosion test results (Hartley et al. 2001).

% Chloride	%	Corrosion Rate (mils per year)		
Salt	Carbohydrate	One Week	Three weeks	Six weeks
15% NaCl	Nil	5.97	4.66	5.48
15% $MgCl_2$	Nil	2.58	1.93	1.73
15% $MgCl_2$	4.1	0.89	0.61	0.40
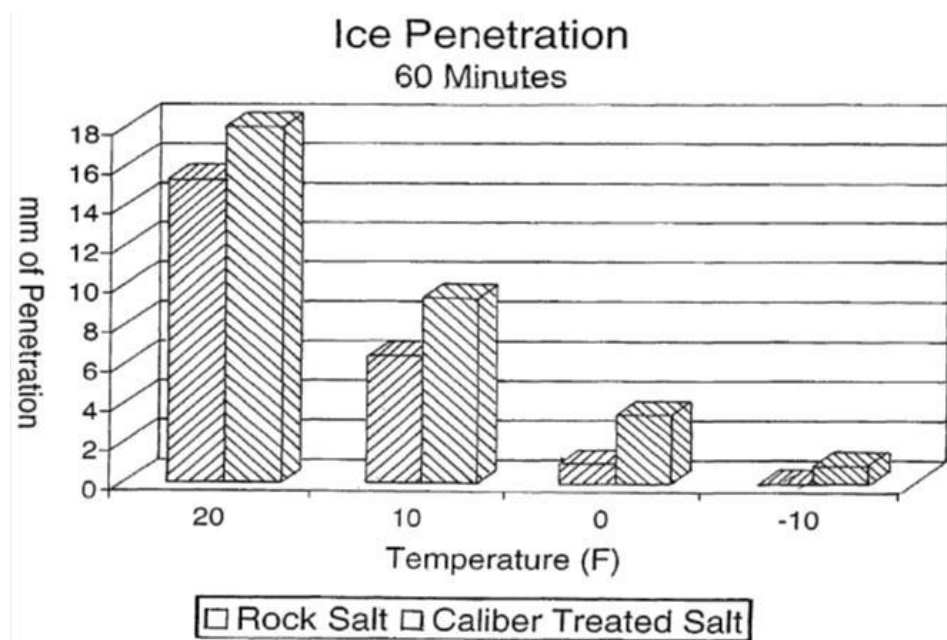
Figure A-14: Ice-penetration results of various deicers at different temperatures (Bytnar 2009).
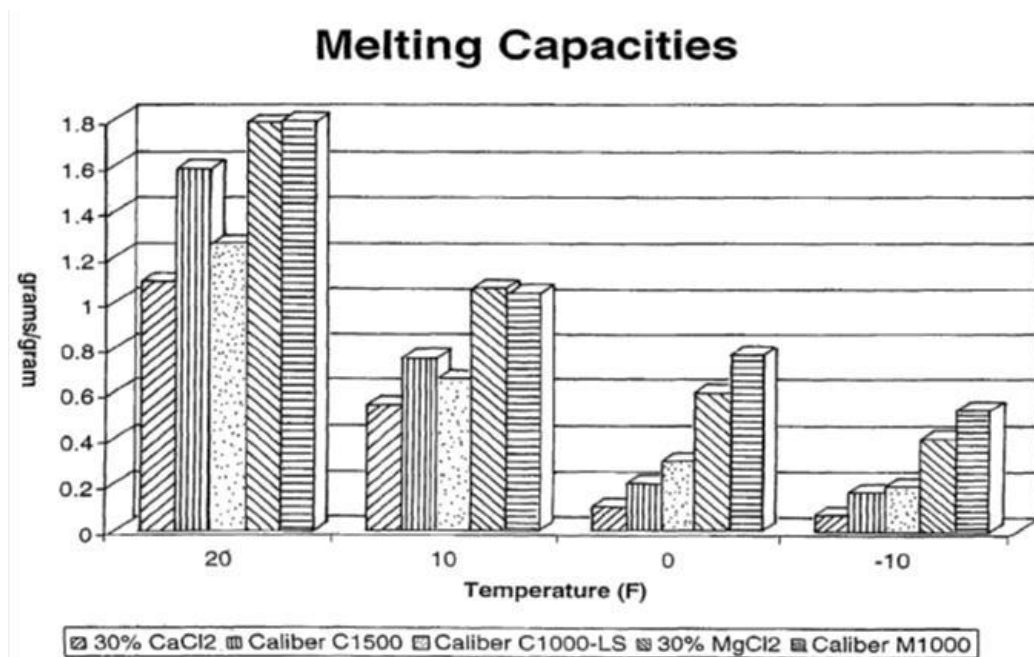
Figure A-15: Melting capacity results of various deicers at different temperatures (Bytnar 2009).
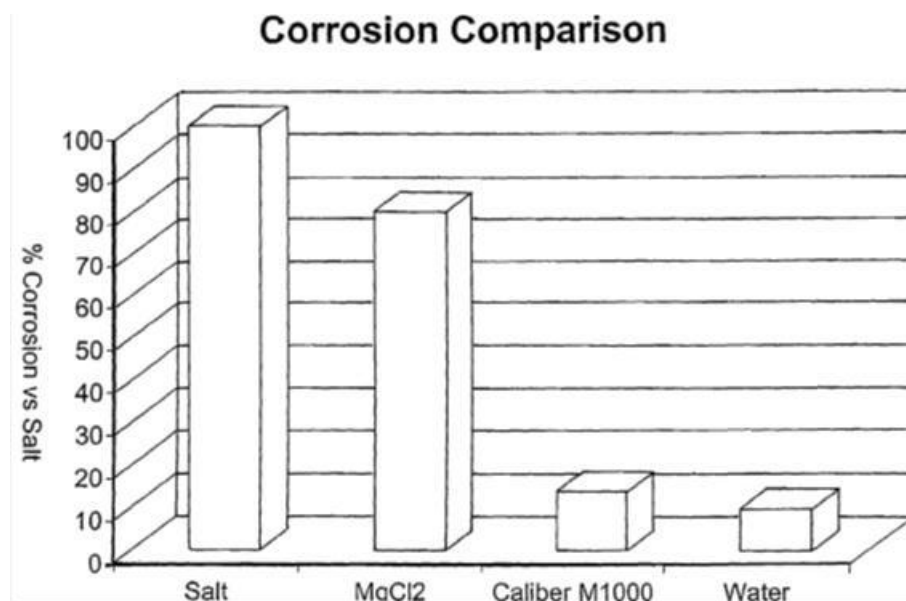
Figure A-16: Corrosion PNS test method results of various deicers (Bytnar 2009).

On the contrary, the use of agricultural by-products such as molasses or distillers' solubles as corrosion inhibitor additives creates some potential complications. To achieve improved corrosion inhibition, high concentrations are required, which affect ice-melting capacity and increase biological oxygen demand. The major constituents in most agricultural by-products are

sugars, thus Koefod proposed the approach of oxidizing the monosaccharide aldehyde group to create a carboxylic acid such as gluconic acid, saccharic acid, and tartaric acid. These compounds can be used as corrosion inhibitors at lower concentrations, which results in lower costs and improved ice-melting capacity. The NACE Standard TM0169-95 corrosion test method was used to determine corrosion inhibitor effectiveness. Steel washers were exposed to a 3% sodium chloride solution with various inhibitors during this cyclic immersion test. Test results are shown in Table A-14 and Table A-15. It was determined that this alternative approach yields effective corrosion inhibitors at lower costs and concentrations (Koefod 2010a).

Table A-14: Corrosion test results (Koefod 2010a).

Mild Steel Corrosion Rates in 0.153 M Sodium Chloride and Corrosion Inhibitors	
Corrosion Inhibitor	Corrosion Rate (mpy)
None (control)	54.4
2.45 mM Glucose	48.8
24.5 mM Glucose	38.8
2.45 mM Gluconate	23.8
2.45 mM Saccharate	13.4
2.45 mM D-Gulonate	20.4

Table A-15: Corrosion test results (Koefod 2010a).

Mild Steel Corrosion Rates in 0.153 M Sodium Chloride and Corrosion Inhibitors	
Corrosion Inhibitor	Corrosion Rate (mpy)
None	51.6
4.0 mM Gluconate	26.5
4.0 mM Glucose	50.0
40.0 mM Glucose	45.4
80.0 mM Glucose	38.8
4.0 mM meso-tartrate	24.0
4.0 mM tartrate	27.5
4.0 mM L-(−) mannose	42.2
4.0 mM L-mannonate	27.4

An investigation by Taylor et al. (2010), which focused on developing an improved agricultural-based deicer by using agricultural by-products in deicer formulations, determined that the most effective deicer formulation consisted of 80% glycerol and 20% NaCl. The NCHRP 577 report provides an evaluation of snow and ice control materials and classifies deicing materials

according to Table A-16. The organic material is considered deicers made from agricultural by-products.

Table A-17 shows the general properties of common chloride salts used as deicers, whereas Table A-18 shows the general properties of organic-based deicers. Recent developments in agricultural-based deicers have been explored, and multiple patents have been produced. Table A-19 summarizes selected patents. Glycerol is abundant and commonly used in agricultural deicer formulations. Glycerol is acquired as a by-product of soap manufacturing, biodiesel processing, or multiple common industrial processes known as transesterification, hydrolysis, or saponification. Multiple tests concluded that the deicer solution of 80% glycerol and 20% NaCl was the most effective (Taylor et al. 2010). This deicer formulation is more cost-effective and less corrosive.

Table A-16: Classification of deicing materials (Taylor et al. 2010).

Material Type	Snow and Ice Control Material	Primary Components
Chloride Salts	Sodium Chloride (NaCl)	Na, Cl
	Calcium Chloride ($CaCl_2$)	Ca, Cl
	Magnesium Chloride ($MgCl_2$)	Mg, Cl
Organic Products	Calcium Magnesium Acetate (CMA)	Ca, Mg, $C_2H_3O_2$
	Potassium Acetate (KAc)	K, $C_2H_3O_2$
	Agricultural By-Products	Complex sugars
	Manufactured Organic Materials	Varies with product (e.g., glycol, methanol)
Nitrogen Products	Urea	Urea, Ammonia
Abrasive	Abrasives	Varies with the source of the material

Table A-17: General properties of chloride salts (Taylor et al. 2010).

Material	Chemical Formula	Forms Used	Eutectic Temperature ºC(ºF) @% Concentration	Approximate Annual usage Tonnes (Tons) North America	Median Cost (USD) per Ton (Survey of Internet contracts)
Sodium Chloride	NaCl	Primarily solid, but increasing use of liquid	-21 (-5.8) @ 23.3%	21,080,000 (22,291,000) (Salt Institute)	$36
Calcium Chloride	$CaCl_2$	Mostly liquid brine, some solid flake	-51 (-60) @ 29.8%	Not available	$120
Magnesium Chloride	$MgCl_2$	Mostly liquid brine, some solid flake	-33 (-28) @ 21.6%	Not available	$195
Blended Chlorides	Varies with product	Solid and Liquid	Varies with product	Not available	$142

Table A-18: General properties of organic products (Taylor et al. 2010).

Material	Chemical Formula	Forms Used	Optimum Eutectic Temperature ºC(ºF)@% Concentration	Median Cost (USD) per Ton (Survey of Internet contracts)

Calcium Magnesium Acetate	CMA	Mostly liquid with some solid	-27.5 (-17.5) @ 32.5%	$1,280
Potassium Acetate	KAc	Liquid only	-60 (-76) @ 49%	Not available
Agro By-products	Not Available	Liquid only	Usually blended with chloride-based products	Blends $108
Other Organic Materials	Glycols Methanol	Liquid only	Varies with product	Not available

Table A-19: Patents for existing deicing agents from agricultural products (Taylor et al. 2010).

Product Name	Reference	US Patent No.
Desugared molasses	Bloomer, 2002	6416684
Monoalkyl esters	Chauhan et al., 2006	7048871
Starch	Gambino et al., 1998	5849356
Processed agricultural by-product	Hartley et al., 2007	7208101
Corn wet-milling by-products	Janke et al., 1999a	5965058
Cheese brewing by-products	Janke et al., 1999b	5919394
Beer brewing by-products	Johnson et al., 1999	5922240
Urea	Kerti et al., 2001	6319422
Particulate plant material	Koefod, 2000	6156227
Monohydric and polyhedric alcohols	Lockyer et al., 1998	5772912
Alkalinically reduced sugars	Montgomery et al., 2003	6605232
Succinate salts	Berglund et al., 2001	6287480
Alkali metal acetate	Dietl et al., 2005	6955770
Calcium chloride and urea	Ossian et al., 1997	5683619
Non-chloride based liquid deicer	Seo, 2007	7276179
GEOMELT®	Road Solutions, Inc., 2007	-
Magic Minus Zero™ and Magic Salt™	MagicSalt.info, 2007	-
Icenator Liquid Deicer	eHealth Solutions, 2005	-
Bare Ground Solution	Bare Ground Systems, 2003	-
Caliber M1000	Glacial Technologies, 2008	-

New research and development are focused on improving commercial agricultural deicer formulations. Many existing commercial products are meant to improve deicing performance, lower costs, lower environmental impact, and reduce corrosiveness. The most common commercially available deicers made from agricultural by-products include GEOMELT®, Magic Minus Zero™ and Magic Salt™, Icenator, Bare Ground, and Caliber M1000. GEOMELT® is a

deicing fluid made from a sugar beet source that passes Pacific Northwest Snowfighters specifications. Magic Minus Zero™ is a noncorrosive, effective anti-icer made from a combination of magnesium chloride and a distilling process by-product. Magic Salt™, rock salt treated with liquid Magic Minus Zero™, is also considered an effective ice-melting product. Icenator is a noncorrosive liquid deicer made from by-products of corn processing that increases the surface friction of asphalt when dry. Bare Ground is a similar corn-based liquid deicer/anti-icer combined with magnesium chloride. Additionally, Caliber M1000, a noncorrosive deicer/anti-icer, contains a mixture of 30% magnesium chloride and an agricultural product derived from corn, which improves the eutectic point and anti-icing properties. Caliber M1000 is noncorrosive, effectively penetrates snow and ice, and prevents bonding at the road surface (Taylor et al. 2010).

3.   Additives for Corrosion Inhibition

Corrosion researchers are concentrating on various preventative strategies in order to mitigate the harmful effects of corrosion. Recently, the focus encompasses the use and creation of effective, nontoxic inhibitors. Corrosion inhibitors, as defined by the International Organization for Standardization (ISO), are "compounds that when present in a corrosive system at a sufficient concentration, decrease the corrosion rate of metals without significantly changing the concentration of any of the corrosive reagents." Corrosion inhibitors cause changes in the state of the protected metal surface through adsorption or formation of compounds with metal cations. This results in a reduction of the active surface area of the metal and a change in the activation energy of the corrosion process. The adsorption and formation of protective layers on metals is greatly dependent on the ability of both the inhibitor and metal surface to form chemical bonds and the charges of the surface and inhibitor (Kuznetsov 2002).

Currently, chromate inhibitors demonstrate the highest corrosion inhibitor performance, but are toxic and harmful to the environment. The focus of recent research is on creating non-toxic oxyanions for use as corrosion inhibitors. Some of these compounds include molybdate, organic thioglycolates, and phosphonates, while some inorganic compounds include phophates, borates, silicates, and surfactants. As environmental concern increases and green alternatives become more prevalent, the utilization of renewable agricultural by-products as corrosion inhibitors will offer many advantages. An investigation performed by Kharshan et al. (2012) demonstrated the potential of using corn-derived by-products produced from ethanol production as effective corrosion inhibitors. Other possibilities for inhibitors include rare earth metal salts (El-Meligi 2010). Inhibitors are incorporated into coating systems, in which the coating contains a physical barrier layer and a conversion layer with an inhibitor that chemically impede the corrosion process and play a key role in corrosion protection. Current research on the applications and effectiveness of proposed corrosion inhibitor compounds is reviewed to identify nontoxic, cost-efficient corrosion inhibitors.

Organic compounds are commonly used as corrosion inhibitors. Previous research has determined that surface adsorption occurs when quaternary amines are used as corrosion inhibitors, which prevent aggressive anions to adhere to the metal surface. The ability of N-coco-amine-2-proprionic acid ($C_{14}H_{29}N(C_2H_4COOH)_2$) to inhibit the corrosion of mild steel exposed to 5% NaCl at pH 6.5 was tested. N-coco-amine-2-proprionic acid is a tertiary amine with two carboxylic acid groups. The inhibitor at a concentration of 10 ppm was tested on samples that

had been pre-corroded. The 10 ppm inhibitor concentration was the most effective. It was determined that the more significant the corrosion before application of the inhibitor, the lower the inhibition efficiencies. The inhibitor provided inhibition efficiencies above 90% depending on the amount of pre-corrosion; that value dropped after an hour of exposure. The protection is the result of oxygen ions being adsorbed to the anodic sites of the substrate surface, preventing Fe^{2+} from diffusing away from the surface. Some pitting corrosion occurred, likely due to incomplete coverage of anodic sites with inhibitor (Malik 1999). An additional study focusing on the corrosion inhibition of tertiary and quaternary amines on mild steel was conducted. A tertiary amine with two carboxylic acid groups ($C_{14}H_{29}N(C_2H_4COOH)_2$), a tertiary amine with one carboxylic acid group (($C_{14}H_{29})N(CH_3)(C_2H_4COOH)$), a quaternary amine ($[CH_3(CH_2)_{15}](CH_3)_3N^+Br^-$), and another quaternary amine ($C_{14}H_{29}N^+(C_2H_6)(C_6H_5)Cl^-$) were all tested. The tertiary amines acted as anodic inhibitors. At a pH of 6.5 the surface of the metal substrate was mainly positively charged, causing the tertiary inhibitors to be more effective than the quaternary due to their negatively charged constituents (COO^-). However, the quaternary inhibitors were found to be more effective than the tertiary inhibitors at low pH values due to an abundance of positive charges on the substrate surface (Malik 2001).

Further investigation on the use of organic compounds as corrosion inhibitors was performed. Five compounds were studied on steel exposed to 2.5% NaCl and 3.5% NaCl solution, namely 3-amino-1,2,4-triazole (3-ATA), 2-amino-1,3,4-thiadiazole (2-ADTA), 5-*p*-tolyl)-1,3,4-triazole (TTA), 3-amino-5-methylmercapto-1,2,4-triazole (3-AMTA), and 2-aminobenzimidazole (2-ABA). It was found that 2-ABA provided the best inhibition, with an inhibition efficiency of 88% in the 2.5% NaCl solution and 94% in the 3.5% solution. The diazole and triazole derivatives overall were found to be mediocre at inhibiting corrosion. The inhibition was found to be related to the shape of the compound, with planar molecules providing better protection (Sahin et al. 2002).

Potassium acetate exhibits low corrosion rates toward aluminum alloys, magnesium alloys, titanium alloys, and mild steel, which contribute to its popularity as a runway deicer. However, it is considered very corrosive toward zinc and galvanized steel. A deicing fluid formulation is proposed to minimize corrosion to galvanized steel and improve carboxylate salt deicers. Research has shown that supplementing potassium acetate with a corrosion inhibitor of soluble silicate salts results in a drastically reduced corrosion rate for galvanized steel. Silicate salts have low solubility in solutions with pH values lower than 12.5, which is an unacceptable value for deicing fluids. The solubility of a silicate salt is increased with the addition of sodium gluconate. Immersion testing of galvanized steel in potassium acetate solutions revealed weight loss measurements of 55.5 mils per year for a solution of only potassium acetate and 0.6 mils per year for potassium acetate supplemented with sodium gluconate. The addition of the corrosion inhibitors sodium gluconate and sodium metasilicate effectively decreased the corrosion rate (Koefod 2010b). Furthermore, immersion corrosion tests of aluminum and carbon steel revealed successful corrosion inhibition with the use of 98% sodium formate and 2% sodium metasilicate (Gurkaynak et al. 2004).

Although organic compounds have shown good general corrosion inhibition properties, research into the possibility of developing organic inhibitors for pitting corrosion is being explored. Wei et al. (2003) focused on the inhibition of pitting on stainless steel by N-lauroylsarcosine sodium salt (NLS). The 304 stainless steel was exposed to 0.1 M NaCl solution with a neutral pH. It was

found that the concentration of NLS played a very large role in inhibition efficiency. The concentration of 30 mM was found to provide total inhibition. The inhibition mechanism is the result of adsorption of the NLS to the metal substrate with significant density. The stainless steel surface is negative in the presence of chloride ions at neutral pH, and the adsorption of NLS only enhances the negative characteristic. It is believed that inhibition is the result of the NLS layer causing a blocking effect due to its negative charge (Wei et al. 2003).

The corrosion inhibition of phosphonocarboxylic acid salts (PCAS) and fatty amines (FA) to carbon steel exposed to 200 mg/L NaCl solution was explored. The association of FA with PCAS resulted in mixed inhibition. The FA inhibited both the anodic and cathodic corrosion reactions, and the PCAS inhibited the anodic reaction. When used by itself, FA provided high inhibition efficiencies at much lower concentrations than the concentrations required for PCAS to reach the same inhibition efficiencies. Adding FA to solutions containing low concentrations of PCAS in solution was also found to be effective. The most effective mixture, however, consisted of 200 mg/L PCAS and 50 mg/L FA that resulted in cooperative adsorption of the compounds to the substrate surface. This combination of inhibitors is biodegradable and non-toxic, which may contribute to potential widespread use (Ochoa et al. 2002).

Previous research on the inhibiting effect of compounds that decrease corrosion rates by forming deposits on the surface of aluminum alloys gave rise to the investigation of similar corrosion inhibiting properties of salicylaldoxime, 8-hydroxyquinoline, and quinaldic acid. Aluminum alloys have a favorable strength-to-weight ratio, making them a very widely used material in the aerospace industry. However, the separation of the intermetallic particles causes these alloys to become susceptible to localized corrosion. The presence of the inhibitors caused the formation of a thin adsorptive protective layer on the surface of the alloy. This layer prevents both the dissolution of Mg, Al, and Cu from the active intermetallic sites and the adsorption of chloride ions onto the surface, as shown in Figure A-17. This research provides consistent evidence that organic compounds capable of forming insoluble complexes within intermetallic zones have the potential to create an enhanced inhibiting response. These organic inhibitors are believed to be as effective as mercaptobenzothiazole, Ce, and La salts. Visual observation shows low corrosion attack on the surface of the samples immersed in an electrolyte solution with 0.05g/L organic inhibitors (Lamaka et al. 2007).
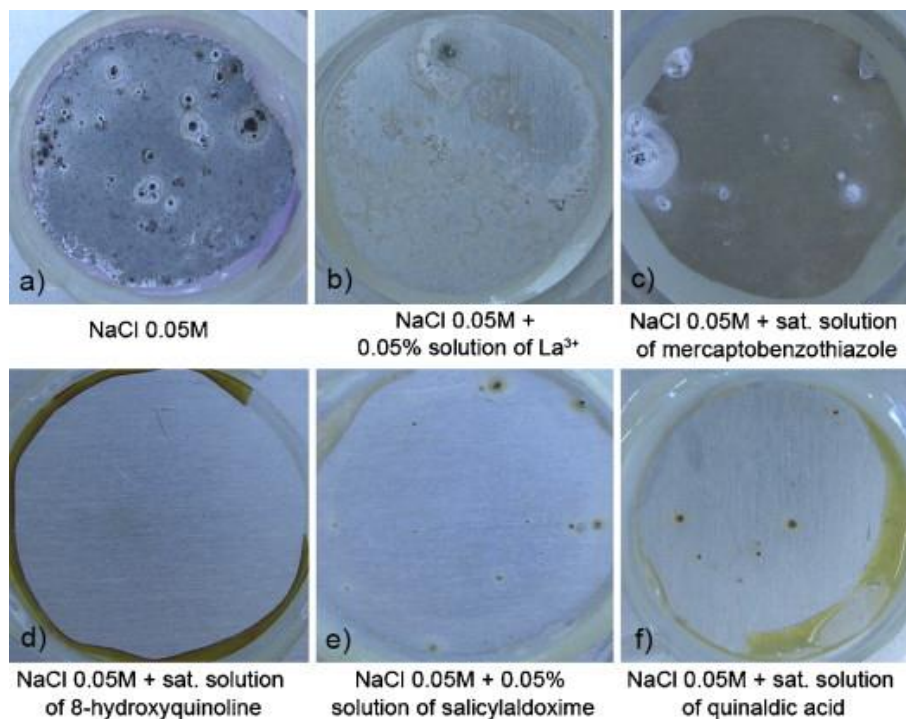
Figure A-17: Photos of the AA2024 samples immersed for 2 weeks in 0.05 M NaCl with and without inhibitors (Lamaka et al. 2007).

A new development in corrosion inhibitors is being focused on providing an effective, naturally renewable, environmentally safe additive for use in chloride salt deicer formulations. It was found that using dry ground plant material, such as alfalfa, wheat, grass, linseed, clover, soybeans, cottonseeds, or fruits, as a corrosion inhibitor with sodium chloride reduced the corrosive effects on ferrous metals. Dried and ground alfalfa with a particle size of 1500 to 150 microns and a moisture content of around 12 weight percent was used as a corrosion inhibitor with deicing salts. During corrosion testing, 1010 carbon steel panels were immersed in a solution of 3% by weight sodium chloride blended with 3% by weight of ground alfalfa and another solution of only 3% by weight sodium chloride solution. Each week the old solutions were replaced with new solution of the same composition. After one month, the test panels were removed and cleaned with hot water, concentrated hydrochloric acid, and Rodine 213. The corrosion rate of the panel immersed in the salt/alfalfa mixture was found to be 7.3 mils per year, and the panel immersed in the sodium chloride solution had an average corrosion rate of 18.0 mils per year. Ice-melting tests revealed that a mixture of sodium chloride rock salt with 3% ground alfalfa and 1.75% magnesium chloride solution with 30% magnesium chloride by weight yielded 13.2 milliliters of melt after 60 minutes at 15°F, whereas just rock salt yielded 13.8 milliliters (Koefod 2000).

Research has shown potential successful inhibitors for the corrosion protection of steel. Inhibitors that are used to protect carbon steel from corrosion were tested in atmospheric corrosion exposure testing consisting of 2 wt.% NaCl and 1 wt.% Na_2SO_4. The best performing inhibitors were sodium dihydrogen orthophosphate, sodium benzoate, sodium nitrite, and sodium nitrate as the corrosion rate was decreased. Application of 10 or 100 mM for a day of sodium dihydrogen orthophosphate gave the best protection, sodium benzoate (10, 100, or 1000 mM

treatments) and sodium nitrite (100 or 1000 mM treatments) performed similarly, closely followed by sodium nitrate (Kahraman et al. 2002). A follow-up study on the inhibition provided by sodium dihydrogen orthophosphate exposed to 2 wt.% NaCl determined that the application of 10 mM solution for one day reduced the corrosion rate to 0.06 mmpy on the treated carbon steel samples compared with the 0.135 mmpy corrosion rate of untreated samples. In atmospheric exposure, it was found that weight loss measurements after 15 days resulted in 0.096 mmpy for untreated and 0.04 mmpy for treated. The difference became greater after 6 months, where weight loss measurements found were 0.1 mmpy for untreated and 0.032 mmpy for treated, which exhibits significant inhibition performance (Al-Mathami et al. 2004).

A similar study further evaluated the corrosion inhibition provided by sodium dihydrogen orthophosphate, dicyclohexylamine nitrite, and sodium benzoate on carbon steel exposed to wet/dry cycling and immersion testing. The wet/dry cycling test exhibited that 10 mM sodium dihydrogen orthophosphate provided the greatest inhibition effectiveness with a corrosion rate of 431.8 µm/y, followed by 100 mM dicyclohexylamine nitrite with a corrosion rate of 812.8 µm/y, then 100 mM sodium benzoate with a corrosion rate of 965.2 µm/y. Lastly the untreated sample exhibited the corrosion rate of 1524 µm/y. Overall the 10 mM sodium dihydrogen orthophosphate reduced the corrosion rate by 70% (shown in Table A-20). Contradictory to the previous results, when the same inhibitors and concentrations were used in immersion exposure, dicyclohexylamine nitrite and sodium benzoate outperformed dihydrogen orthophosphate (shown in Table A-21). However, the higher corrosion rates obtained with the cyclic testing were found to better match corrosion rates found in field testing (Saricimen 2009).

Table A-20: Inhibitor efficiency under wet/dry cycling conditions (Saricimen 2009).

W/D cycle	100 mM SOB Effectiveness (%)	100 mM DICHAN Effectiveness (%)	10 mM SODHOP Effectiveness (%)
0	33.8	33.8	66.2
1	41.0	41.0	70.5
10	62.0	71.7	84.1
20	42.7	35.3	68.3
30	52.3	51.2	65.9
60	31.7	49.1	74.6

Notes: W/D, wet/dry; control, untreated; SOB, sodium benzoate; DICHAN, dicyclohexylamine nitrite; SODHOP, sodium dihydrogen orthophosphate; effectiveness (%) = [CR(C), CR(IT)] × 100/CR(C); CR, corrosion rate; C, control; IT, inhibitor treated

Table A-21: Inhibitor efficiency under continuous immersion conditions (Saricimen 2009).

Days	100 mM SOB Effectiveness (%)	100 mM DICHAN Effectiveness (%)	10 mM SODHOP Effectiveness (%)
0	42.5	42.5	*63.0*
1	28.5	43.9	30.8
10	*55.2*	*64.1*	33.6
20	38.7	38.7	24.5
30	46.8	40.4	18.0

Notes: W/D, wet/dry; control, untreated; SOB, sodium benzoate; DICHAN, dicyclohexylamine nitrite; SODHOP, sodium dihydrogen orthophosphate; effectiveness (%) = [CR(C), CR(IT)] × 100/CR(C); CR, corrosion rate; C, Control; IT, inhibitor treated

Proposed phosphonic acid corrosion inhibitors were investigated in a study that tested the corrosion inhibition ability of a 2-carboxyethyl phosphonic acid (2-CEPA) – Zn^{2+} system and an ethyl phosphonic acid (EPA) – Zn^{2+} system on steel exposed to 60 ppm Cl^- at neutral pH. The 2-CEPA – Zn^{2+} provided better inhibition, reaching an inhibition efficiency of 98% at 200 ppm, compared with an inhibition efficiency of 58% provided by EPA at 200 ppm. The increased inhibition provided by the 2-CEPA system was attributed to a greater concentration of the Fe^{2+} - CEPA complex on the metal substrate surface than the concentration of Fe^{2+} - EPA complex of the EPA system. The protective films composed of Fe^{2+} - CEPA and Fe^{2+} - EPA complexes respectively were found to dissolve over time resulting in decreased ability to inhibit corrosion. It was found that the systems inhibited both the anodic and cathodic corrosion reactions (Rajendran et al. 2000). In another study, the system composed of ethyl phosphonate (EPA) and Zn^{2+} exposed to 60 ppm Cl^- was found to perform better with concentrations of 300 ppm EPA and 300 ppm Zn^{2+}, reaching an inhibition efficiency of 88% and corrosion rate of 1.87 mdd. The greater concentration may be attributed to a greater concentration of $Zn(OH)_2$ in addition to the Fe^{2+}-EPA and iron oxides (Rajendran et al. 1998a). An additional study focused on the corrosion inhibition of mild steel exposed to an aqueous solution with a concentration of 60 ppm Cl^- provided by amino (trimethylene phosphonic acid) (ATMP), molybdate, and Zn^{2+}. Testing of the three inhibitors found that none by itself provided much inhibition (Zn^{2+} actually accelerated corrosion), nor did any combinations of two except for Zn^{2+} and molybdate, which reached an inhibition efficiency of 90%. Combining all three was found to provide the best inhibition, with an optimal mixture concentration of 50 ppm ATMP, 50 ppm Zn^{2+}, and 300 ppm molybdate. The aforementioned mixture was able to provide 96% inhibition efficiency and limit the corrosion rate to 0.62 mdd due to the formation of a protective film composed of $ZnMoO_4$, Fe^{2+}-ATMP, $Fe_2(MoO_4)_3$, and $Zn(OH)_2$ (Rajendran et al. 1998b).

A synergistic approach to corrosion inhibition of carbon steel was investigated by the use of tertiary butyl phosphonate (TBP), zinc ions, and citrate. The ternary formulation of Zn^{2+}/TBP/Citrate formed a protective film composed of $Zn(OH)_2$ and Fe^{2+}/Fe^{3+}-TBP-citrate

compounds, reducing the corrosion rate of carbon steel mainly by influencing the cathodic reaction. The ternary formulation works synergistically and was found to be effective in conditions with low chloride concentrations at near neutral pH values (pH=5-8). Binary systems containing only Zn^{2+} and TBP were found to be much less effective than the ternary system. The optimal ternary mixture consisting of 50 ppm Zn^{2+}, 75 ppm TBP, and 150 ppm citrate was able to reach an inhibition efficiency of 96% (Narmada et al. 2006).

Furthermore, an additional study examined the inhibition of calcium gluconate and sodium molybdate on carbon steel; both inhibitors are non-toxic and inexpensive. When calcium gluconate is used alone, it often suffers from dissolution of gluconate from the substrate surface. The combination of calcium gluconate and sodium molybdate prevents the previously mentioned dissolution, which is determined to synergistically provide corrosion inhibition. It was also found that increasing the concentration of one of the inhibitors allowed for a reduction in the other without any negative effects. For example, the combination of 150 ppm sodium molybdate and 50 ppm calcium gluconate demonstrated an inhibition efficiency of 96.9%. Another combination of 50 ppm sodium molybdate and 150 ppm calcium gluconate exhibited an inhibition efficiency of 96.8%, and lastly a mixture of 200 ppm sodium molybdate and 200 ppm calcium gluconate provided an inhibition efficiency of 97%. This suggests that a high concentration of just one of the inhibitors is critical for high corrosion inhibition performance (Shibli and Kumary 2004).

4.   Additives for Enhancing Ice-Melting Capacity or Salt Solubility

In an attempt to improve ice-melting performance and decrease corrosiveness, Koefod (2008) developed a deicer mixture containing a salt such as sodium chloride and a radiation absorber, which is an agent that absorbs radiation and converts it to heat. Radiation absorbers are chemicals, having high molar absorptivity, capable of absorbing high amounts of solar radiation and converting it to heat by displaying high quantum yields. This particular deicer mixture is composed of concentrations by weight of 90–99% sodium chloride, up to 5% magnesium chloride, up to 1000 ppm triethanolamine, and up to 1000 ppm of Napthol Green B, radiation absorber (Koefod 2008).

5.   Other Additives for Snow and Ice Control Chemicals

Deicer compositions contain a freezing point depressant and often various additives to enhance chemical properties and performance. Additives can have a significant impact on the overall effectiveness of snow and ice control products. Additives are incorporated into deicer formulations for specific functionality, for example, as corrosion inhibitors. Additives are most commonly present in snow and ice control chemicals in low concentrations. Common additives include thickeners, surfactants, antioxidants, stabilizers, fire inhibitors, and pH buffers. Each additive is used for a certain property. Surfactants, which are compounds that lower the surface tension of a liquid, are generally used as wetting agents to increase product coverage and decrease adhesion of ice on surfaces. A list of reported surfactants is shown in Table A-22 (ACRP 2008).

Table A-22: Surfactants used in snow and ice control compounds (adapted from ACRP 2008).

Chemical Compound	Reference
Aliphatic alcohol ethoxylates	Ashwari and Coffey, 1993
Brij 35 (polyoxyethylene dodecyl ether)	Simmons et al., 2007
Alkyl glycosides	Simmons et al., 2007
Decyl alcohol ethoxylate	Corsi et al., 2003
Emerest 2660 (PEG-12 oleate)	Westmark et al., 2001
Emsorb 6900 (PEG-20 sorbitan oleate)	Westmark et al., 2001
Ethylene oxide / propylene oxide block copolymers	Ashwari and Coffey, 1993; Nieh, 1992
Lauryl Alcohol Ethoxylate	Corsi et al., 2003
Lauryl alcohol phosphoric acid-ester Ethoxylate	Corsi et al., 2003
Nonyl phenol ethoxylate	Nieh, 1992
Octyl phenol ethoxylate	Nieh, 1992
Oleic acid diamine	Bloom, 1986
Oleyl propylene diamine	Bloom, 1986
Palmitic acid diamine	Bloom, 1986
Siponate A-2466, sodium dodecylbenzene sulfonate	Boluk et al., 1999
Siponate DDB-40, sodium dodecylbenzene sulfonate	Boluk et al., 1999
Siponate DS, sodium dodecylbenzene sulfonate	Boluk et al., 1999
Sodium alkylbenzenesulfonate	Konig-Lumer et al., 1982
Surfonic N-40, 4-mole nonylphenol ethoxyate	Ashrawi and Coffey, 1993; Coffey et al.,1995
Surfonic N-60, 6-mole nonylphenol ethoxylate	Ashwari and Coffey, 1993; Coffey et al.,1995
Surfonic N-95, 9.5 mole nonylphenol ethoxylate	Nieh, 1992
Tergitol TMN-10, branched secondary alcohol ethoxylate	Boluk et al., 1999

Antioxidants are used to prevent chemical or physical degradation and are often present in low concentrations. Antioxidants inhibit the oxidation of compounds within snow and ice control compounds. Simmons et al. incorporates potassium sorbate, sodium azide, 2-methyl-4,5-trimethylene-4-isothiazoline-3-one, or sodium sorbate as antioxidants into various deicer formulations (ACRP 2008).

Thickeners are used to increase the viscosity of snow and ice control chemicals, which increases holdover time and decreases rates of runoff. Thickeners are usually polymers containing carboxylate salts that become dissociated, creating net negative charges that repel one another, effectively uncoiling the polymer. This effect causes entanglement of polymer strands, which thickens the mixture. Thickener efficiency is affected by water and salt concentration. High salt content or low water content will cause an increase in polymer chain unfolding (Dow). A list of common thickeners is shown in Table A-23.

Table A-23: Common thickeners used in snow and ice control compounds (adapted from ACRP 2008).

Chemical Compound	Reference
polyacrylic acid	Ashwari and Coffey, 1993; Nieh, 1992
Carboxymethylcellulose	Ma and Comeau, 1990
Hydroxyethylcellulose	Ma and Comeau, 1990
Iota-carrageenan	Tye et al., 1987
Kappa-carrageenan	Tye et al., 1987
Polyvinylpyrrolidone	Simmons et al., 2007
Welan gum	Westmark et al., 2001
Xanthan gum	Lockyerm et al., 1998; Ma and Comeau, 1990; Westmark et al.,2001

Snow and ice control compounds are usually required to have a near neutral pH with values of approximately 7 to 11 to prevent any harmful effects. Simple compounds such as sodium hydroxide, potassium hydroxide, or ethanol amines are used as pH buffers and can be added to deicers to ensure that neutral pH is achieved. Various pH buffers are listed in Table A-24 (ACRP 2008).

Table A-24: Various pH buffers found in snow and ice control compounds (adapted from ACRP 2008).

Chemical Compound	Reference
Diethanolamine	Boluk et al., 1999
Dipotassium phosphate	Hu et al., 1998
Disodium phosphate	Nieh, 1992
Monoethanolamine	Boluk et al., 1999
Potassium hydroxide	Boluk et al., 1999; Hu et al., 1998; Konig-Lumer et al., 1982
Sodium dihydrogenphosphate	Simmons et al., 2007
Sodium hydrogenphosphate	Simmons et al., 2007
Sodium hydroxide	Ashwari and Coffey, 1993; Boluk et al., 1999; Hu et al., 1998
Triethanolamine	Boluk et al., 1999

Furthermore, anti-spalling additives are sometimes used to prevent harmful spalling effects of sodium chloride on concrete. Commonly used anti-spalling additives include gelling agents, which attract moisture and expand, creating a seal within the concrete pores. This provides a barrier within the concrete, preventing exposure to moisture and brine. Kuhajek and Waatti (1992) proposed the use of hydroxyethyl cellulose as an effective anti-spalling additive in a concentration of around 5% by weight.

Agricultural additives used in snow and ice control materials are mostly composed of reduced organic biomass developed from various agricultural sources such as corn, rice, wheat, or beets. Although these additives are frequently supplemented with chloride-based products, non-chloride-based products have been shown to possess desired characteristics such as overall performance and corrosion inhibition (Levelton Consultants 2007).

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