MANAGING THE ENVIRONMENTAL IMPACTS OF CHEMICALS USED FOR SNOW AND ICE CONTROL

by

Scott Patrick Jungwirth

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ABSTRACT

Departments of Transportation (DOTs) and other winter maintenance agencies are continually challenged to provide safe, reliable winter highways in a cost-effective and eco-friendly manner, while minimizing adverse effects to the environment, vehicles, and transportation infrastructure. Increasing 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) have directed agencies to explore alternatives. The objective of this project is to provide winter maintenance agencies various strategies to effectively reduce the environmental impacts related to winter maintenance operations by presenting strategies focused on alternative deicer compounds, mitigation measures, and management procedures. A series of anti-icers designed to reduce the environmental footprint of deicers and to meet the varying requirements of highway anti-icing performance, cost-effectiveness, and minimized corrosion impacts was developed. The research was accomplished through literature review, agency surveys, and laboratory investigation. A review of various new developments and available products is presented in order to identify the current state of the art and gain a better understanding of commercially available snow and ice control materials. Performance evaluations are presented with respect to ice melting capacity, corrosion effects, and impacts to the environment of various deicers to determine trends and future research needs. In addition, it was identified that roadway maintenance equipment in cold climates is exposed to high amounts of chloride-based deicers that are inherently corrosive. This work aims to identify current approaches available to manage the risk of deicer corrosion to equipment assets, including design considerations, materials selection, and maintenance strategies. Furthermore, this research summarizes the current practices and methods available to mitigate the water quality risks associated with chloride based deicers. Two common approaches used for reducing the impacts of chloride based deicers were examined. The first method known as a proactive approach focuses on reducing the amount of chloride based deicers introduced into the environment. The second method known as a reactive approach consists of effective practices used to reduce the impacts of chloride based deicers after they have been introduced into the environment, which is accomplished using treatment methods and controlling chloride transport through the environment.

1. INTRODUCTION

Statement of the Problem

Significant environmental impacts related to soil and water quality degradation and corrosion and infrastructure impacts are caused by the continued use of traditional deicing chemicals. Many challenges are presented to winter highway maintenance agencies in terms of reducing environmental impacts and the detrimental effects to vehicles and transportation infrastructure, while effectively maintaining roadways and improving safety. In the US, a total of approximately 20 million tons of salt is applied onto roadways, which has significantly increased exposure and accumulation in the environment (Bester et al., 2006). In certain regions such as the state of Minnesota, as high as nine tons of road salt is typically applied per lane mile in one winter season (Ye et al., 2009). Chloride salts including sodium chloride (NaCl), magnesium chloride ($MgCl_2$), and calcium chloride ($CaCl_2$) are the most commonly used snow and ice control materials due to abundance and low cost. Chloride salts readily dissolve in water and do not undergo degradation; therefore they are extremely mobile and accumulate in the environment over time, increasing the environmental risk (Fay et al., 2014). Chloride deicers migrate from road surfaces and cause negative effects on water, soil, vegetation and aquatic species (Fay et al., 2014). High chloride concentrations above the Environmental Protection Agency (EPA) standard have been observed in groundwater and surface water throughout the US as a result of winter maintenance operations (Fay et al., 2014). It has been determined that 10% to 60% of applied chloride salts enter the subsurface and accumulate in the groundwater (Environment Canada, 2010). Therefore, there is a need to explore possible strategies to ultimately reduce the risk to the environment associated with winter maintenance operations. Figure 1 depicts the various environmental impacts of roadway deicer.

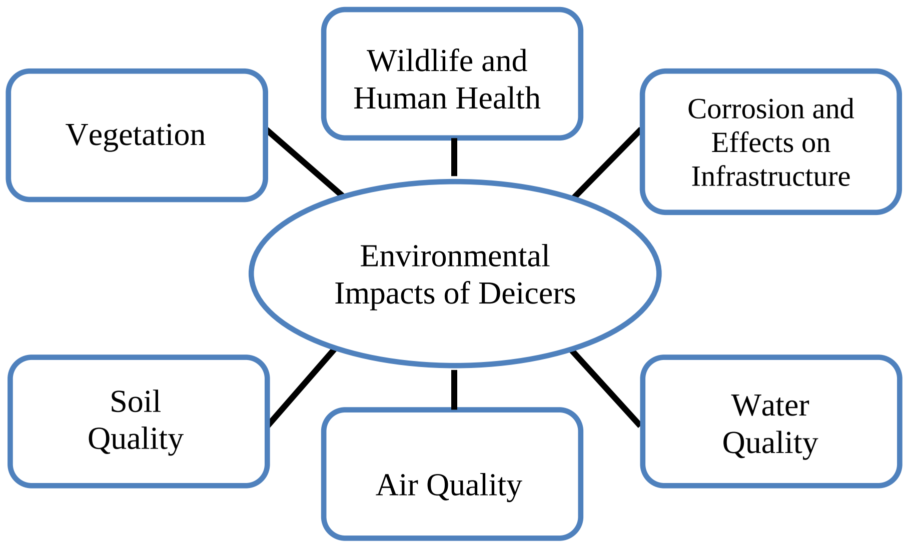

Figure 1: Environmental impacts of deicers.

This crosscutting issue also has significant economic implications. It has been reported that winter maintenance operations in the U.S. costs approximately $2.3 billion dollars annually and the costs associated to corrosion and environmental impacts adds at least $5 billion (FHWA 2005).

Research Objectives

The objective of this project is to provide winter maintenance agencies with various strategies to effectively reduce the environmental impacts related to winter roadway maintenance operations. Methods focused on alternative deicer compounds, mitigation measures, and management procedures are presented. Specifically, this research consists of multiple phases in an effort to improve the knowledge of the environmental impacts of roadway deicers and provide alternative mitigation solutions through reactive strategies and proactive techniques to ultimately reduce environmental and corrosion impacts of deicers.

The first phase consists of a review of chemicals used for snow and ice control with a subsequent laboratory evaluation of selected commercially available products used for snow and ice control to identify research needs and potential development opportunities. This approach consists of reducing the risk to the environment by reducing the salt usage, which is achieved by utilizing more environmentally friendly alternative deicers that are currently available or developing more effective snow and ice control materials through waste utilization. The development of alternative deicer compounds will successfully recycle a waste product to produce a more effective deicer compound, thus reducing the amount of salt applied to highways. An environmental life-cycle assessment as described by Michael Fitch et al. (2012), which involves determining five distinct environment impacts of deicers based on energy use, greenhouse gas emissions, water use, chloride emissions, and biochemical oxygen demand determined that salt brine is the best option for winter maintenance agencies to reduce environmental impacts.

Therefore, the utilization of a waste stream would provide favorable results with respect to environmental life-cycle assessment, since a waste compound is recycled and used in a brine solution. 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.

In addition to the environmental risks of deicers on soil and water, chloride deicers pose a significant risk to maintenance equipment and roadway infrastructure. Equipment exposure to chloride deicers causes significant corrosion over time and early deterioration can negatively affect performance, reliability and the service life of maintenance equipment. Therefore, various mechanisms of corrosion and strategies to reduce the detrimental effects and associated costs of chloride deicers to winter maintenance equipment are explored. Protecting maintenance equipment against the effects of corrosion will have positive effects on the environment by extending the service life of equipment fleets and reducing maintenance costs and energy consumption and environmental contaminants associated with metallic corrosion.

Lastly, specific strategies aimed at reducing the environmental impacts of chloride roadway deicers and alternative methods to remove chlorides from the environment are presented. Source control and the effective chloride management applications of various techniques including the use of stormwater best management practices can reduce the impacts of roadway deicers on the environment Figure 2 depicts an overview of the focus of this research and the respective chapters discussing specific aspects.

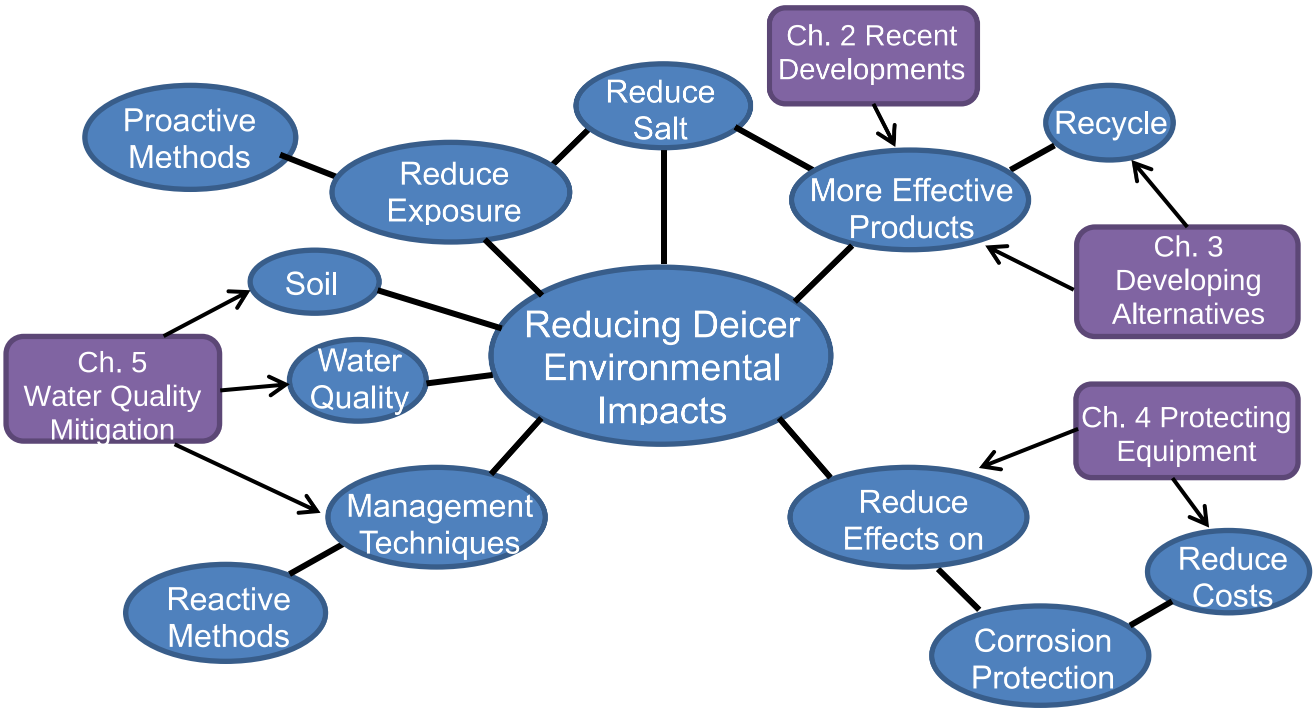

Figure 2: Overview of thesis objectives.

<u>Structure of the Thesis</u>

The structure of this thesis is presented as follows. Chapter one introduces the problem and the research objectives. Chapter two consists of a review of recent developments and knowledge related to chemicals used for snow and ice control and provides some background information. Chapter three includes the laboratory methodology and evaluation and analysis of commercially available liquid deicers along with the information on the development of locally sourced salt brine additives. Chapter four discusses corrosion mechanisms and strategies to protect winter maintenance equipment against chloride deicers in an effort to reduce costs and increase service life. Chapter five discusses various mitigation strategies to reduce the environmental impacts of chloride deicers through proactive and reactive approaches. Chapter six provides a summary of the key findings and overall knowledge gaps.

CHAPTER TWO

2. CHEMICALS USED FOR SNOW AND ICE CONTROL: STATE OF THE ART

Contribution of Authors and Co-Authors

Manuscript in Chapter 2

Author: Scott Jungwirth

Contributions: Collected and analyzed data and existing literature. Wrote draft of manuscript.

Co-Author: Dr. Xianming Shi

Contributions: Provided guidance and feedback on first drafts of manuscript.

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Introduction

Although chloride based deicers are the most common snow and ice control products, organic compounds derived from agricultural by-products are increasing in popularity. Many new and emerging products for snow and ice control are becoming commercially available. A review of various new developments and available products is presented in order to identify the current state of the art and gain a better understanding of commercially available snow and ice control materials. Performance evaluations are presented with respect to ice melting capacity, corrosion effects, and impacts to the environment of various deicers to determine trends and future research needs.

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 a 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 to be harmful to the environment due to contributions to eutrophication. Chloride based products are the most commonly used deicers, however, organic products such as potassium acetate, calcium magnesium acetate, and products derived from agricultural processes are becoming more popular for snow and ice control. The purpose of this review is to present the current knowledge of chloride based deicers and organic deicers to gain a better understanding and identify knowledge gaps within the literature. In addition, this work aims to identify new and emerging products and technologies used for snow and ice control and make some comparisons to the more traditional deicer products. Figure 3 shows an outline of the research approach.

Figure 3: Outline showing research approach.

Currently Available Liquid Deicers

The most common chemicals used for snow and ice control are sodium chloride (NaCl), magnesium chloride, ($MgCl_2$), calcium chloride ($CaCl_2$), calcium magnesium acetate (CMA), and potassium acetate (KAc) (Cuelho, 2010). Due to availability and low costs, chloride salts are the most widely used snow and ice control chemical with NaCl being the most prevalent (Fay et al., 2008). It is used in either a solid or liquid form and is effective over a wide range of temperatures (Cuelho, 2010). Application rates for anti-icing range from 20 to 50 gallons per lane mile. However, $MgCl_2$ brines feature higher performance at lower temperatures and research has shown that $CaCl_2$ is more effective than NaCl due to its ability to attract moisture and stay on roadways (Ketcham et al., 1996, Shi et al., 2009a, Warrington, 1998). Since chloride salts are highly corrosive to metals, corrosion inhibitors are usually added to reduce harmful impacts. The primary chemical constituents of various deicers are shown in the Table 1 (Taylor et al., 2010).

Table 1: Classification of Deicing Materials (adapted from 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

Chloride blends such as a mixture of 85% salt brine, 10% De-ice, and 5% $CaCl_2$ have been shown to be a cost effective alternative with good field performance for anti-icing applications or pre-wetting techniques (CTC & Associates, 2011). In addition, Ohio DOT has reported a significant increase in salt residual on roadways when using a blended salt brine with 10-15% agro-based products, which can improve longevity (Ohio DOT, 2011)

In addition to chloride products, organic products such as acetates and agricultural based chemicals are becoming more common with snow and ice control methods. For example, KAc is less corrosive and has a low effective temperature and causes minimal impact on soils and the environment. However, KAc is expensive and significantly damages galvanized steel, concrete and asphalt pavement (Shi, 2008, Shi et al., 2009a.)

New product developments have been focused on using agricultural products for snow and ice control. The addition of agricultural products to winter maintenance chemicals can significantly reduce the freezing point thus increasing effectiveness (Koefod, 2008). Nixon and Williams (2001) have identified the advantages of agricultural products and suggest that these products can be combined with chloride based products to reduce corrosion and increase ice melting performance. Agricultural products have low impacts to the environment and highway infrastructure and have low eutectic and effective temperatures. These products are usually produced through the fermentation and processing of beet juice, corn, molasses, or other agricultural derivatives (Cheng and Guthrie, 1998; Albright, 2003). Hallberg et al. (2007) reported that glucose/fructose and unrefined sugar is mixed with sand to prevent freezing and used in salt brine for anti-icing. Agricultural based additives provide improved ice-melting performance, reduce corrosion effects, and tend to last longer when applied to roadways; however, these additives usually increase costs (Fischel, 2001; Kahl, 2004). Agricultural products are typically mixed with common deicers or anti-icers to reduce costs while improving performance (Nixon and Williams, 2001). When compared to salt brine, a product derived from beet molasses was reported to outperform the salt brine in field tests with a lower application rate (Fu et al., 2012).

Concerns over the widespread use of agricultural based products have delayed winter maintenance agencies from adopting these products. Issues such as toxicity, due to high phosphate, nitrate, or total organic content, to the aquatic ecosystems near roadways, high costs, and quality control concerns present some challenging considerations (Fischel, 2001). Moreover, high levels of phosphorous promote the growth of algae, which reduces the available oxygen for other aquatic biota (Fischel, 2001). Most agricultural based products are composed of chloride salts and low molecular weight carbohydrates made from sugar beets, molasses or corn. The general properties of agricultural based products are summarized in Table 2 (Taylor et al., 2010).

Table 2: General properties of organic products (adapted from Taylor et al., 2010).

Material	**Chemical Formula**	**Forms Used**	**Optimum Eutectic Temperature $^{o}C(^{o}F)@\%$ 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

Emerging Liquid Deicers

As agricultural based products become more widely used, new research and development is focused on improving deicer formulations. Existing products are focused on improving performance, lowering costs and environmental impact, and reducing corrosiveness. The most common commercially available agricultural based liquid deicers are GEOMELT®, Magic Minus Zero™ and Magic Salt™, Icenator™, Bare Ground™, and Caliber M1000™. GEOMELT is made from a derivative of sugar beets and has been approved by the Pacific Northwest Snowfighters as an effective deicer. Magic Minus Zero is a noncorrosive anti-icer composed of a mixture of magnesium chloride and a by-product of a distilling process and Magic Salt, which is an effective deicer, is a rock salt treated with liquid Magic Minus Zero. A noncorrosive liquid deicer made from corn by-products known as Icenator increases the surface friction of asphalt when dry. Similarly, Bare Ground is a corn based liquid deicer/anti-icer combined with magnesium chloride. Caliber M1000 is a similar product composed of 30% magnesium chloride and corn based derivatives. Caliber M1000 has been reported to be noncorrosive, while effectively penetrating snow and ice to prevent bonding at the road surface (Taylor et al., 2010). A product recently developed by Natural Solutions, known as ICEBAN, is prepared from the organic by-products in the processing of alcohol, cheese, or corn.

Furthermore, the anti-icing fluid Ice Bite® has been approved by the Pacific Northwest Snowfighters as an effective anti-icer and is effective at low temperatures (Road Solutions, Inc.). It is made from an all-natural agricultural product and is usually mixed with traditional salt brines to reduce corrosion and improve ice melting at lower temperatures.

Recent developments in agricultural based deicers have been explored and multiple patents have been produced. Table 3 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 by multiple common industrial processes known as trans-esterification, 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 while being less corrosive.

An emerging class of liquid deicers features the unique synergy of complex chlorides and mineral products. For instance, AquaSalina™ is a product consisting of natural brine and corrosion inhibitor. According to the vendor, the product contains 10-11% $CaCl_2$, 7-8% NaCl, 2-3% $MgCl_2$, and 1% KCl. AquaSalina™ is produced from natural resources instead of fresh water, thus preserving valuable water resources and has been recently approved by the Pacific Northwest Snowfighters. AquaSalina™ has been claimed to enhance the performance of rock salt and to feature higher ice melting capacity and colder effective temperatures than salt brine.

Due to increasing environmental concerns and high corrosion costs associated with chemical deicers and anti-icers, recent research and development for snow and ice control chemicals has been focused on producing less corrosive, environmentally friendly snow and ice control chemicals. One common approach to achieve such specific properties has been the implementation of waste products, such as bio-derived components, into snow and ice control chemicals to reduce environmental impacts and costs while minimizing effects of corrosion.

Additives such as Boost® are proprietary formulas based on organics such as sugar or alcohol to suppress the freezing point of salt brine. The use of calcium chloride with Boost® in Michigan has been reported to reduce application rates and decrease the amount of salt applied to roadways by as much as 38%, thus reducing chloride loading to the environment (Michigan DOT). However, these additives can be costly but are necessary in cold climates to produce a solution with a lower melting point (similar to $MgCl_2$). The anti-icers available on the market have increased concerns over their corrosion to metals (chlorides), impact on concrete and asphalt (acetates), and toxicity to aquatic resources (agro-based products). Agencies are continually searching for alternatives that maximize the benefits of acetates and agro-based products while minimizing their drawbacks. 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.

Table 3: Patents for deicing agents made 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 polyhydric 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	-

Recently, bio-derived freezing point depressants have been developed for airport runway applications. For example, glycerol is currently being identified as a potential freezing point depressant. For each gallon of biodiesel produced, approximately 0.35 kg

(0.76 lb) of crude glycerol is also produced and there exists a 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 showed great potential for airport runway applications, they have never been used in commercial anti-icers or deicer applications. For highway applications, a different set of priorities exists 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 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 effects, and other negative impacts need to be assessed. Subsequently, field operational tests need to be conducted to validate their effectiveness at a given application rate under a given road weather scenario.

Laboratory testing has demonstrated that the AMS 1435A certified potassium succinate (KSc) anti-icing liquids for airport runway applications significantly reduce the corrosion of alloys and concrete scaling, relative to potassium acetate (KAc) solution and feature low biological oxygen demand corresponding to a BOD of 0.15 g O_2/g fluid, and outstanding deicing performance compared 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 fermentation-based biotechnology has facilitated significant cost reduction of producing succinate salts. 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 addressing the needs of winter highway operations (Berglund et. al., 2003).

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) proposed a procedure for the practice of utilizing fermentation products to create road deicer products. It was determined that calcium magnesium propionate is equally as effective as calcium magnesium acetate as a freezing point depressant (Mathews 1994). Furthermore, it has been 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 (Klyosov et. al., 2000).

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 displace bonded water and create a hydrophobic surface, which makes it difficult for ice crystal formation. The main component in this deicing fluid is glycerol, which is supplemented with a small amount of a deicing salt. It was demonstrated that this deicing fluid is nontoxic with a median lethal dose (LD_{50}) of 58,000 mg/L for fathead minnow (Samuels et. al., 2006). Glycerol is becoming a popular freezing point depressant in new agro based deicer formulations mostly due to the low cost, low environmental impact, and abundant quantity.

Evaluation of Liquid Deicers

Comprehensive evaluation and analysis of the performance characteristics and negative impacts of deicers provides winter maintenance operations with valuable information such as performance, costs, corrosiveness, impacts to the environment and infrastructure. A three step process for evaluating deicers proposed by Nixon et al., (2007) consists of identifying key characteristics of the deicing chemical, finding the test methods for each characteristic and combining the test results into a composite measure of the effectiveness of a given product. Another method of differentiating between liquid anti-icing chemicals based on performance identified critical properties such as freezing point depression, environmental impacts, corrosion, stability, consistency of viscosity, handling, conductivity and documentation and an overall score is developed and ranked according to specific agency needs (Nixon and Williams, 2001).

Evaluation of liquid deicer performance has been the focus of many research projects in recent years. Shi et al. (2009a) reported laboratory test results aimed at evaluating the performance and impacts of alternative deicers compared with traditional chloride-based deicers.

Many factors are taken into consideration when selecting a chemical for winter road maintenance such as performance characteristics, costs, environmental risks, and application rates required for various road weather scenarios. Typical performance properties consist of ice melting capacity, ice penetration, ice bonding, and thermal properties. The eutectic and effective temperatures of a deicer are the most important indicators to determine performance with respect to penetration power and the ability to undercut and break the bond between the ice and road surface.

The eutectic temperature is the minimum temperature at which a deicer solution can remain in liquid form. Figure 4 shows the eutectic curves for the most commonly used liquid deicers including $MgCl_2$, NaCl, $CaCl_2$, and KAc with solution concentrations (FHWA, 1996). The low point on each curve indicates the eutectic point, which is the lowest freezing point. The eutectic point is the lowest temperature and maximum concentration at which the deicer solution will not freeze. As the temperature approaches the eutectic temperature the melting rate decreases. In the range of 0°F to 32°F (-18°C to 0°C), chemicals with lower eutectic temperatures generally demonstrate faster ice melting rates (FHWA, 1996). Furthermore, the effective temperature is the lowest temperature limit at which the material is effective within 15-20 minutes of application and is the lowest temperature a deicer should be used to achieve effective ice melting (Ohio DOT, 2012; Shi, 2011).

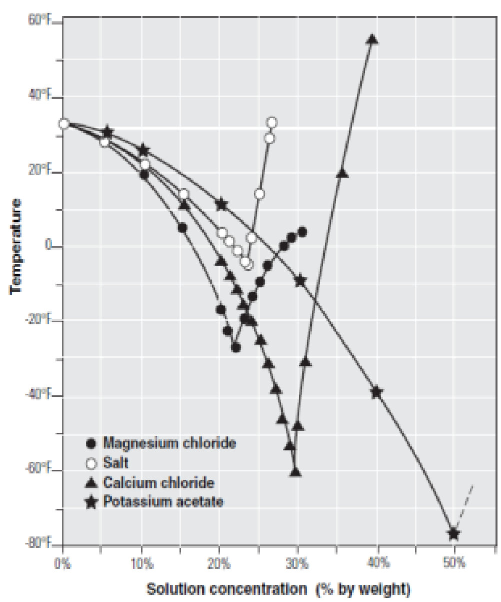


Figure 4: Eutectic curves of four common chemical solutions (FHWA, 1996).

Acetates are also promising alternate deicers and exhibit high performance in lab and field studies. Fay et al. (2008) reported that CMA was the only chemical that continued to melt ice after 30 minutes. Additionally, field application results showed that CMA provided long residual benefits under certain conditions when applied before a storm and decreased the number of applications (Wyant, 1998; Perchanok et al., 1991). Agricultural based products were found to be effective at 23°F (-5°C) (Fay et al., 2008). These agro-based products melt snow faster and at lower temperatures and provide more consistent, longer-lasting residuals than $MgCl_2$ (Fischel, 2001). Fischel (2001) compared the eutectic temperatures and effective temperatures of selected liquid deicers at their specific solution concentrations. The results are summarized in Table 4, which shows that Caliber M1000, potassium acetate, and calcium chloride have low eutectic and effective temperatures, whereas CMA has higher eutectic and effective temperatures. The magnesium chloride deicers, calcium chloride and potassium acetate deicers are most effective at low temperatures. CMAK is moderately effective at low temperatures and the least effective deicer at low temperatures was found to be CMA. Note that deicers with low eutectic and effective temperatures work well at low temperatures.

Additional laboratory testing of Caliber deicing products was performed by Bytnar (2009). Ice penetration tests and ice melting capacity tests demonstrated good performance for Caliber products. Ice penetration tests were performed using untreated rock salt as a control and comparing the performance to rock salt treated with Caliber. The rock salt treated with Caliber had better penetration at four temperatures as shown in Figure 5. Figure 6 shows a comparison of ice melting capacities at various temperatures for three Caliber products, 30% $CaCl_2$ and 30% $MgCl_2$. Caliber M1000 had great ice melting performance with ice melting capacities greater than or equal to 30% $MgCl_2$.

Furthermore, corrosion testing following the PNS test method demonstrated that Caliber M1000 had minimal corrosion impacts with significantly lower percent corrosion than salt and $MgCl_2$ as shown in Figure 7 (Bytnar, 2009).

Table 4: Eutectic and effective temperatures of selected deicers.

Deicer	**Concentration**	**Eutectic/Effective Temperature (ºF)**	**Reference**
FreezGard-Zero® with Shield LS®	22% $MgCl_2$	-27/5	Envirotech Product Information Sheet
Ice-Stop™ CI	21.6% $MgCl_2$	-28/5	Product Specification Sheet
Caliber™ M1000	27% $MgCl_2$	-85/-10	Product Specification Sheet
Liquidow* Armor*	30% $CaCl_2$	-59/-25	Product Information Sheet
CMA25® (25% aqueous solution)	100% CMA	+1/20	K. Johnson, Cryotech, personal communication
Potassium Acetate (CF7®) (50% aqueous solution)	100% potassium acetate	-76/-15	K. Johnson, Cryotech, personal communication
CMAK™ (50:50 blend of CMA25 and CF7)	100% CMAK	-25/0	K. Johnson, Cryotech, personal communication

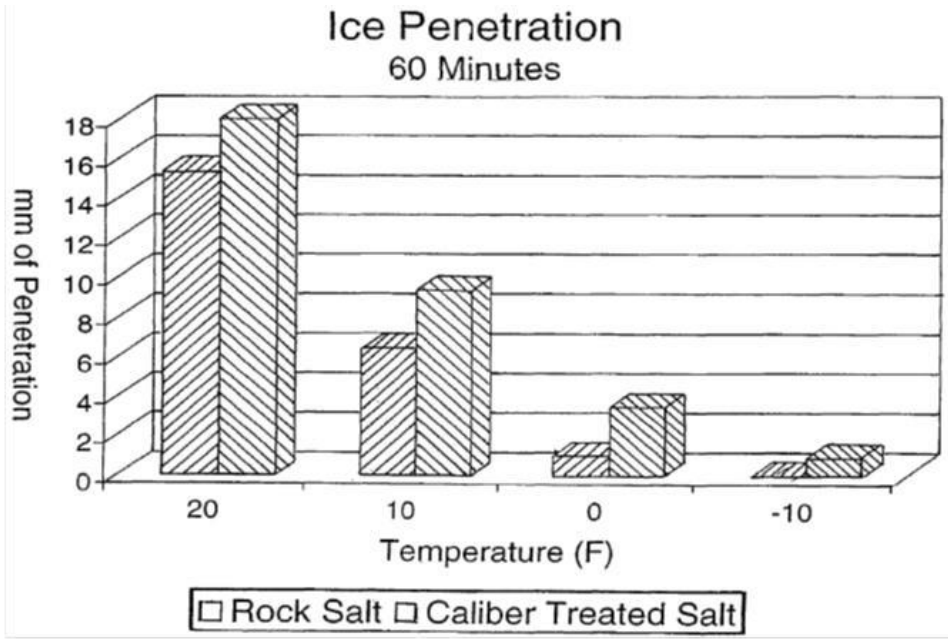


Figure 5: Ice penetration results of various deicers at different temperatures. (Bytnar, 2009).

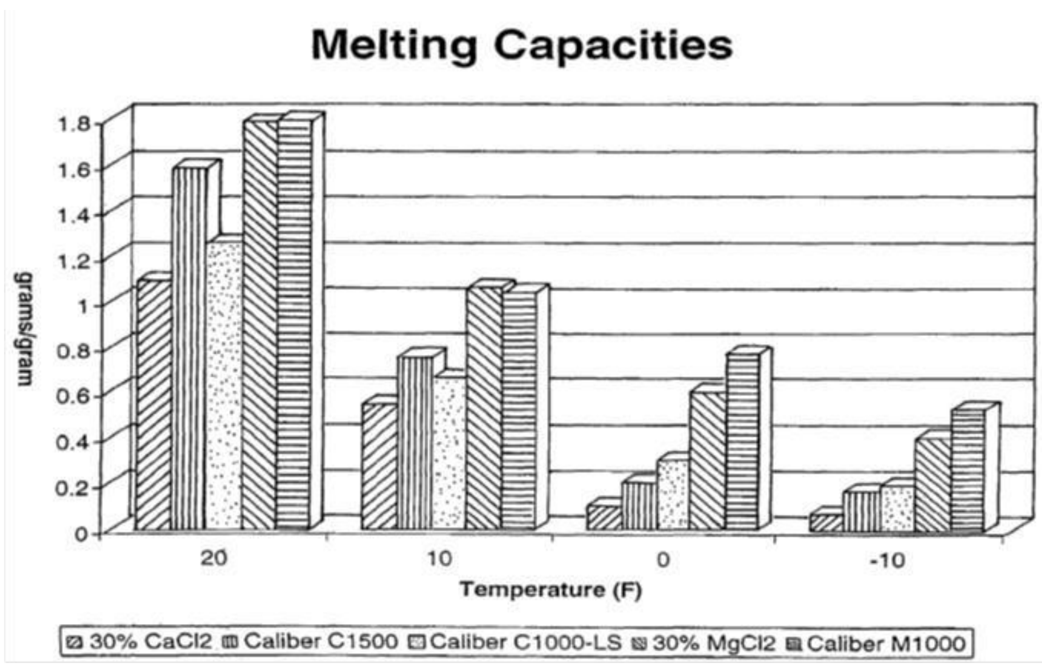


Figure 6: Ice melting capacity results of various deicers at various temperatures (Bytnar, 2009).

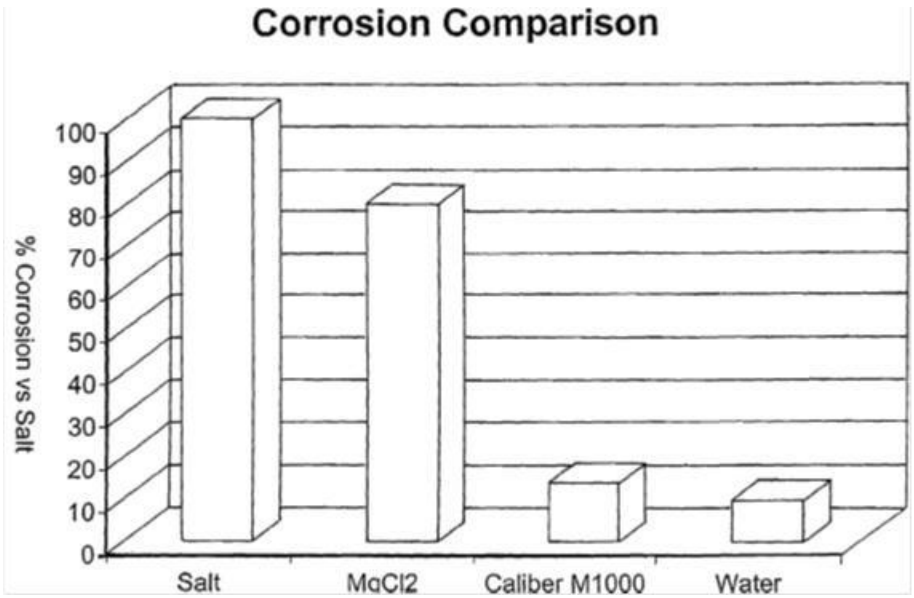


Figure 7: Corrosion results from PNS test method of various deicers (Bytnar, 2009).

In recent years anti-icing compounds developed from agricultural by-products (ABP) have been produced alone as deicers or as additives to enhance the performance of commonly used deicers. These chemical additives help keep roads clear by providing a faster reaction time and longer residual effects (Shi, 2011; Fischel, 2001; Kahl, S., 2004). It was reported that adding beet juice into salt brine would help the salt stay on the pavement for longer and thus improve the overall performance of the brine. The chloride based liquid deicer/anti-icer "Geomelt S30" has been used in Southern Ontario (Soudki et al., 2011). It contains an organic additive derived from desugared beet juice (Geomelt 55 concentrate) that is blended with NaCl brine. The same effectiveness of other deicers is achieved with reduced use of Geomelt and it adheres to road surfaces better.

Ice Ban™ is a concentrated liquid residue made from fermented corn by-products and can be used alone or mixed with a solution of 30% magnesium chloride. Fischel (2001) has compared the effectiveness of Ice Ban to magnesium chloride deicers and Ice

Ban was reported to have faster melting effects at lower temperatures than magnesium chloride solutions. A more consistent, longer lasting residual effect than magnesium chloride was also observed (Fischel, 2001). Controlled field trials conducted in New York indicate that applications of Ice Ban Magic can "significantly reduce the amount of salt needed in follow-up applications during the course of a snow storm" (HITEC/CERF, 1999).

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 (Shi 2008; Shi et al., 2009a). Therefore, advancement is needed to develop less corrosive, highly effective, and environmentally safe deicers. Battelle has been able to successfully modify the trans-esterification process in the production of biodiesel to produce a usable deicing product. 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 hydrochloric acid (HCl) to neutralize the sodium hydroxide (NaOH), which creates an acetate or formate salt and glycerin. In addition, glycerin naturally behaves as a corrosion inhibitor. Table 5 shows various formulations of deicing fluids made from biodiesel by-products. Test procedures including ice melting, ice penetration, and ice undercutting were performed on the bio-based deicing fluids at various temperatures. Figure 8 and Figure 9 display the ice melting performance results of various deicers at 25°F. The results reveal that the proposed new deicing fluids have comparable performance to the commercially available potassium acetate. Figure 10 displays the freezing points of the various bio-based deicers. It was determined that 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 5: 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

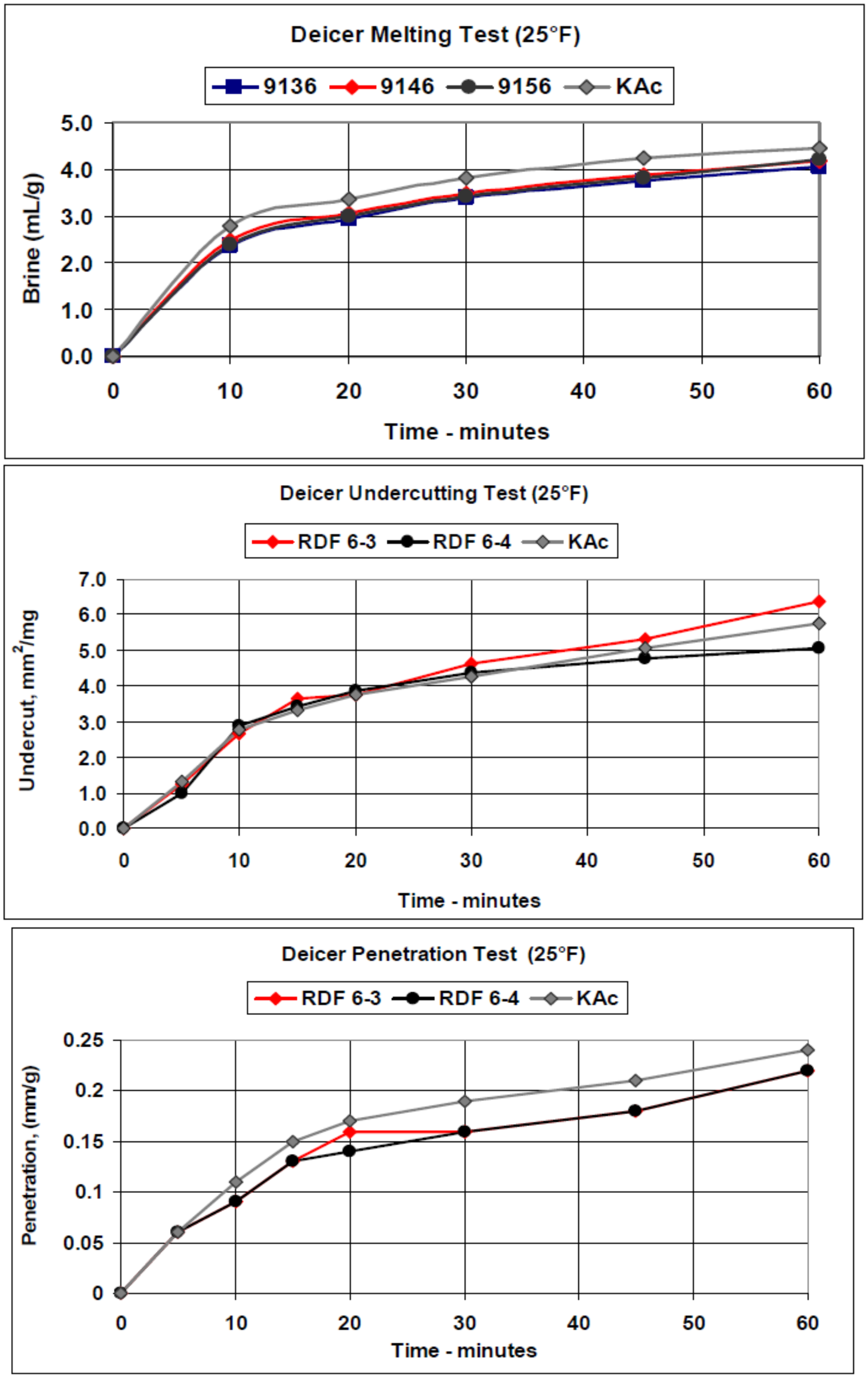


Figure 8: Ice melting performance at 25°F (a) Ice Melting (b) Ice Undercutting (c) Ice penetration (Chauhan et al., 2009).

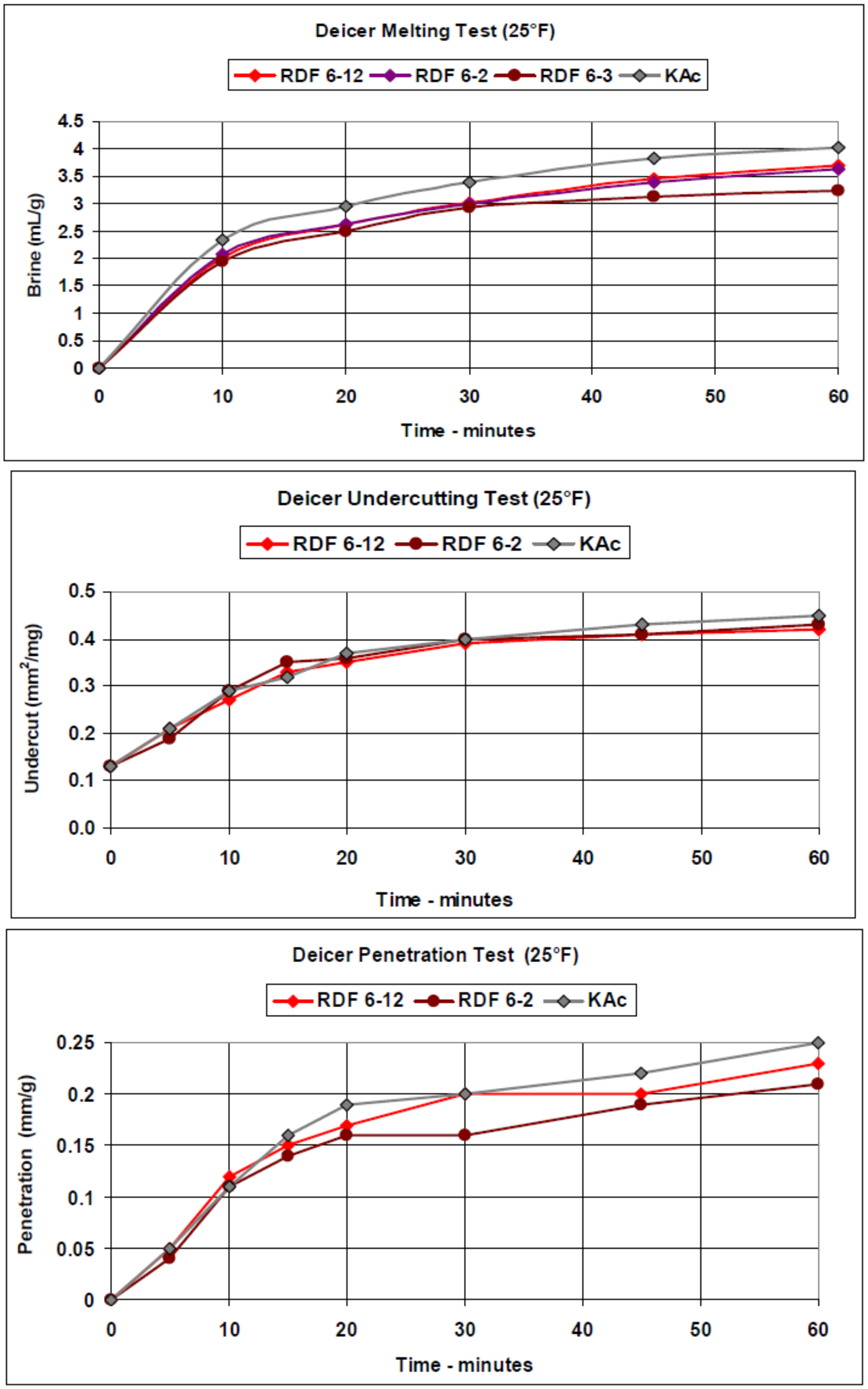


Figure 9: Ice melting performance at 25°F (a) Ice Melting (b) Ice Undercutting (c) Ice penetration (Chauhan et al., 2009).

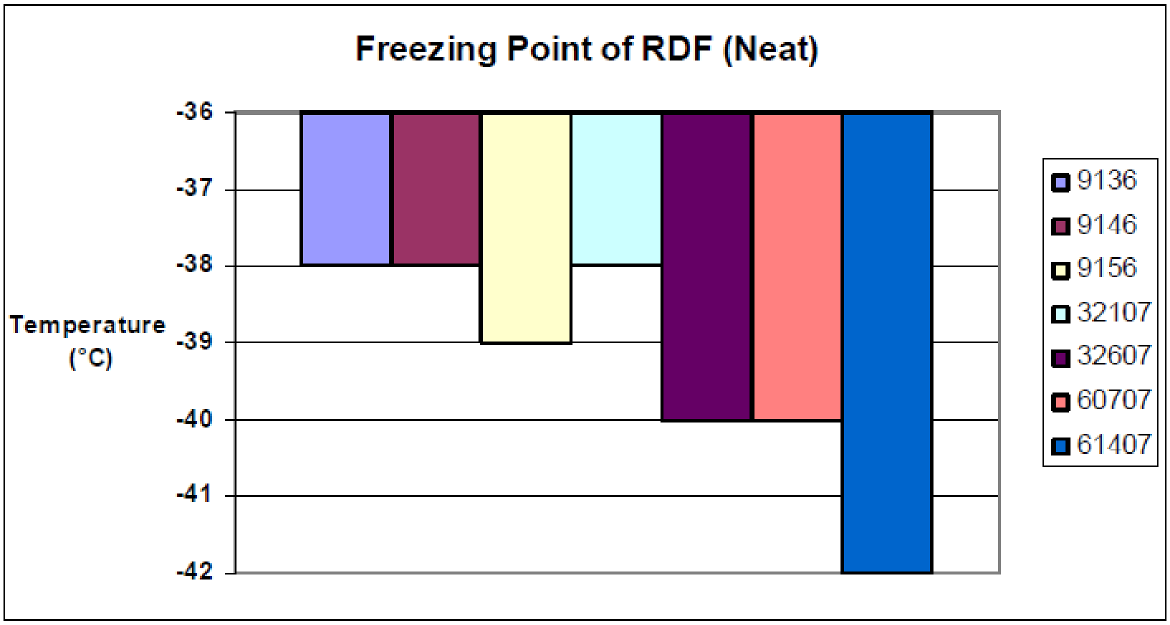


Figure 10: Freezing points of various deicers. (Chauhan et. al. 2009)

A recent study by Fay and Shi examined the performance properties of commonly used deicers at various temperatures. Figure 11 displays the results from the SHRP H205.1 and H205.2 ice melting capacity test methods, corresponding to 60 min 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. In addition, data was collected for ice penetration of selected deicers using SHPR H205.3 and H205.4 test methods. These results are shown in Figure 11 and Figure 12. The results show that the liquid deicers outperformed the solid deicers (Fay and Shi, 2011). This study was able to demonstrate a wide range of performance among commonly used deicers and show some of the challenges required in the development of new deicers.

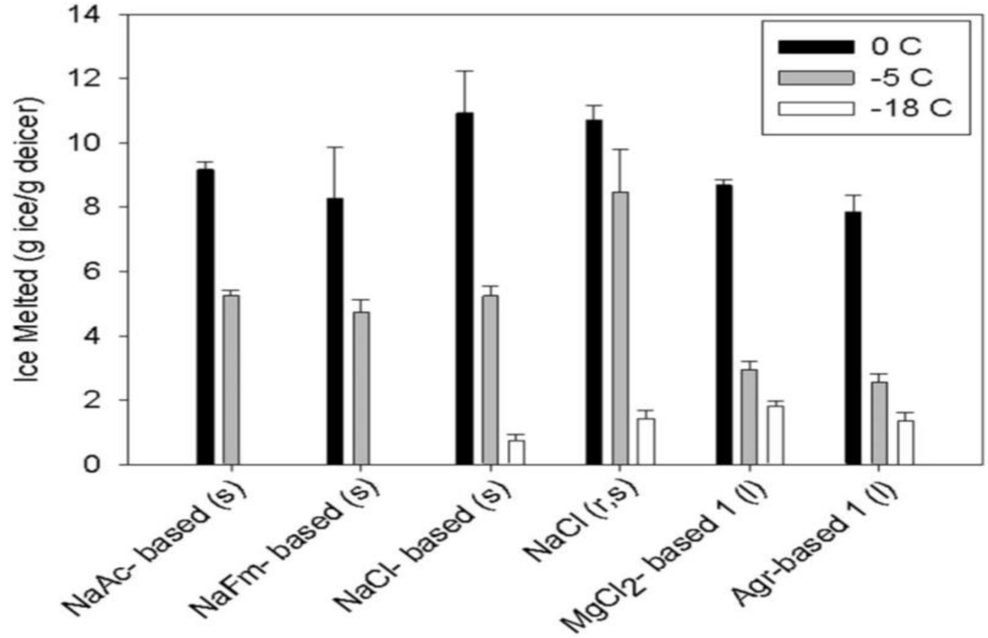


Figure 11: Data from SHRP ice melting capacity test after 60 minutes exposure to deicers (Fay and Shi, 2011).

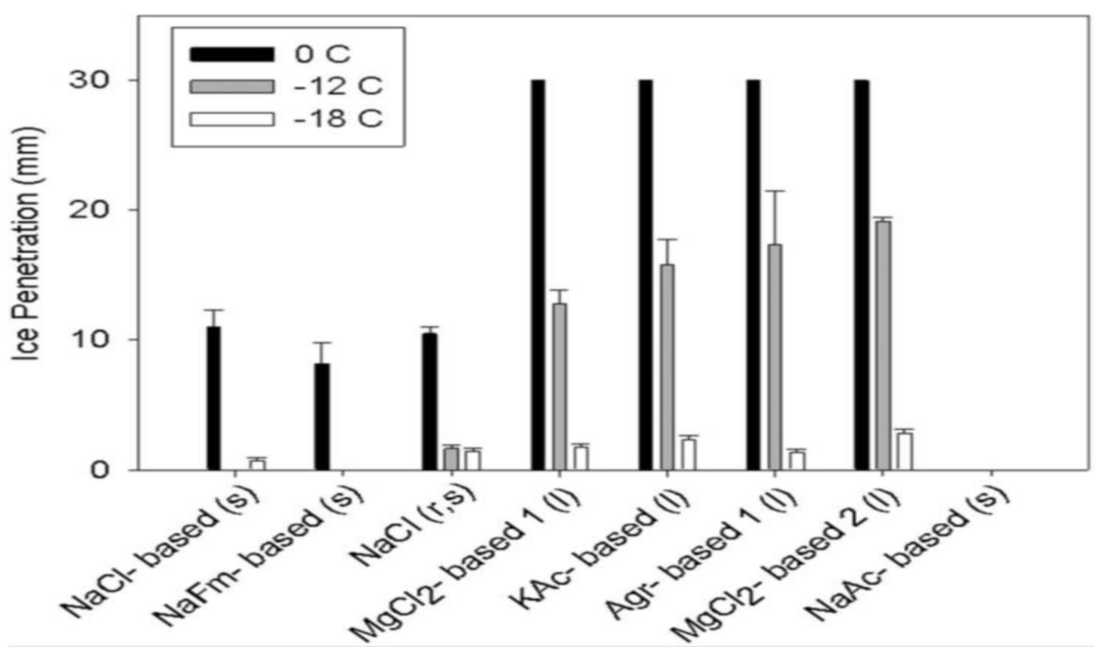


Figure 12: Results from SHRP ice penetration test after 60 minutes exposure to deicers (Fay and Shi, 2011).

Environmental Impacts of Deicers

Extended use and increased applications of chemical deicers for winter maintenance operations has resulted in increased concentrations of deicer constituents in the environment. Water quality, air quality, soil, vegetation and toxicity to aquatic species are negatively affected by the continued use of deicing chemicals; however, the degree of impact depends on various factors and can be attributed to the types of salts used (Ramakrishna and Viraraghavan, 2005). Winter maintenance agencies are now more concerned with evaluating the environmental impacts when selecting appropriate types of deicers. When solid deicers are applied to roadways, some of the product will bounce and scatter off the road and end up on the surrounding soil and vegetation or become transported by wind currents to the surrounding environment (Blomqvist 1998, Environment Canada and Health Canada 1999). Liquid deicers tend to remain on roadways longer and are considered to have less impact on the environment than sand and solid salts (CDOT, 2013). Liquid deicers can also reduce the need for applying abrasives and solid salts, thus reducing impacts to air quality, roadside vegetation, and aquatic biota (CDOT, 2013). Chloride based deicers pose a significant risk to the environment and can cause increased chloride concentrations in surface and ground water.

It is well documented that chloride deicing chemicals greatly affect soil structure and vegetation near roads and have negative impacts on water quality and various organisms (Crowther and Hynes, 1977; Dickman and Gochnauer, 1978; Barrick and Davidson, 1980; Demers and Sage, 1990; Lewis, 1999; Butler and Addison, 2000;

Robidoux and Delisle, 2001; Bryson and Barker, 2002; Czerniawska-Kusza et al., 2004; Mineau and Brownlee, 2005; Sanzo and Hecnar 2006; William and Little, 2011). Road runoff with high levels of NaCl can reduce the quality of surface and ground waters several months after application (Thunqvist, 2004). Increasing concentrations of Na^+ and Cl^- is known to affect soil structure, dispersion, permeability and osmotic potential and can cause loss of soil stability and osmotic stress for vegetation and microorganisms (Morin et al., 2000). High levels of sodium (Na^+) can affect soil properties by exchanging with available nutrients in the soil complex and can lead to cation leaching and nutrient deficiencies (Bouzille et al., 2001).

Table 6 provides a summary of the potential environmental effects, corrosion, cost and performance of common deicers, which was developed by Fischel (2001). Each of the deicers discussed in the report has potential negative impacts on the environment. In some cases, the common alternative deicers such as CMA, $MgCl_2$ and $CaCl_2$ are believed to be less detrimental to the environment than conventional NaCl. For example, $MgCl_2$ is more effective than NaCl at lower temperatures and requires a reduced application rate thus causing reduced chloride loading to the environment, and it also benefits the forests and soils. CMA is a more corrosion resistant deicer but may result in decreased dissolved oxygen in receiving waters (Daniel, 2010).

Table 6: Summary table comparing potential environmental effects, corrosion, cost and performance of selected deicers (Adapted from Fischel, 2001)

Deicer/ Parameter	Inhibited $MgCl_2$	Caliber+ $MgCl_2$	Ice Ban +$MgCl_2$	Inhibited $CaCl_2$	CMA	CMAK	Potassium Acetate
Chemicals	Trace metals[1]	Trace metals[1], phosphorus, ammonia	Trace metals[1], phosphorus, ammonia, nitrates	Trace metals[1], ammonia, nitrates.	Trace metals[1]	Trace metals[1], ammonia, nitrates.	Trace metals[1]
Soil	Improves structure, increases salinity	Improves structure, increases salinity, oxygen depletion	Improves structure, increases salinity, oxygen depletion	Improves structure, increases salinity	Improves structure; oxygen depletion	Improves structure; oxygen depletion	Improves structure; oxygen depletion
Water Quality	Increases salinity	Increases Salinity Oxygen depletion	Increases Salinity Oxygen depletion	Increases salinity	Oxygen depletion	Oxygen depletion	Oxygen depletion
Air Quality	Minimal air pollution	Minimal air pollution	Minimal air pollution	Minimal air pollution	Minimal air pollution	Minimal air pollution	Minimal air pollution
Aquatic Organisms	Relatively low toxicity	Relatively low toxicity	Moderate toxicity	Relatively low toxicity	Relatively low toxicity	Moderate toxicity	Moderate toxicity
Terrestrial Vegetation	Chlorides damage vegetation	Chlorides damage vegetation	Chlorides damage vegetation	Chlorides damage vegetation	Minimal damage to vegetation	Minimal damage to vegetation	Minimal damage to vegetation
Terrestrial Animals	Does not attract wildlife	Does not attract wildlife	Does not attract wildlife	Does not attract wildlife	Not expected to attract wildlife	Not expected to attract wildlife	Not expected to attract wildlife
Corrosion	Low corrosion	Low corrosion	Low corrosion	Low corrosion	Non-corrosive	Non-corrosive	Non-corrosive
Performance	Moderately effective at low temperature	Effective at low temperature	Effective at low temperature	Effective at low temperature	Not effective at low temperature	Effective at low temperature	Effective at low temperature
Cost	Low cost	Relatively low cost	Relatively low cost	Relatively low cost	High cost	High cost	High cost

1 – Trace metals that may be present include arsenic, barium, cadmium, chromium, copper, lead, mercury, selenium, and zinc.

Corrosion and Infrastructure Impacts

Long exposure times and continued use of deicers for snow and ice control can cause significant damage to vehicles, bridges, and maintenance equipment. Liquid deicers leave a residual, which can cause corrosion to vehicles (CDOT, 2013). Shi et al., (2009c) reported that deicers pose detrimental effects on Portland cement concrete (PCC) infrastructure, thus reducing the structural integrity of the concrete, as indicated by mass change, expansion, and loss in the dynamic modulus of elasticity and strength. Furthermore, deicers cause corrosion damage to motor vehicles, concrete structures, and steel bridges (Shi et al., 2009b). However, the corrosion of metals is a function of humidity, dissolved oxygen levels, debris, and type of metal (Jones et al., 1992). Fischel, (2001) reported corrosion test results for various metals shown in Table 7. Calcium chloride and sodium chloride were considered the most corrosive and CMA was the least corrosive.

Table 7: Corrosion test results from various studies (adapted from Fischel, 2001).

Ranking	HITEC(1998) (flat steel)	McCrumm, 1992 (bridge steel-laboratory testing)	McCrum, 1992 (bridge steel-field testing)	Addo, 1995 (mild steel)	Vancouver City Council, 1998 (unprotected steel)
Least Corrosive	70% Ice Ban + 30% $MgCl_2$	Inhibited $MgCl_2$ (FreezGard+ PCI)	CMA	$MgCl_2$	CMA
Low corrosion	Inhibited $MgCl_2$	CMA	-	-	-
Moderate corrosion	-	-	Inhibited $MgCl_2$	$MgCl_2$ (FreezGard)	$MgCl_2$
Most Corrosive	NaCl	NaCl	NaCl	NaCl (Ice Slicer)	NaCl and $CaCl_2$

Recent Developments

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 typically contain chlorides, which are highly corrosive. Berglund et. al. (2003) has 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 wastes, 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. It is proposed that this formulation may also be used as an anti-icing agent and integrated 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 these steep water solubles to chloride salts. Similarly, Kharshan et. al. (2012)

demonstrated the successful increased corrosion protection of carbon steel using corn extracts. Table 8 displays the typical composition of steep water. It is suggested that an amount of 20 to 60 gallons per lane mile of the steep water deicer be applied to effectively clear snow and ice from roadways. When applied to roadways, the 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 also showed active ice melting temperatures as low as 7.5°F, whereas the salt, sand mixture ice melting stops around 20°F (Janke et. al., 1997). Additionally, Montgomery et. al. (2003) 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. Furthermore, corrosion testing resulted in little effect on mild steel as shown in Table 9. Mild steel bolts were immersed in various concentrations of steep water and showed no oxidation after four months. Mild steel bolts were sprayed with various concentrations of steep water and 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 8: Typical compositon of steep water (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%

Table 9: Corrosion results (Janke et. al. 1997).

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

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, availability, non-corrosive, and environmentally acceptable. During the cheese making process, milk is coagulated and strained leaving a liquid behind known as whey. This liquid is condensed to 50% solubles and is used as an additive in livestock feed. 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 five percent by weight chloride salts compared to a solution of five percent salts. Also, the whey composition can be used as an anti-icer in which it is 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 with 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). Janke et. al. also proposed an additional noncorrosive, environmentally safe deicer composition made from condensed solubles acquired from the processing of wine. This wine by-product deicer has a low freezing point of -20°F and (Janke et al., 1998b)

Although the deicer compositions presented by Janke et. al. offer viable alternative deicers to chloride salts, some negative characteristics are encountered. By-products from the fermentation or processing of cheese are biologically reactive, which can result in continued growth of organisms after application. This can produce undesirable strong odors and cause foaming. Furthermore, distillation and fermentation by-products tend to have a strong odor, which may not be suitable for residential areas. Thus a deicer formulation made from a waste product of processing sugar beet molasses is proposed. Sugar beets are processed to remove the 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 10. It was discovered that this waste product is an effective freezing point depressant and can be utilized directly from the manufacturer without further processing. It does not contain any alcohols or microorganisms thus being 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 between ¼ -1 inch thick are shown in Table 11. 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 et al show comparable results.

Table 10: Composition of desurgared 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%

Table 11: 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.

The use of agricultural by-products such as molasses or distiller's solubles as corrosion inhibitor additives creates some potential complications. To achieve improved corrosion inhibition, high concentrations are required which affects the ice melting capacity and increases 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. 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

12 and Table 13. It was determined that this alternative approach yields effective corrosion inhibitors at lower costs and concentrations (Koefod 2010a).

Table 12: 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 13: 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

Additives for Corrosion Inhibition

Corrosion research is concentrating on various preventative strategies in order to mitigate the harmful effects of corrosion caused by deicing products. Recently, the main focus is the use and development of effective, nontoxic inhibitors. Corrosion inhibitors, as defined by 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 both the ability of 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; however, they are toxic and harmful to the environment. Recent research focuses 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 (Kharshan et. al. 2012).

Potassium acetate exhibits low corrosion rates towards aluminum alloys, magnesium alloys, titanium alloys and mild steel, which contributes to its popularity as a runway deicer. However, it is considered very corrosive towards 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 significantly reducing the 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 enhanced 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).

New developments in corrosion inhibitors are 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, cotton seeds, 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 is used as a corrosion inhibitor with deicing salts. During corrosion testing, 1010 carbon steel panels are immersed into 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).

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 formulation for specific functionality such 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 (ACRP 2008).

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 on water quality. Simple compounds such as sodium hydroxide, potassium hydroxide, or ethanol amines are used as pH buffers and can be added to deicers to ensure neutral pH is achieved. Various pH buffers are listed in Table 14 (ACRP 2008).

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).

Table 14: 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

Conclusion

The state of the art of chemicals used for snow and ice control was reviewed and the findings were reported to gain a better understanding and identify knowledge gaps within the literature. Development of new snow and ice control chemicals has been actively progressing over the past several years in order increase performance and reduce impacts associated with conventional snow and ice control materials. An overwhelming number of products for snow and ice control are commercially available and various new options for developing environmentally friendly deicer formulations have been explored. These options offer great alternatives to the traditional chloride based deicers by reducing impacts to the environment and minimizing corrosion effects, which is associated with chloride based deicers. Table 15 outlines a summary comparison of chloride based deicers and organic based deicers.

Table 15: Comparison of chloride based deicers and organic based deicer.

Chloride Based Deicers	**Organic Based Deicers**
$NaCl$, $MgCl_2$, $CaCl_2$	CMA, KAc, Geomelt, Agricultural products
Good performance. Most commonly used deicer. Relatively inexpensive	Good performance at low temperatures. Reduced corrosion and environmental impacts.
High costs due to corrosion. Low performance at low temperatures.	Potential for utilizing by-products or waste products. Can be added to chloride deicers to enhance performance. May contain high BOD levels.

It can be most cost effective to utilize local materials available within a specific location where the snow and ice products will be used. However, since many of the raw materials for agricultural based products are limited in certain regions more research is needed to develop deicer formulations from renewable resources specific to the state of Alaska since snow and ice control chemicals are expensive due to shipping costs. Future work in the development of deicers should involve the exploration of local products, which may be driven by local industries to better utilize by-products or waste products that can be processed into deicer formulations with minimal processing. In addition, specific road weather scenarios and the priorities of local maintenance agencies need to be taken into consideration when developing new snow and ice control chemicals.

3. EVALUATION AND DEVELOPMENT OF LIQUID DEICERS FOR WINTER HIGHWAY MAINTENANCE OPERATIONS

Introduction

Liquid deicers are increasingly popular for winter maintenance operations since they offer better performance for snow and ice control and are environmentally friendly alternatives to abrasives and solid salts. Commercially available products are composed of a variety of chemicals and widely vary in terms of performance and cost. Due to availability and low costs, sodium chloride is the most commonly used product for snow and ice control, followed by magnesium chloride (Fay et al., 2008). However, increasing environmental concerns and high corrosion costs associated with chloride based chemical deicers and anti-icers have caused recent developments to focus on producing less corrosive, environmentally friendly snow and ice control chemicals made from renewable agricultural sources. For example, Ice Bite® is a commercially available anti-icer derived from sugar beets. Similarly, products such as Caliber M1000 and BOOST are composed of organic agricultural derivatives.

Each product contains specific advantages, which make it more suitable for a specific road weather scenario. However, there is a need to directly compare the performance of these commercially available products in terms of ice melting capacity, corrosion to carbon steel, and impact to Portland cement concrete under identical conditions. Results of laboratory testing procedures will assist in the proper selection of a product depending on priorities determined by winter maintenance agencies. In addition, results from the laboratory testing will assist in the guidance of developing new formulations for high performance, cost effective additives for snow and ice control.

The use of liquid deicers offers various benefits to winter maintenance agencies and has been becoming more prevalent in recent years. Liquids stay on roadways better than solids and improve overall performance (Duane 2006). Liquid deicers can be used for anti-icing applications, which prevents snow and ice from bonding to pavement surfaces; therefore, increasing the effectiveness of mechanical removal such as plowing. Anti-icing has been shown to decrease applications of chemicals and maintenance costs while improving level of service and decreasing accident rates (EPA, 1999, O'Keefe and Shi, 2006). In addition, prewetting salt or other solid chemicals is performed with liquid deicers to reduce bounce and scatter, improve performance and reduce overall chemical usage (Blackburn et al., 2004). A recent study by Michigan DOT reported that the addition of a liquid deicer such as an agricultural product increases the ice melting process and reduces salt loss (MDOT, 2012). According to Max Perchanok of the Ontario Ministry of Transportation, liquid deicers can be applied to achieve bare pavement conditions if a thin layer of ice or snow is present after plowing. Direct liquid application, which is the method of directly applying liquid deicers to the roadway during a storm event, can also be an effective use of liquid deicers (Peterson et al., 2010).

Agricultural based chemicals are becoming more popular due to the harmful effects caused by chloride based deicers (Better Roads 2001). Many research projects have investigated the performance and use of chloride based deicers for winter maintenance operations; however, research is needed to investigate the benefits of using agricultural products as liquid deicers for winter highway maintenance and directly compare these products to traditional salt brine (Shi et. al 2013a, Shi et. al 2013b). In addition, a recent study performed by Levelton Consultants has identified cost and performance as the two main criteria in which deicers used in the field are selected, whereas there are generally more factors to consider (Levelton, 2007). Therefore, an extensive evaluation and analysis of various liquid deicers used for winter highway maintenance was performed to determine performance characteristics using laboratory techniques. The selected products were evaluated based on ice melting capacity, corrosiveness and impact to Portland cement concrete.

A total of four agricultural based deicer formulations and a salt brine control were evaluated. The salt brine control was made using water and rock salt at a 23 wt.% concentration. Product A is a 30 wt.% $MgCl_2$ solution produced from naturally occurring minerals in the Great Salt Lake. Product B is an all-natural product derived from renewable resources. Product C is an agricultural product made from beets and Product D is a blended mixture of salt brine and Product C at a volume ratio of 60:40.

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).

Anti-icing has been gradually accepted and adopted by North American maintenance agencies as a proactive approach to winter highway safety and mobility.

There is a need to better utilize industrial by-products such as distillery by-products. The addition of additives to salt brine may enhance anti-icing performance at cold temperatures at reasonable costs and decrease the environmental risks associated with winter maintenance operations.

Deicers or anti-icers 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 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 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 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.

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 likely reduce the costs of winter road maintenance for the State of Alaska and boost local economic growth.

Research Approach

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. Patents were examined to understand the state of the art and identify active ingredients and additives for eco-friendly anti-icing formulations.

Concurrent to the literature review, information was gathered from winter maintenance professionals 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 conducted for the Colorado DOT (Shi et al. 2009a) identified some desirable attributes of anti-icers and deicers such as low cost-per-lane mile, low effective temperature, high ice-melting capacity, ease of application and some key negative concerns over their use, which included 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 emphasis 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. To this end, research is needed to develop anti-icing liquids tailored to address the specific user requirements.

Preliminarily performance testing of the identified freezing-point depressants, corrosion inhibitors, and other additives was performed. 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 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.

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 or electrochemical test was used to assess the corrosiveness of these anti-icer blends to carbon steel.

Formulation Development

The process of developing alternative deicers consists of many steps before winter maintenance agencies can apply them onto roadways. The first step is to obtain the by-products and then develop potential mixtures. Then laboratory testing is needed to determine the best formulations and subsequent field testing is needed before the liquid deicer is commercially available. Figure 13 shows a flow chart of the process of developing alternative liquid deicers using waste products.

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.

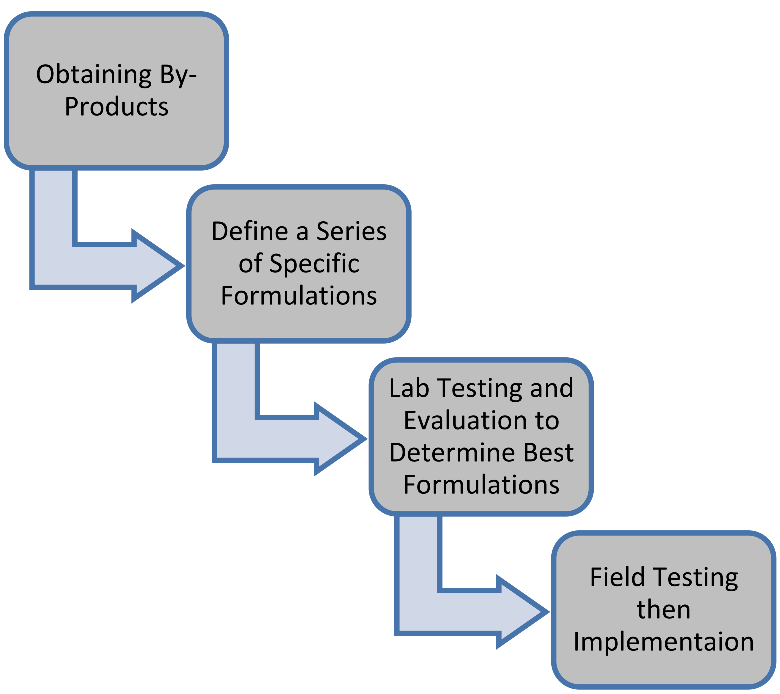


Figure 13: Flow chart showing the process of developing alternative deicers.

Differential scanning calorimetry (DSC) data analysis revealed favorable ice-melting properties for both distillery by-products, which are labeled Sample 1 and Sample 2. Potassium acetate, urea, and potassium succinate demonstrated effective ice-melting characteristics. Subsequently, potassium gluconate and sodium metasilicate exhibited optimal corrosion-inhibition properties. Therefore, these compounds were selected to be the main components in the deicer formulations generated by the design of experiments. The mix design contained three components: two that varied with percent concentration and one that had 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. All mix formulations were subjected to further DSC and EIS testing to determine the mix designs with the highest performance. Table 16 shows the specific components of each mix formulation.

Table 16: Mix design formulations.

Mix Number	Corrosion Inhibitors	Sample 1	Sample 2	Component 3	Salt Brine
3	1% KGluc 0.2%NaMetaSil	7%	5%	2% KAc	23% NaCl
4	1% KGluc 0.2%NaMetaSil	5%	5%	2% urea	23% NaCl
6	1% KGluc 0.2%NaMetaSil	3%	3%	2% KSuc	23% NaCl
12	1% KGluc 0.2%NaMetaSil	7%	5%	2% KSuc	23% NaCl
13	1% KGluc 0.2%NaMetaSil	5%	3%	2% urea	23% NaCl
16	1% KGluc 0.2%NaMetaSil	7%	3%	2% KAc	23% NaCl
19	1% KGluc 0.2%NaMetaSil	5%	4%	2% KAc	23% NaCl
20	1% KGluc 0.2%NaMetaSil	7%	4%	2% KSuc	23% NaCl

Table 16 Continued

Mix Number	Corrosion Inhibitors	Sample 1	Sample 2	Component 3	Salt Brine
22	1% KGluc 0.2%NaMetaSil	7%	4%	2% KAc	23% NaCl
27	1% KGluc 0.2%NaMetaSil	7%	5%	2% urea	23% NaCl
28	2% KGluc	10%	10%	10% Boost	18.4% NaCl
29	4% KGluc	10%	10%	10% Boost	18.4% NaCl
30	3% KGluc	10%	10%	8% Boost	18.4% NaCl
31	-	10%	10%	10% Boost	18.4% NaCl
32	-	-	-	13.3% Boost	20% NaCl
33	4% KGluc	15%	15%	10% Boost	18.4% NaCl
34	1.5% urea	7%	7%	-	18.4% NaCl
35	0.5% KGluc 0.1%NaMetaSil	2.5%	0.5%	3% Boost 1.0% urea	21% NaCl
36	0.5% KGluc 0.1%NaMetaSil	2.5%	0.5%	5% Boost 1.0% urea	21% NaCl
13X	1% KGluc 0.2%NaMetaSil	5%	-	2% urea	23% NaCl
13Y	1% KGluc 0.2%NaMetaSil	-	1%	2% urea	23% NaCl
13Z	1% KGluc 0.2%NaMetaSil	5%	1%	2% urea	23% NaCl
3A	1% KGluc 0.2%NaMetaSil	7%	5%	2% KAc	7% $MgCl_2$ 8.1% NaCl
3B	1% KGluc 0.2%NaMetaSil	7%	5%	2% KAc 3% MgSil	7% $MgCl_2$ 8.1% NaCl
3C	1% KGluc 0.2%NaMetaSil	7%	5%	2% KAc 3% CaSil	7% $MgCl_2$ 8.1% NaCl
22A	1% KGluc 0.2%NaMetaSil	7%	4%	2% KAc	7% $MgCl_2$ 8.1% NaCl
22B	1% KGluc 0.2%NaMetaSil	7%	4%	2% KAc 3% KSil	7% $MgCl_2$ 8.1% NaCl

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

Methodology

DSC Thermogram Test

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 energy necessary to maintain a near-zero temperature difference between the test substance and an inert reference material, with the two subjected to an identical (heating, cooling, or constant) temperature program. A DSC measurement typically requires only a few milligrams of the sample, which is sealed in an aluminum capsule. By measuring the heat flow of deicing and anti-icing compounds, DSC measurements provide insight into their freeze/thaw behavior, effective temperatures, and ice-melting capacity. The DSC method, described below, was developed based on trial and error, and eventually led to a deicer dilution ratio and a cooling/heating rate that provide reliable, reproducible, and useable results. The DSC machine used for test method development was a TA Instruments Q200.

To test liquid deicers, a diluted deicer solution at a ratio of 2:1 by volume was prepared and placed into an empty aluminum sample pan and the mass of the deicer solution was recorded. The sample was then placed into the TA Instruments Q200 sample container and subjected to a heating and cooling cycle with a temperature range of 25°C to -60°C. The samples were run in triplicate. The peak in the warming cycle of the thermogram was integrated to determine heat flow (J/g) and peak temperature. The ice melting capacity was then calculated using the average values of heat flow and peak temperature according to the method outlined in Akin and Shi (2010).

Ice Melting Performance Test

Ice melting performance of 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.

Corrosion Evaluation

The corrosive effects of selected deicers 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 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 and were purchased from Ad-Tek, Inc. The metal coupons were cleaned using hydrochloric acid and then rinsed in tap water and 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 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 to a 3% volume-to-volume ratio with deionized water (3 parts liquid deicer to 97 parts deionized water). The two controls consisted of 3% weight-to-volume solution of reagent grade NaCl and pure deionized water. After 72 hours the coupons are cleaned in a solution of hydrochloric acid containing stannous chloride and antimony chloride, which stops the reaction of the hydrochloric acid with steel once the corroded particles are removed. The final weight of the coupons is then recorded.

Deicer Impact on Concrete

The effects of diluted liquid deicers on Portland cement concrete 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 a 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 requires 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 were 3% NaCl and de-ionized water.

Splitting Tensile Strength

After the specimens experienced ten freeze-thaw cycles, the splitting tensile strength was determined according to ASTM C496 / C496M – 11. The splitting tensile data was collected using a MTS model 880. First, the diameter and length of each specimen were determined using the average of three measurements. The specimen is then positioned in the testing machine and a load rate of 100-200 psi/min is applied. The maximum applied load at failure is then recorded. The splitting tensile strength is calculated using the equation $T = 2P/\pi ld$, where l is the length (in) and d is the diameter (in).

Results and Discussion

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 14 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, as shown in Figure 15, 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.

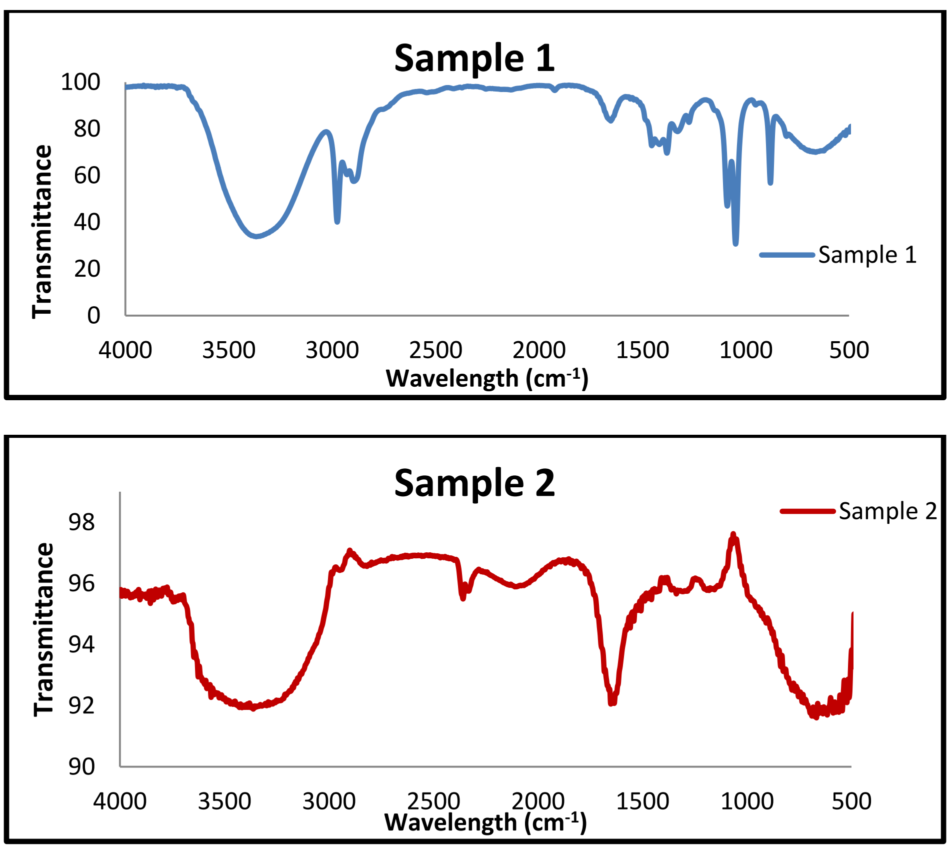
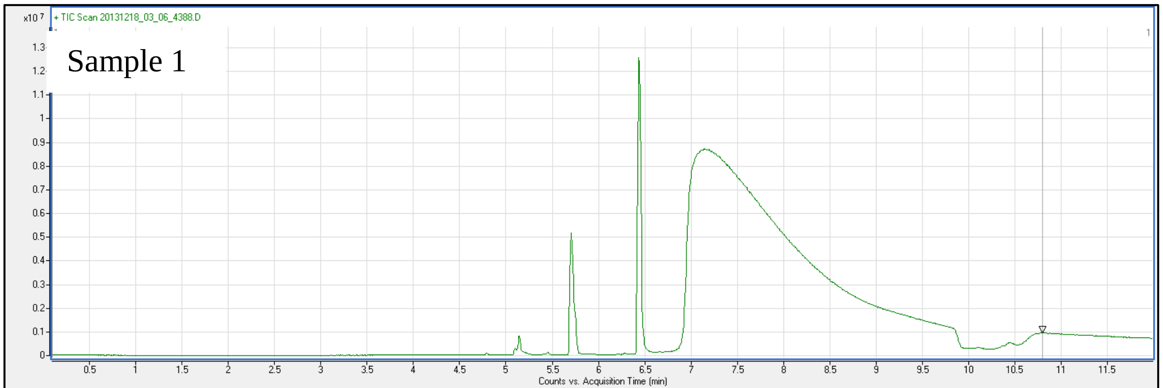
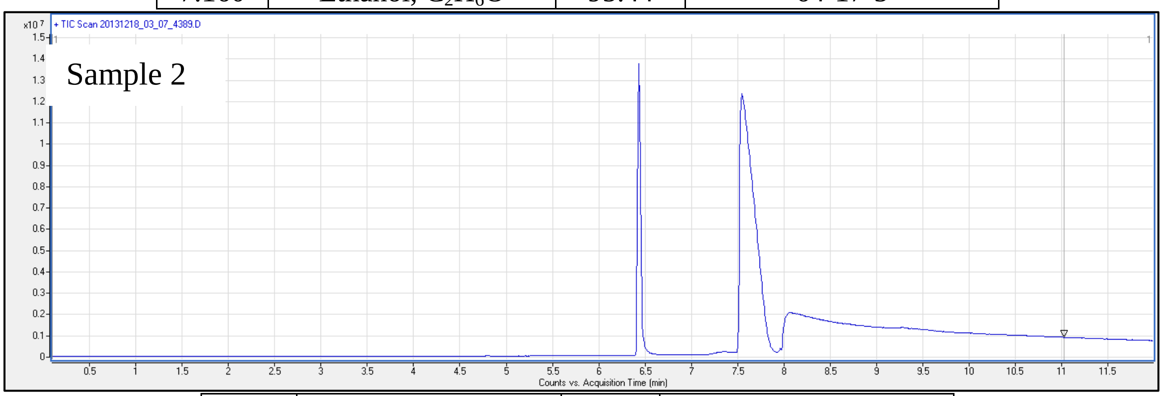


Figure 14: Fourier Transform Infrared spectroscopy results for Sample 1 and Sample 2.



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 15: Gas chromatography results of sample 1 and 2.

Ice Melting Performance: Commercially Available Deicers

Five liquid deicers were tested at both 15°F and 5°F. The ice melting behavior of the selected liquid deicers as a function of time for 15°F and 5°F are shown in Figure 16. The ice melting capacity at 60 minutes for 15°F and 5°F is shown in Figure 17. Figure 16 suggests that the liquid deicers reached or approached their maximum ice melting capacity at approximately 30 minutes at 15°F and 5°F. In addition, Product A had the highest ice melting capacity, thus outperforming all other liquid deicers at both 15°F and 5°F. The liquid deicer labeled salt brine control is used as a reference material for direct comparison. Product B outperformed the control at 15°F and had a slightly lower ice melting capacity than the control at 5°F as shown in Figure 16 and Figure 17. Product C and Product D had lower ice melting capacities than the control at 15°F and 5°F, which suggests that Product C is not a suitable liquid deicer at low temperatures.

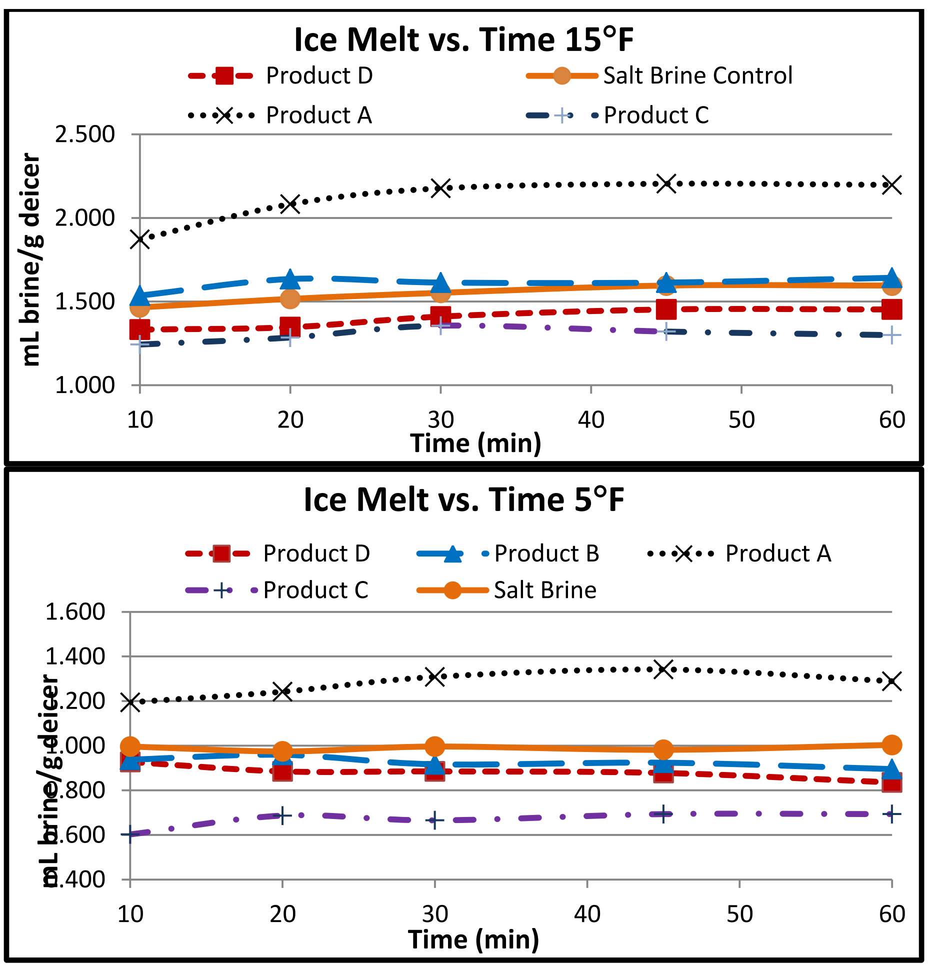


Figure 16: Ice melting behavior with respect to time. (a) 15°F; (b) 5°F.

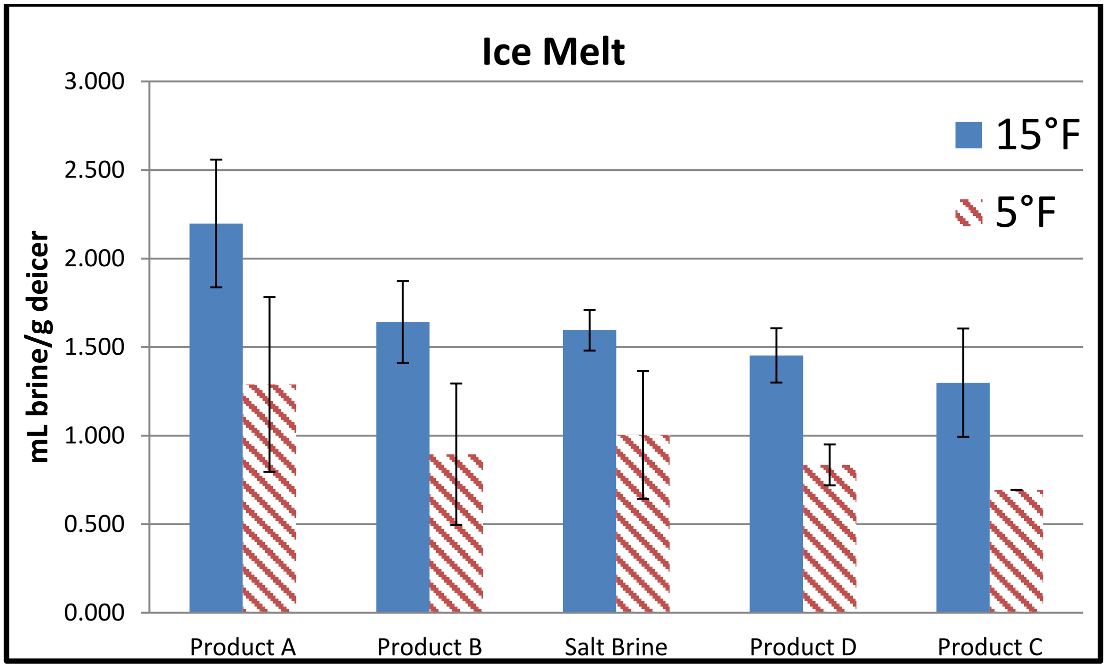


Figure 17: Ice melting capacity at 60 min for 15°F and 5°F.

<u>Ice Melting Performance: Developed Deicers</u>

Initial screening tests were performed using DSC and EIS. These techniques offered the most flexibility in defining potential high performance anti-icing additives by permitting numerous screenings within a short time frame. The EIS data were analyzed to determine the most effective corrosion inhibitors, and the DSC data were evaluated according to the DSC thermogram test protocol to calculate ice-melting capacity. 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.

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 heat flow 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 18 provides a comparison of 23% NaCl, Mix 3, and Mix 22. The DSC test provides the characteristic temperature (T) and heat flow (H) associated with the peaks.

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 heat flow, 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).

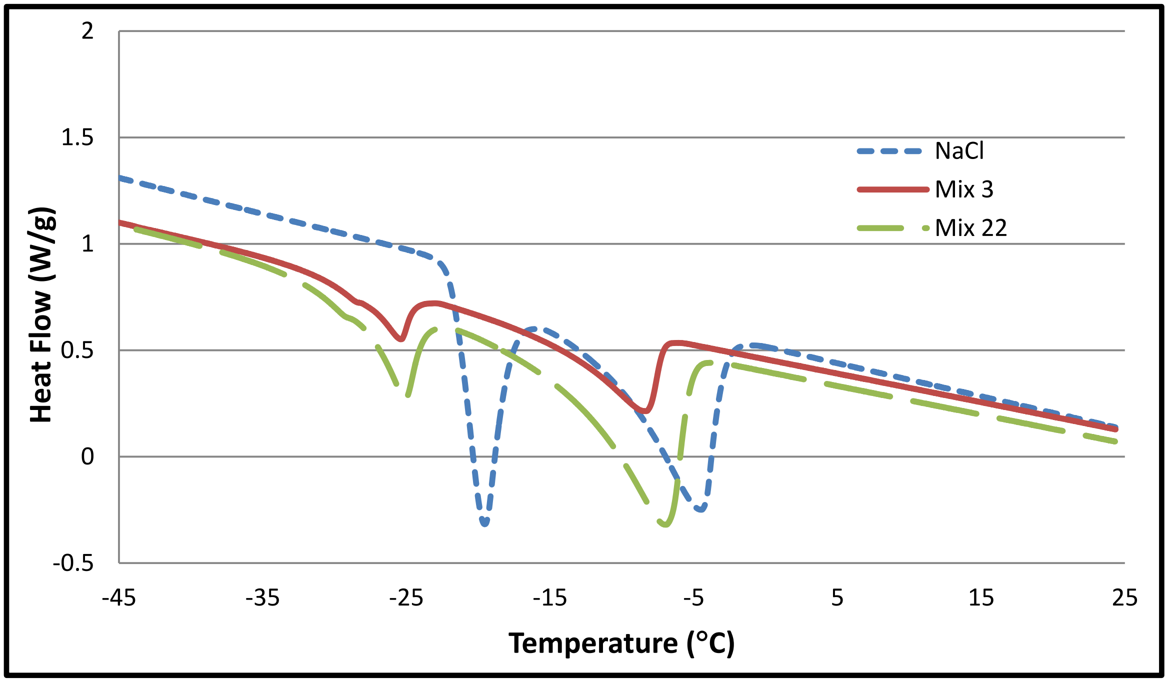


Figure 18: DSC thermograms for 23% NaCl, Mix 3, and Mix 22.

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.

Table 17 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 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 Table 17 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 and 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. Although higher predicted ice-melting capacities showed a strong correlation with high actual ice-melting capacities, DSC screening tests offer effective initial assessments of anti-icing characteristics.

Table 17: Comparison of predicted ice-melting capacity to actual ice-melting capacity

IMC30°F	**Predicted Ice-Melting Capacity (ml brine/g deicer)**	**Actual Ice-Melting Capacity (ml brine/g deicer)**
Mix 3	**4.260**	4.880
Mix 4	**3.842**	4.578
Mix 6	**3.570**	4.577
Mix 13	**3.659**	4.782
Mix 16	**3.306**	4.646
Mix 19	**3.591**	4.587
Mix 20	**3.736**	4.996
Mix 22	**3.527**	5.134
Mix 27	**3.300**	4.593
23%NaCl	**3.664**	3.773

The ten mixes with the highest performance, as determined by DSC, 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. All ten mixes had significantly higher ice-melting capacities at 15°F than the 23% NaCl control as shown in Figure 20. Subsequently, Mixes 22 and 3 were shown to have the highest ice-melting capacities at 30°F and 15°F, respectively, as shown in Figure 19 and Figure 20. Therefore, Mix 3 and Mix 22 were selected to be further evaluated for corrosiveness as described by NACE TM0169-95 PNS Modified Dip Test.

Furthermore, 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.

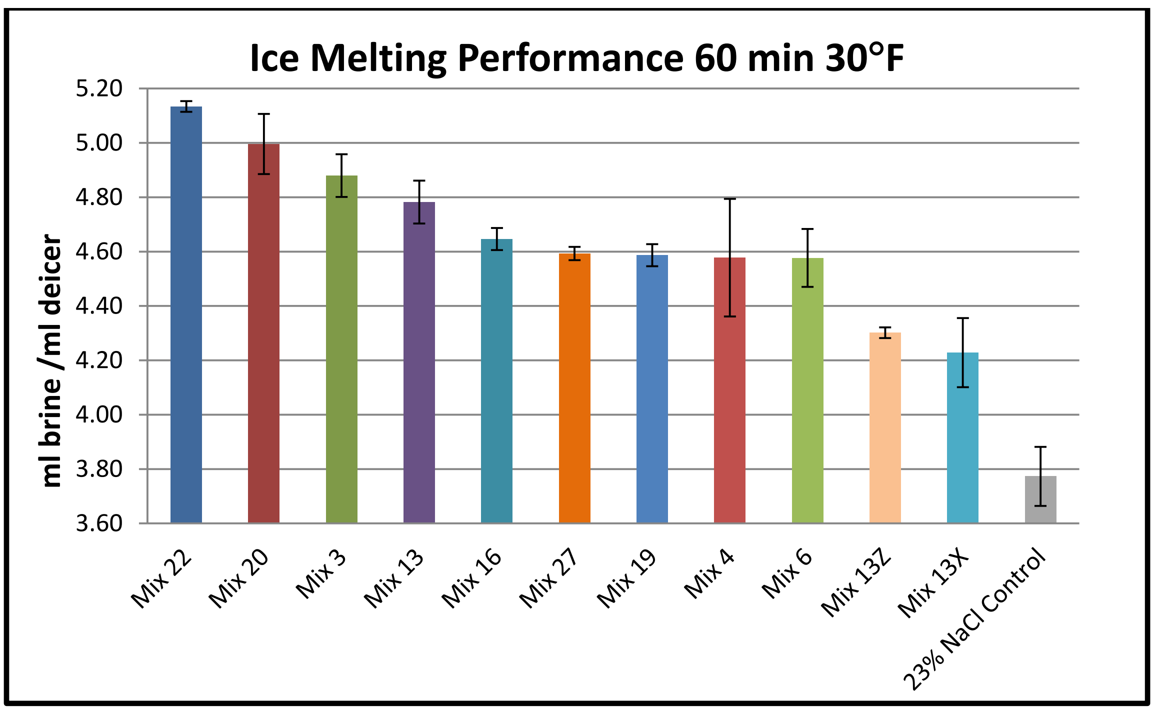


Figure 19: Ice Melting Performance at 60 min at a temperature of 30°F.

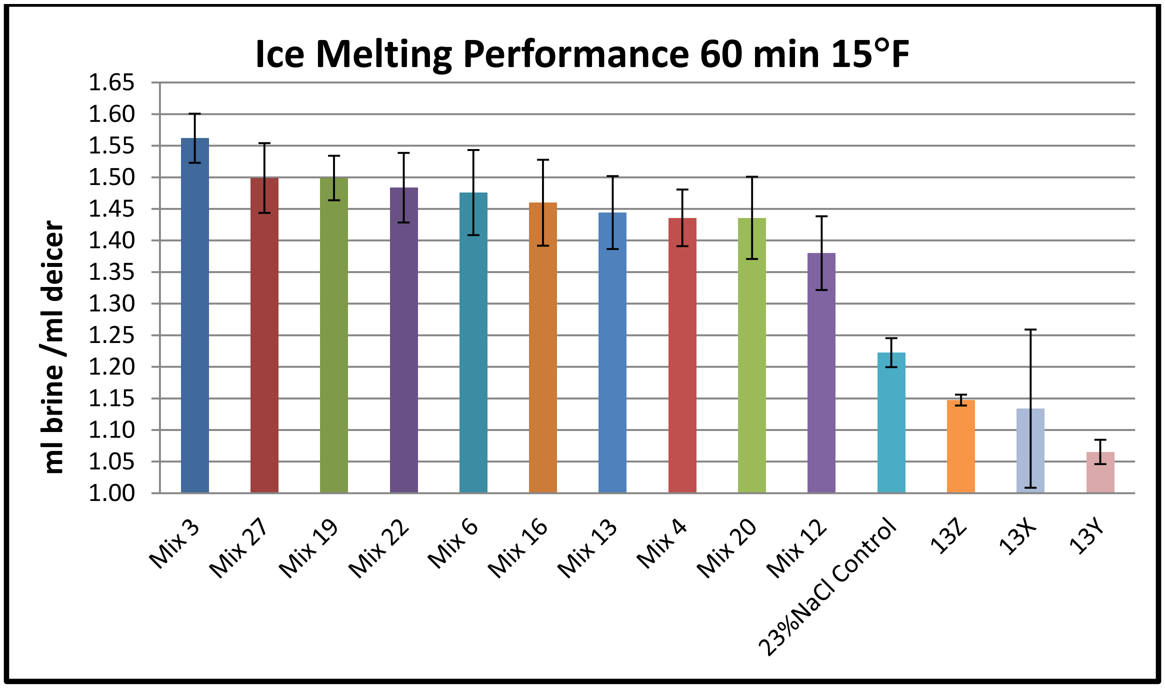
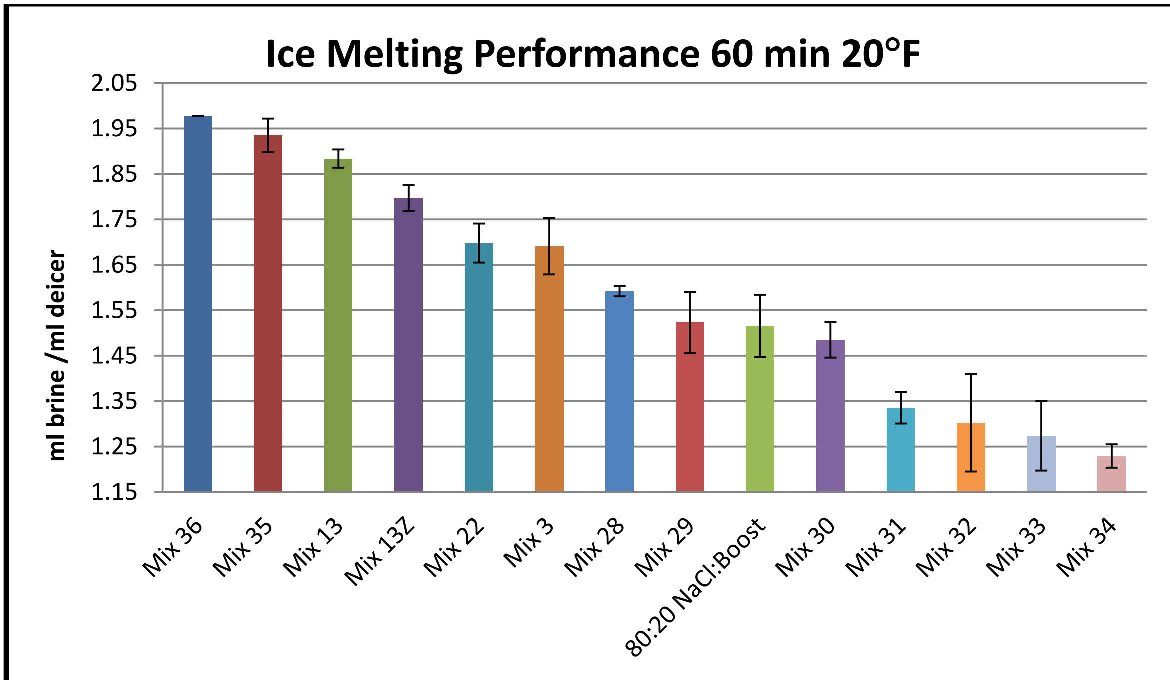


Figure 20: Ice Melting Performance at 60 min at a temperature of 15°F.

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 35 and Mix 36 was shown to be significantly better than the ice melting performance of the control and the cost of Mix 35 and Mix 36 is significantly lower than the control since a lower concentration of Boost was used to achieve better performance. The average ice melting capacities and the corresponding error bars are shown in Figure 21. The ice melting behavior with respect to time at 20°F is displayed in Figure 21. It is 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 compounds.



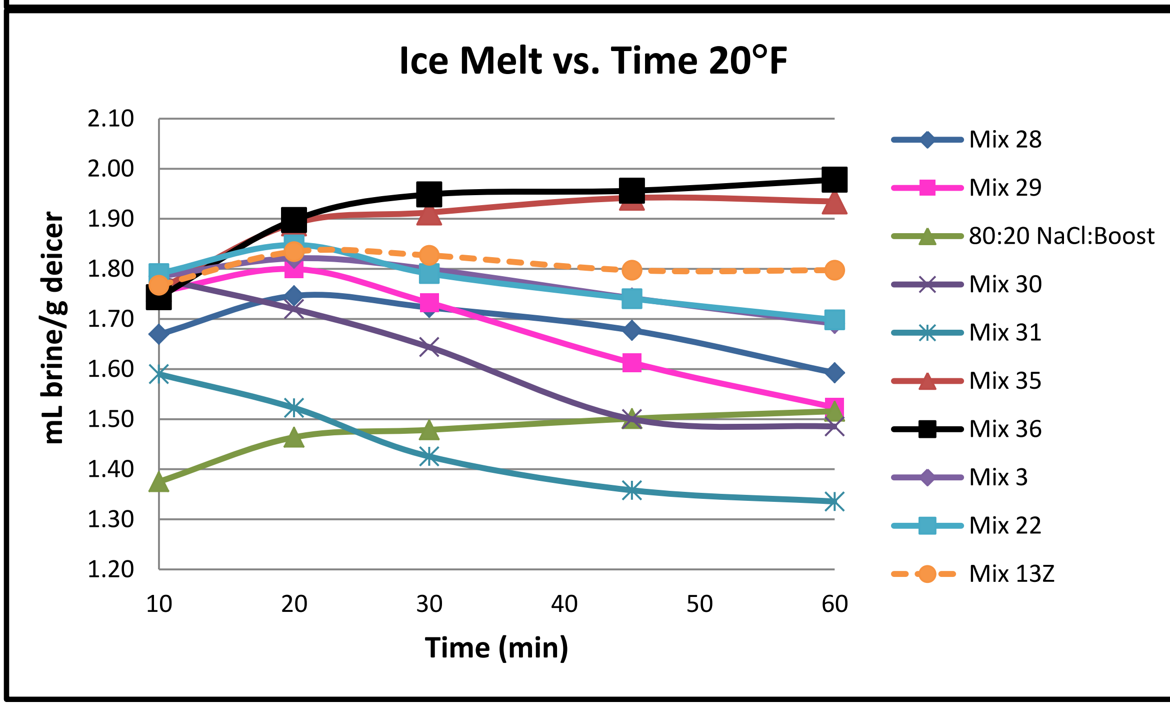


Figure 21: Ice melting test results at 20°F.

Based on the testing data, it has been observed that reducing the total by-products to a total of no more than 8% does not significantly sacrifice the ice melting capacity but effectively minimizes any evaporation of anti-icers. It is also evident that synergistic effects become a major contributor in performance mechanisms. The interactions among the various additives effectively increase the overall ice melting performance and reduce the effects of evaporation.

Corrosion Evaluation:
Commercially Available Deicers

The corrosion test is an evaluation method that provides corrosion rate assessment in terms of mils per year or milli-inch per year (MPY). Corrosion is measured with a control of deionized water and corrections are applied to account for the corrosion observed by the exposure to the deionized water control. The results are expressed in terms of Percent Corrosion Rate (PCR) and comparisons are made to the NaCl control. The PCR value of the NaCl control is 100%, whereas, the PCR value for the deionized water is 0%. Therefore, deicers with a PCR value of greater than 100% are more corrosive than 3% NaCl and deicers with a PCR less than 0% are less corrosive than water. According to Pacific Northwest Snowfighters Association, a deicer with a PCR value of less than 30% is considered acceptable.

The corrosion rates are shown in Figure 22. Product A and Product B demonstrated the lowest corrosion rates near the acceptable PCR value of 30%. In addition, Product A, Product B, Product C, and the Product D showed significantly lower corrosion rates than the salt brine control. Therefore, the results show that the agricultural products have lower impacts on carbon steel than the traditional salt brine. Furthermore, the addition of Product C to the salt brine significantly reduced the corrosion rate when compared to the salt brine alone.

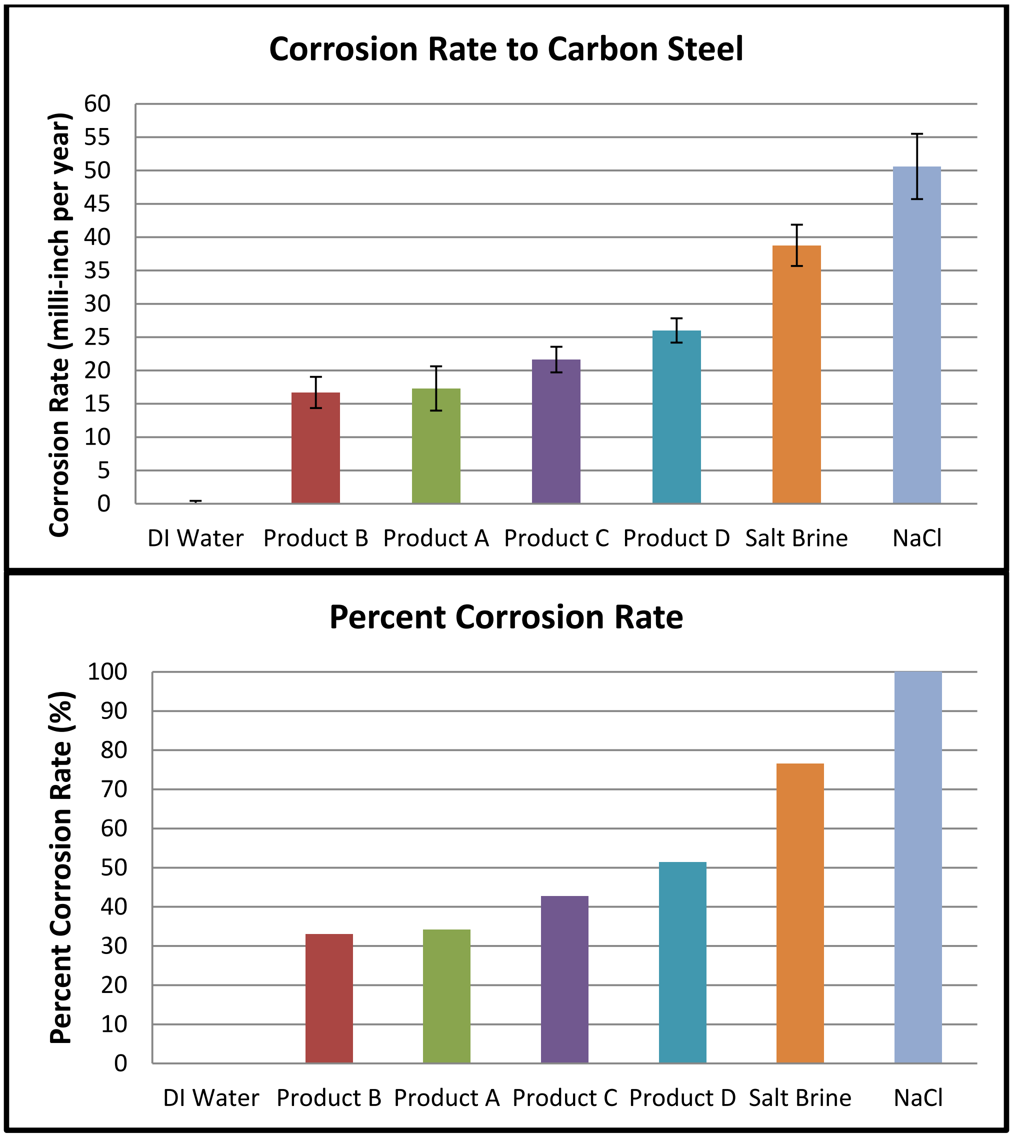


Figure 22: Corrosiveness of selected deicers to carbon steel (a) MPY; (b) PCR.

Corrosion Evaluation: Developed Deicers

The NACE TM0169-95 PNS Modified Dip Test was carried out using Mix 3, Mix 22, Mix 3A, and Mix 22A to compare the effects of corrosion to carbon steel to traditional deicers such as 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% $MgCl_2$. Figure 23 shows the calculated corrosion rates. 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. The corrosion rates for Mix 3, Mix 22, Mix 3A, and Mix 22A were determined to be significantly lower than the corrosion rates of 23% NaCl and 30% $MgCl_2$, which indicates that these formulations contain effective corrosion inhibitors that successfully minimize corrosion to steel. However, more investigation is needed to identify the mechanisms involved. Since Mix 3, Mix 22, and Mix 3A had percent corrosion rates less than 30%, they are considered acceptable corrosion inhibited products. It was determined that Sample 1 and Sample 2 have corrosion inhibition properties to carbon steel, which will significantly reduce long term costs due to corrosion impacts to equipment and various components.

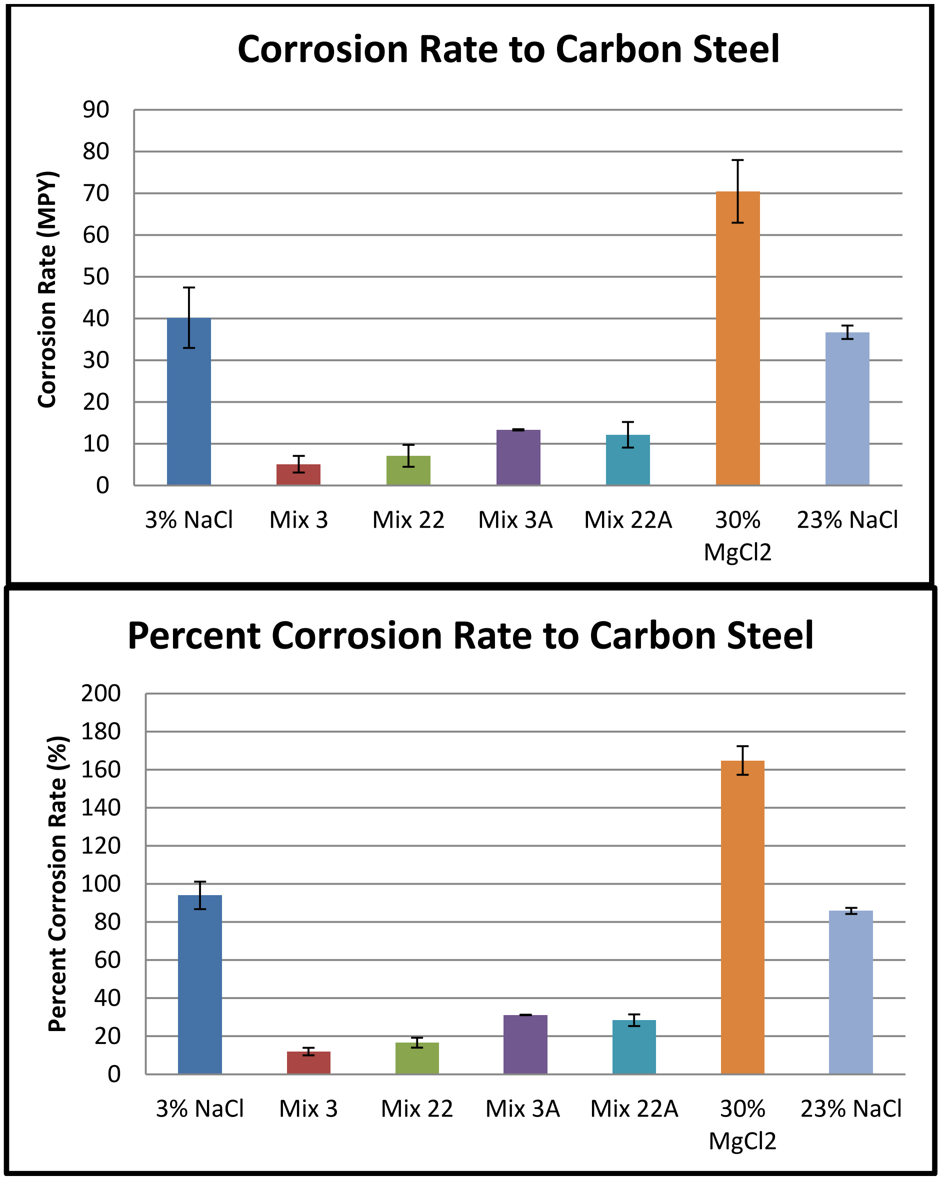


Figure 23: Results of NACE TM0169-95 PNS Modified Dip Test.

Deicer Impact on Concrete:
<u>Commercially Available Deicers</u>

The SHRP H205.8 test method reports the effects of deicers and salt scaling to PCC in terms of weight loss by comparing the final weight to the initial weight of each sample. Mass loss is mostly caused by the physical attack of concrete due to the presence of deicers, which increases the freeze/thaw damage. However, splitting tensile strength measurements can be used to assess the damages related to the chemical interactions between the deicers and the concrete. This chemical damage develops as a result of leaching of calcium rich constituents from the concrete and the weakening of the cementitious phases in the concrete.

The mass loss and splitting tensile strength results are displayed in Figure 24. Product A demonstrated minimal impact to concrete after ten freeze\thaw cycles as minimal weight loss was observed. The specimens exposed to Product A showed lower weight loss and less salt scaling than the specimens exposed to the deionized water. In addition, the specimens exposed to Product D and Product B showed little weight losses of 0.48% and 0.51%, respectively. The salt brine control had the highest weight loss of 1.9%.

Previous research has shown that magnesium chloride demonstrates minimal weight loss and salt scaling to PCC at low concentrations. Since one of the main components of Product A is magnesium chloride, it is estimated to behave similarly to magnesium chloride with respect to impacts on concrete thus resulting in minimal damage.

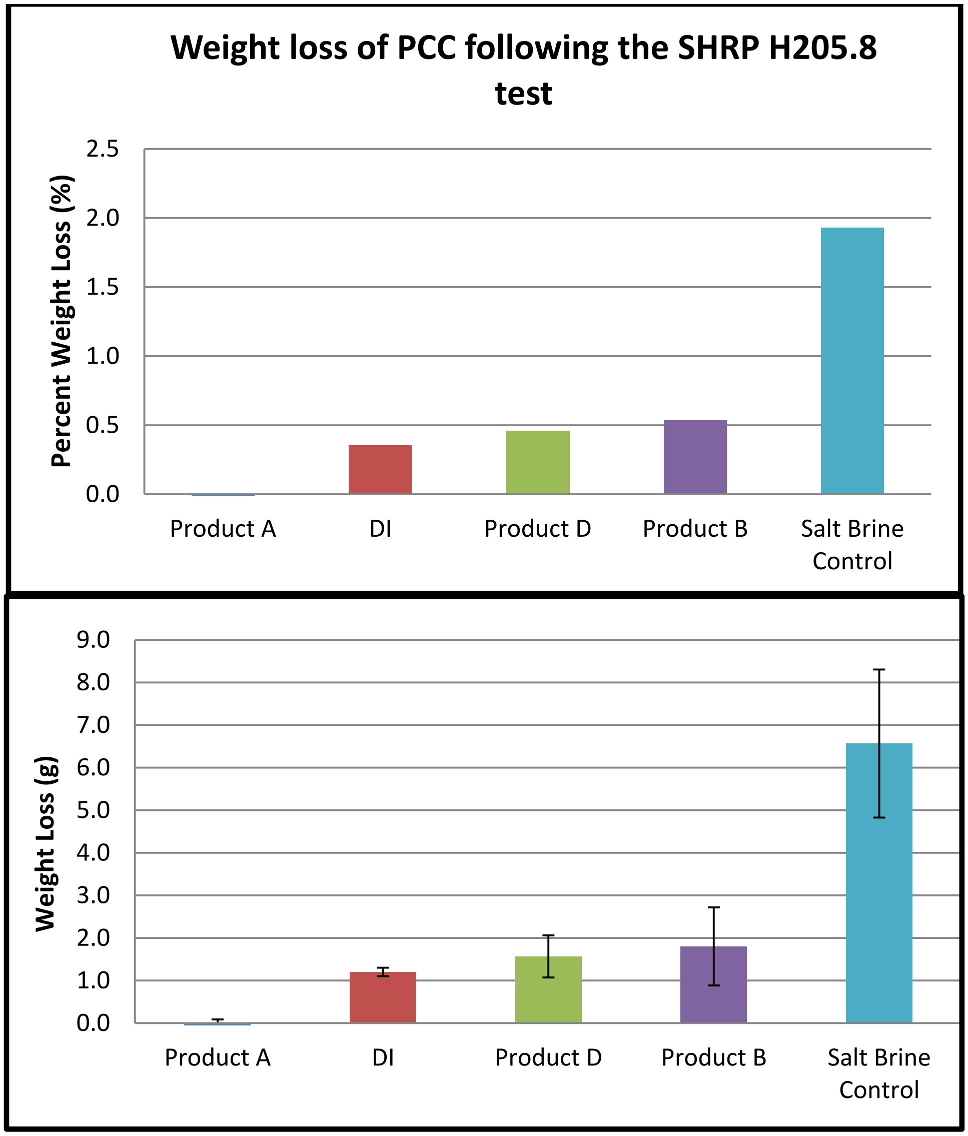


Figure 24: Average weight loss of PCC specimens after 10 freeze/thaw cycles.

In addition to mass loss, splitting tensile strength evaluation determined that the concrete specimens exposed to Product B and Product A had the lowest strength thus the highest reduction in strength after 10 freeze\thaw cycles as shown in Figure 25. Although the concrete specimens exposed to Product A and Product B had minimal physical damage as assessed by weight loss, these concrete specimens had the lowest tensile strength and thus the highest reduction in strength, which can be attributed to the chemical degradation of the cementitious phases in the concrete. Furthermore, it has been shown that magnesium chloride causes significant damage to PCC; therefore, since magnesium chloride is the main component of both Product A and Product B similar impacts are observed (Cody et al. 1996; Mussato et al. 2004; Shi et al., 2009c). The concrete specimens exposed to both of the controls, deionized water and salt brine, showed the highest splitting tensile strength and thus the lowest reduction in strength after ten freeze/thaw cycles.

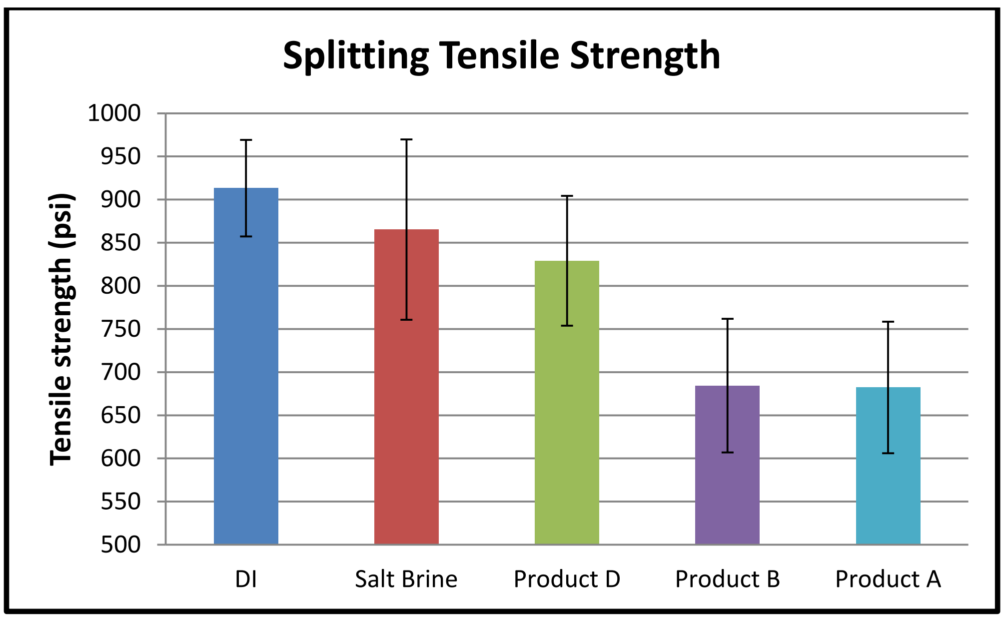


Figure 25: Splitting tensile strength of PCC specimens after 10 freeze/thaw cycles.

<u>Porosity Calculations</u>

An x-ray micro-computed tomography (micro-CT) scanner was used to generate thousands of 2D images for each of the five Portland cement concrete samples that underwent ten freeze/thaw cycles in the presence of water or a specific deicer solution.. A total of five separate non-air entrained concrete samples were exposed to salt brine, deicer products A, B, C, and D, respectively. A representative image is shown for each in Figure 26- Figure 30. The porosity of each concrete sample was calculated from the images to determine the effects of the deicer and freeze/thaw exposure on the concrete. Table 18 shows the results of the micro-CT porosity calculations. It was determined that the porosity of the sample exposed to salt brine and product D showed a decrease in porosity compared to the control (deionized water). Since product D contains a high amount of salt brine, it behaved similarly to the salt brine. It is hypothesized that during the freeze/thaw cycling the salt brine initiated chemical reactions with the cement hydrates causing the formation of products within the cement matrix, which decreased the overall porosity of the concrete sample while showing the symptoms of spalling to the outside surface. This mechanism was likely responsible for the observed reduction in strength for the concrete samples exposed to salt brine and product D. In contrast, products A and B contain $MgCl_2$, which causes leaching of Ca^{2+} cations from the cement paste. This mechanism has been proven to reduce strength in Portland cement concrete (Cody et al. 1996; Mussato et al. 2004; Shi et al., 2011). The concrete samples exposed to products A and B behave similarly to concrete samples exposed to $MgCl_2$. A significant decrease in strength was observed along with an increase in porosity relative to the control, which is due to leaching of the Ca^{2+} cations causing the degradation of the cement paste. In both cases (exposure to $MgCl_2$ or NaCl deicer solutions), the underlying mechanisms for porosity and strength changes merit further investigation and additional chemical analyses are needed to shed more light on them. This study, however, has illustrated that the two types of deicers deteriorate concrete by different mechanisms and the porosity measurements do not have direct correlation with strength readings of the concrete samples.

Table 18: Results of micro-CT porosity calculations.

Deicer	**Porosity (%)**
Salt Brine	2.418
Product D	2.556
Water Control	3.263
Product A	3.368
Product B	4.222

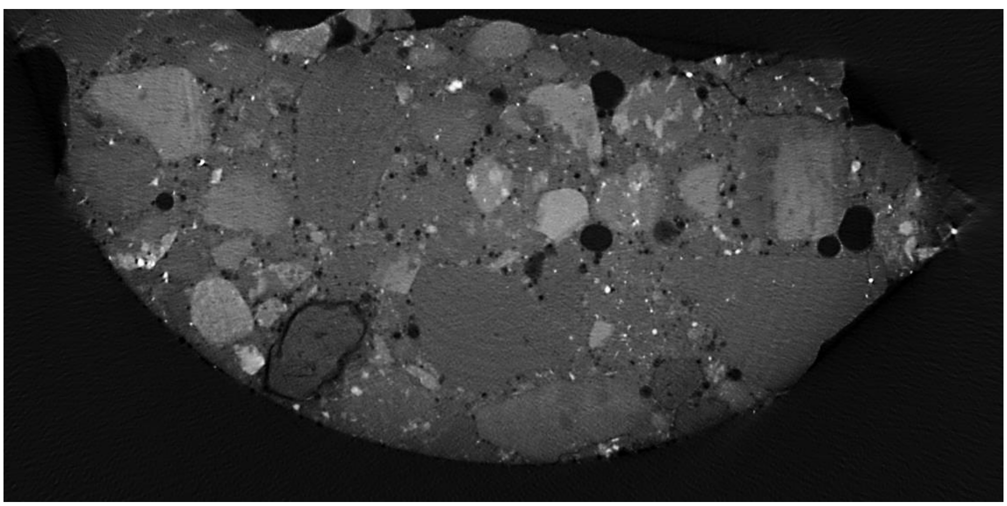


Figure 26: Micro-CT image of concrete sample exposed to salt brine.

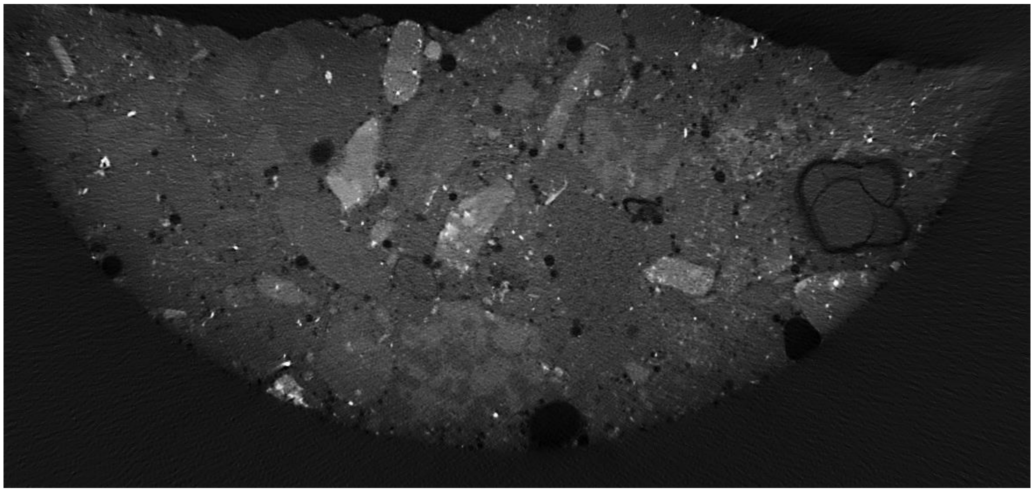


Figure 27: Micro-CT image of concrete sample exposed to Product D.

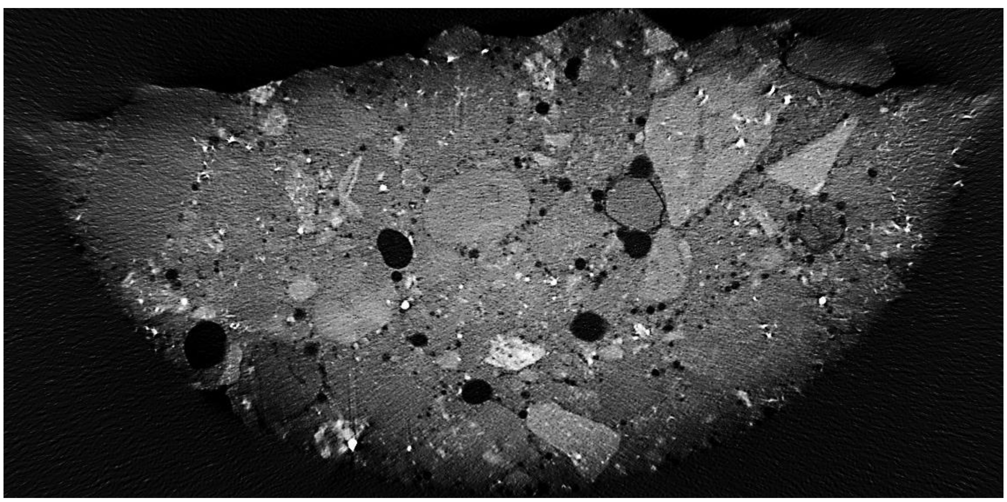


Figure 28: Micro-CT image of concrete sample exposed to water.

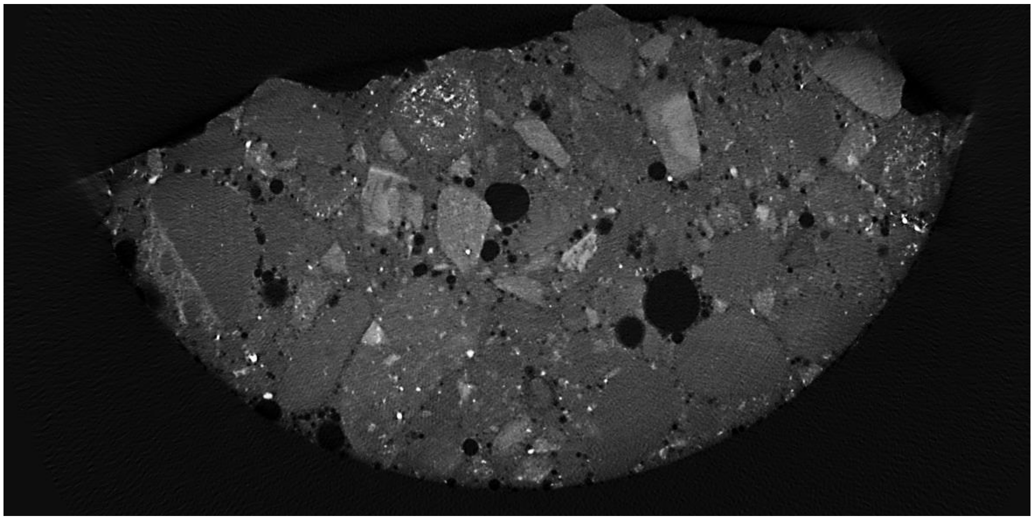


Figure 29: Micro-CT image of concrete sample exposed to Product A.

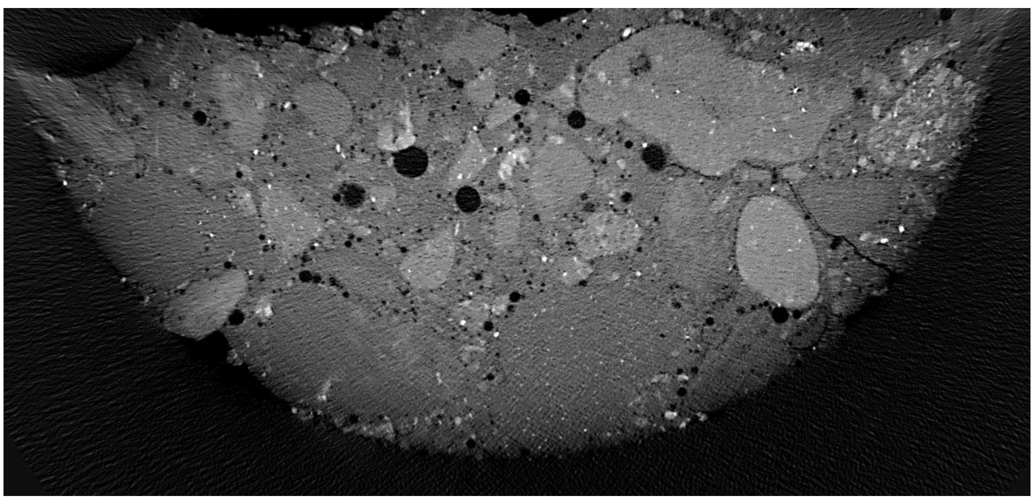


Figure 30: Micro-CT image of concrete sample exposed to Product B.

Deicer Impact on Concrete: Developed Deicers

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). Therefore, 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 Figure 31, illustrate the significant differences among various anti-icer formulations. 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 3A and Mix 22A had significantly lower impacts on the PCC specimens. Damage of PCC in the presence of NaCl or NaCl-based deicers can be explained by the role of NaCl in dramatically accelerating the freeze/thaw cycles and thus worsening the physical and chemical damages. Magnesium chloride did not seem to 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 results 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 assuming a 3-to-100 dilution ratio 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). A longer exposure time with the $MgCl_2$-based deicers will likely cause considerable damage to concrete as well.

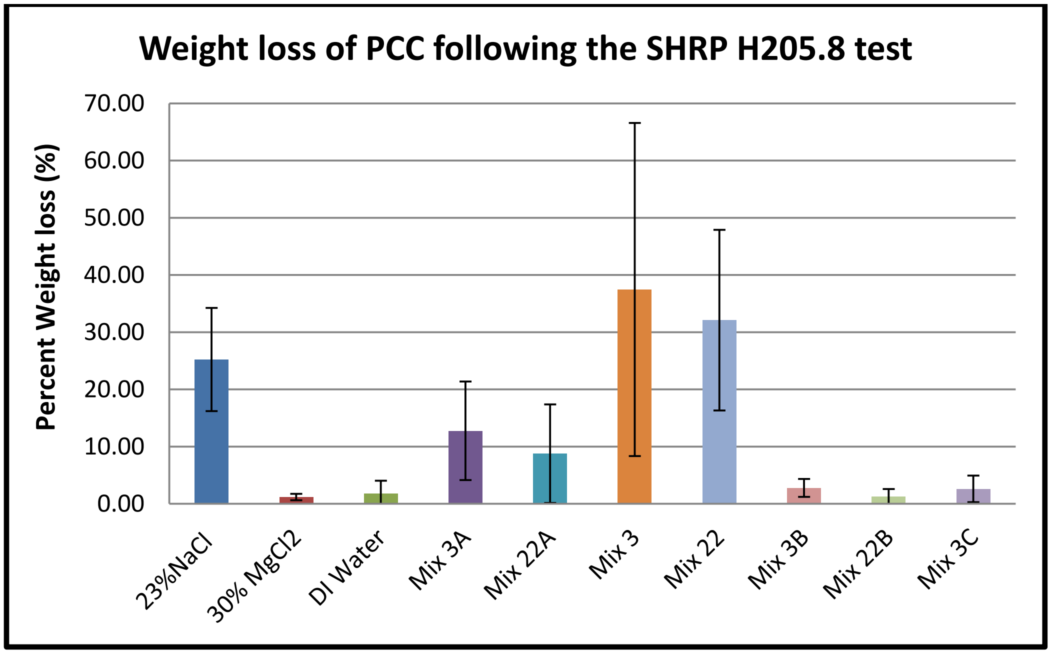


Figure 31: Results of freeze/thaw weight loss of PCC following SHRP H205.8.

Concluding Remarks

There are considerable data gaps with respect to the quantification of deicer performance and impacts especially for new and emerging products derived from agricultural sources. This research identified a specific set of liquid deicers made from agricultural resources and subsequently evaluated their performance and impacts to carbon steel and Portland cement concrete. It was determined that Product A had the highest ice melting capacity at both 15°F and 5°F and that all of the agricultural products had ice melting performance similar to the salt brine control. In addition, it was demonstrated that Product A and Product B have significantly lower corrosion rates to carbon steel than the salt brine control. All of the agricultural products showed significant corrosion inhibition properties to carbon steel. Lastly, Product A and Product B had minimal physical impacts to PCC; however, specimens exposed to Product A and Product B had the highest reduction in splitting tensile strength after ten freeze/thaw cycles. All of the agricultural products tested showed a reduction in splitting tensile strength as a result of chemical degradation of the cementitious paste in the concrete, which causes a decrease in strength. Therefore, it is recommended to avoid using agricultural products near concrete infrastructure.

Agricultural products made for snow and ice control offer promising ice melting performance with reduced impacts to metals and can be effective alternatives to conventional chloride based deicers. Additionally, products made from agricultural processes can assist to reduce the environmental impacts observed from the continued use of chloride based deicers and by utilizing sustainable resources thus reducing waste products.

Additional research is needed to fully understand the effects of using snow and ice control products derived from agricultural processes and to further evaluate performance of agricultural products. Additional performance testing need to be performed, which consist of field testing or pilot studies in which products are used for various applications by winter maintenance agencies and direct observations can be made to assist overall snow and ice control. Environmental impacts such as toxicity and effects on water, vegetation and soils need to be evaluated in order to increase widespread use of agricultural based products. Furthermore, specific priorities for certain winter maintenance agencies need to be taken into consideration when selecting potential alternative deicers as specific priorities significantly change based on location and agency needs.

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, Mix 3A, and Mix 22A— that have minimal 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, Mix 3A and Mix 22A 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.

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. Further research will also help the value-added utilization of distillery by-products. Extensive research and development in the utilization of distillery by-products is needed to effectively advance the production of bio-based anti-icer formulations in a cost-effective and environmentally conscious approach. 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.

Applications

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 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 ADOT&PF end users and other stakeholders in producing formulations that meet user needs, are environmentally safe, and can be readily implemented. This research will help the value-added utilization of industrial by-products.

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.

CHAPTER FOUR

4. PROTECTING MAINTENANCE EQUIPMENT AGAINST CHLORIDE ROADWAY DEICERS: CORROSION MECHANISMS, TEST METHODS, AND PROACTIVE APPROACHES

Contribution of Authors and Co-Authors

Manuscript in Chapter 4

Author: Scott Jungwirth

Contributions: Collected and analyzed data. Conducted site visit to gather information. Wrote draft of manuscript.

Co-Author: Dr. Xianming Shi

Contributions: Provided guidance and feedback on first draft of manuscript.

Co-Author: Nicholas Seeley

Contributions: Reviewed and summarized literature.

Co-Author: Yida Fang

Contributions: Reviewed and summarized literature. Performed laboratory testing.

Manuscript Information Page

Scott Jungwirth, Xianming Shi, Nicholas Seeley, Yida Fang

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Introduction

Roadway maintenance equipment in cold climates is exposed to high amounts of chloride-based deicers that are inherently corrosive. As such, various structural, hydraulic, and electrical components on maintenance equipment are vulnerable to the deleterious effects of chloride roadway deicers and their premature deterioration can negatively affect the performance, reliability and service life of the equipment fleet. This work aims to shed more light on this important asset management issue, by providing an overview of the relevant corrosion mechanisms, corrosion-prone parts, and test methods. More importantly, this work presents an overview of current approaches available to manage the risk of deicer corrosion to equipment assets, including design considerations, materials selection, and maintenance strategies. The information aims to enable equipment engineers and managers to gain a better understanding of this technical issue and to make more informed decisions in corrosion risk management.

In the last two decades, the northern regions of North America have experienced a gradual increase in the use of roadway deicers. Meanwhile, concerns over the potentially negative effects of roadway deicers on the transportation infrastructure (Shi et al., 2011, Shi et al., 2010a, Shi et al., 2009a, http://www.coe.montana.edu/me/faculty/Shi/DeicerRebarANNs.pdf Shi et al., 2012, Pan et al., 2008) and the natural environment have significantly increased (Fay and Shi, 2012, Levelton Consultants 2008, Fay et al., 2013, Shi et al., 2009b). Meanwhile, the corrosive effects of roadway deicers on motor vehicles, particularly on roadway maintenance equipment, have been a less documented yet equally important issue (Shi et al., 2009c, Li et al., 2013). Roadway maintenance equipment in cold climates is exposed to high amounts of chloride-based deicers that are inherently corrosive (Shi et al., 2013a, Shi and Akin, 2012, Shi et al., 2013b, Fay and Shi 2011). As such, various structural, hydraulic, and electrical components on the maintenance equipment are vulnerable to the deleterious effects of chloride roadway deicers (as shown in Figure 32) and their premature deterioration can negatively affect the value, performance, reliability and service life of the equipment fleet and increase its life-cycle cost and safety risk (Li et al., 2013, Menzies, 1992).

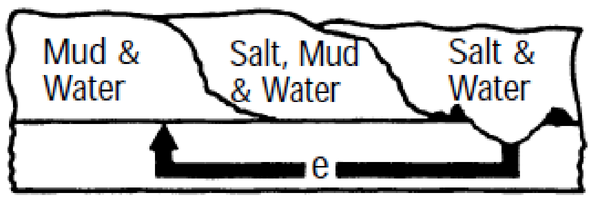
Figure 32: Side-discharge salt spreader showing extensive corrosion.

The implementation of best engineering practices and anti-corrosion technologies could reduce the cost of metallic corrosion from 25% to 30% (Menzies, 1992). Yet, the knowledge underlying the corrosion and corrosion mitigation for metals at the risk of chloride-based deicers remains scattered. In this context, this work provides an overview of the relevant corrosion mechanisms, corrosion-prone parts, and test methods. More importantly, this work presents an overview of current approaches available to manage the risk of deicer corrosion to equipment assets, including design considerations, materials selection, and maintenance strategies. The information aims to enable equipment engineers and managers to gain a better understanding of this technical issue and to make more informed decisions in corrosion risk management.

Corrosion Mechanisms

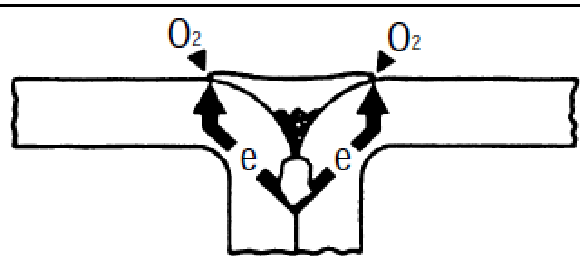
Types of Corrosion

Corrosion is an electrochemical process initiated by an electrolyte present on the surface of a metal, and there are many possible types of corrosion depending on the specific combination of metal and its service environment. General or uniform corrosion occurs over a substantial amount of the metallic surface and is the most predictable type. Yet, in reality, most corrosion occurs in a localized manner (i.e., attacking a specific area of the metal) and is more difficult to predict. Among them, crevice corrosion occurs at the interface of a metal and another surface, often where a confined or stationary area is formed to trap electrolyte, as illustrated in Figure 33 (Light Truck 1999). Commonly, this is observed beneath surface deposits, seals, gaskets, washers, clamps, sleeves, and similar junctions. Pitting corrosion is frequently observed on the surface of metals (e.g., stainless steel) and is often difficult to detect considering the relatively small amount of metal loss during the process.



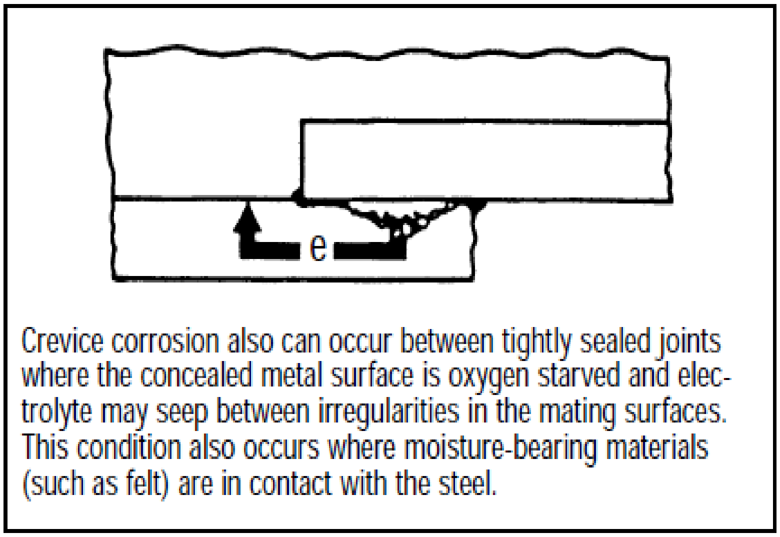
Electrolyte composition gradients are probably the most common cause of corrosion. Clumps of mud frequently collect under car fenders. The varying concentrations of salt and water encourage corrosion.

(a)



Crevice corrosion is caused by a gradient between the oxygen at the surface of the electrolyte and oxygen-starved electrolyte at the bottom of the crevice. Typical of the weldments, sheet-metal joints, and rough surfaces where water may be trapped, the oxygen gradient also causes a rough microfinished surface to corrode faster than a smooth surface.

(b)



(c)

Figure 33: Schematics illustrating crevice corrosion (a) under poultice; (b) at weld joint; and (c) at lap joint (Light Truck 1999).

Intergranular corrosion initiates at grain boundaries of metals (e.g., aluminum alloys) and commonly spreads along adjacent grain boundaries. Galvanic corrosion occurs when two dissimilar metals are in contact with one another in the presence of an electrolyte. As a result, electrical current flows from the metal acting as the anode to the metal acting as the cathode. The presence of residual stresses from the metal's manufacturing processes and cyclic loadings during service are common causes of stress corrosion cracking (SCC) and corrosion fatigue, respectively, which are forms of corrosion exacerbated by the mechanical stress.

In 2005, the authors conducted an investigation of the corrosion of trucks exposed to deicers applied on Montana highways and detected significant crevice corrosion between the conjunction of the winch frame and the truck frame and in conjunctions on the truck frame. In addition, filiform corrosion was observed under the coating near frame corners and on brake chambers. Other forms of less significant corrosion were also observed on the trucks, such as pitting corrosion on the outer surfaces of stainless steel parts and aluminum fuel tanks, galvanic corrosion and SCC in the welding zones or conjunction of dissimilar metals. According to a recent NCHRP report (Levelton Consultants 2008), "crevice corrosion and poultice corrosion typically occur where dirt and moisture are trapped – between adjacent pieces of metal, under gaskets and at fasteners, or on the surface of motor vehicle components. This is compounded by ingress of snow and ice control chemicals that increase the conductivity of the trapped moisture".

Pitting corrosion poses a great risk to the integrity of metal as it is a self-accelerating process featuring a combination of small anode (pitted area) and large cathode (non-pitted area) on the metal. Recent research has discovered that on carbon steel surfaces, an anodic area forms at the location of sodium chloride (NaCl) and a cathodic region forms around it. The size of the cathodic region is proportional to the amount of NaCl coverage (Nazarov and Thierry, 2004). The main corrosion product on carbon steel is lepidocrocite (γ-FeOOH), and the time of wetness has a greater impact on corrosion when the temperature was less than 25^{o}C (Mendoza and Corvo, 1999). Pit growth occurs where the H^+ ions formed during hydrolysis starts to diffuse. Pitting proceeds at the greatest rate near the perimeter of the droplet where corrosion product concentration is lowest, causing corrosion in the lateral direction (Thompson et al., 2007, Hastuty et al., 2010). This lateral corrosion occurs since the metal ions at the perimeter are not saturated and the perimeter is closer to the cathode, causing the metal dissolution to occur at a greater rate (Hastuty et al., 2010). Research has shown that the early corrosion of high-strength steels is characterized by the formation of a layer of corrosion product followed by preferential attack of the ferritic phase. Analysis of corrosion rate revealed that as pit depth increased the rate of corrosion decreased (Tsutsumi et al., 2007). The study examined the corrosion of stainless steel (304 SS) under a thin layer of chloride solution and found the active site of the pit grows to a maximum depth of 10 μm (Sanchez et al., 2008). Stainless steel (430 SS and 304 SS) were subjected to cyclic corrosion testing consisting of 1-hr immersion in chloride-containing solution and a few hours of drying. Pit formation and growth were found to occur before the surface of the metal dries completely (Sanchez et al., 2008). During the drying stage, the surface dryness can lead to passivation of the pit. Pit formation and growth can be induced by thin electrolyte layers that exist during atmospheric corrosion, which cause a buildup of corrosion products over the anodic areas of the metal. This buildup is due to a lack of lateral diffusion, which also causes pits to form in clusters (Sanchez et al., 2008).

During a two-year field study of deicer corrosion to specimens mounted on winter maintenance equipment (Ordine et al., 2000), intergranular corrosion attack was observed on all 5182-O aluminum (Al) specimens as shown in Figure 34 and a few A356 cast Al specimens and general corrosion on all 1008 steel and most A356 cast Al specimens. Initial corrosion of Al alloys consists of an attack on the S-phase and Al-Cu-Fe-Mn-(Si) intermetallics (Stephens et al., 2006), causing them to de-alloy and create trenching around the intermetallic particles (Queiroz et al., 2008). The cooperative corrosion stage is observed as domes of corrosion within a ring of corrosion product occur around clusters of intermetallic particles. After the penetrating attack of the grain boundary network, the corrosion begins to spread laterally. The minor grain attack then develops into more extensive intergranular attack and grain etch-out, forming pits (Queiroz et al., 2008). For pure aluminum, the cathode is the portion of the metal exposed to NaCl and the anodic attack occurs at the border with the adjacent passive metal (Nazarov and Thierry, 2004).

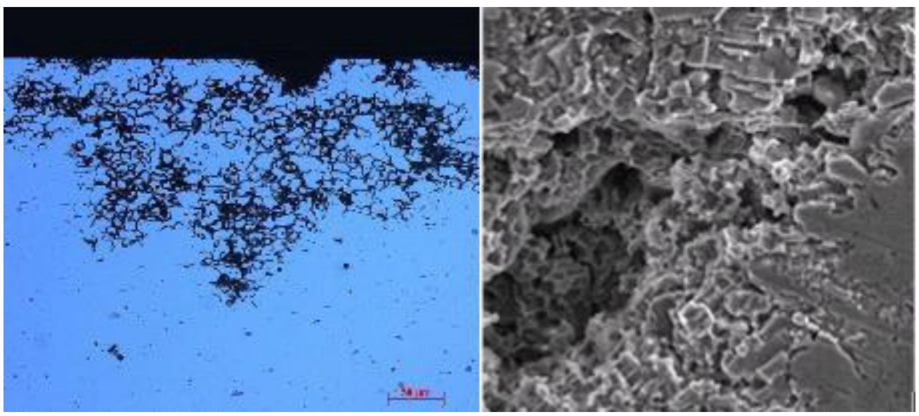


Figure 34: Scanning electron microscope (SEM) evidence of selective attack of grain boundary (left) and Mg_2Al_3 precipitates (right) on Al specimens exposed to field chloride-based deicers (Ordine et al., 2000).

Zinc is commonly used as an anti-corrosion coating for iron and steel and is often applied through hot dipping or electrochemical processes. Zinc is more reactive than the other metals and is thus commonly used as a sacrificial coating. The corrosion mechanism of zinc in a NaCl-containing environment consists of the deposition of the electrolyte on the surface of the zinc followed by the dispersion of an alkaline electrolyte film that extends from the boundary, doubling or tripling the initial radius of the drop. The corrosion product in the center of the initial droplet was found to be zinc hydroxychloride, while sodium carbonate (Na_2CO_3) is present at the perimeters. The rate of corrosion dispersion is related to the electrical potential gradient between the anodic region at the center of the initial droplet and the cathodic region located at the perimeter (Hughes et al., 2011).

Corrosion-Prone Parts

According to a survey of transportation professionals in 2012 (Li et al., 2013), chloride deicer exposure “poses the most significant risk of metallic corrosion to dump trucks, liquid deicer applicators, hoppers, front end loaders, and supervisor trucks or crew pickups”. At the component level, the most severe deicer corrosion risk was found in electrical wiring, frames, brackets and supports, brake air cans, fittings, and spreader chute. Figure 35 shows the distribution of corrosion-related repair costs among the equipment owned by the Washington State Department of Transportation (WSDOT). This indicates that metallic corrosion mostly led to repair costs in four groups: chassis, axles, brakes, frame, steering, suspension, tires & wheels; equipment dependent attachments; engine; and electrical components.

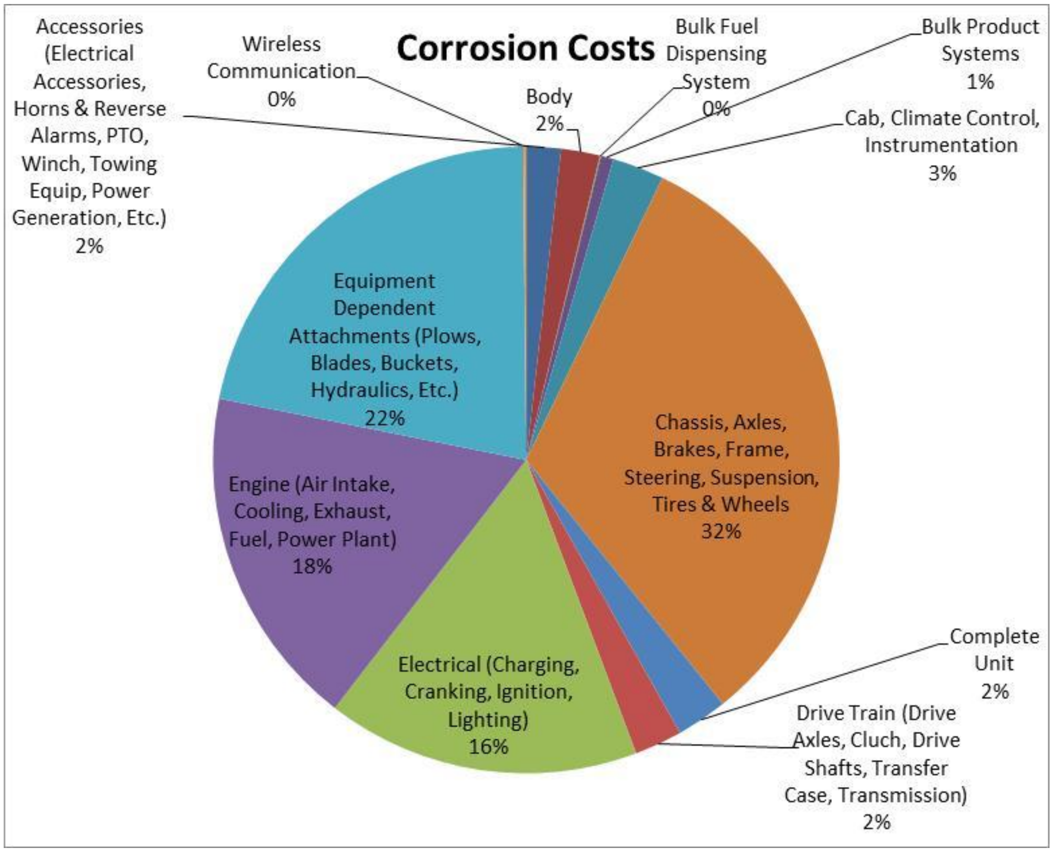


Figure 35: Allocation of corrosion-related repair costs among WSDOT equipment.

The extent of metallic corrosion is directly related to exposure time to chloride deicers. As such, components most significantly impacted by corrosion are often located on the underbody of equipment or in close proximity to the road surface and application devices. Common components most likely to be impacted by roadway deicers are brake shoes, trailer underbodies, trailer landing gear, junction boxes, door headers, sills, bulk heads, mud flap brackets, threshold plates, logistics posts, and roof bows (Neufeld et al., 2002). The structural components of the underbody are normally composed of low-carbon steel and high-strength steel. These underbody components commonly experience pitting, crevice, galvanic, and cosmetic corrosion. Cosmetic corrosion often originates where the coating or paint is damaged or penetrated (Hartley 2010). Sites likely to exhibit corrosion also include areas where dirt and other materials can deposit and remain wet such as metal folds and joints, breaks in painted surfaces, threaded-screws, and beneath coatings that do not adhere well to the surface beneath (Berg et al., 1999).

Corrosion Test Methods

To evaluate the risk of corrosion and the effectiveness of mitigation strategies, a variety of test methods to assess chloride-induced corrosion to metals have been developed. Among them are laboratory test methods and on-site test methods. In order to predict and manage corrosion damage, the original condition with respect to corrosion must be defined, such as environmental corrosivity and exposure time. Accurate corrosion projections are difficult to obtain due to the stochastic nature of corrosion and the time associated with the corrosion process. Accelerated laboratory testing is at the risk of not realistically simulating the field conditions, whereas outdoor exposure testing can be very time consuming **(**Baldi et al., 1989).

Recently, a survey performed by the Steel Structures Painting Council (SSPC) revealed that the salt spray test is the most widely used corrosion assessment method (Kinzie 2003). This test entails exposing mild steel plates of size (150 mm × 100 mm × 2 mm) in a salt spray chamber followed by drying. The metallic samples are often subjected to electrochemical measurements, of which electrochemical impedance spectroscopy (EIS) is particularly useful for revealing the mechanistic information about interfaces (Granata 2005, Collazo et al., 2010, He and Shi, 2009).

The PNS/NACE gravimetric test method is a common procedure for measuring the corrosivity of deicers. It is a modification of the National Association of Corrosion Engineers (NACE) Standard TM0169-95 by the Pacific Northwest Snowfighters (PNS). This test method entails applying 30 ml of a 3% chemical deicer solution per square inch to the surface of a coupon for testing. Then a 72-hr cyclic immersion procedure is used, with a 10-min exposure time in the solution followed by a 50-min air exposure. Electrochemical techniques are suggested as a supplement to this gravimetric method so as to obtain data related to corrosion mechanisms and kinetics in a timely manner (Collazo, 2010). Furthermore, the SHRP H-205.7 test method was developed by the Strategic Highway Research Program (SHRP) to analyze the effectiveness of corrosion inhibitors in deicing chemicals. This test method uses continuous immersion to evaluate the corrosive effects of deicers on metal. As it does not include wet-dry cycling, it does not simulate the field exposure scenario very well and long exposure times are required before significant weight loss can be detected (Shi et al., 2009d).

The U.S. Army has developed an accelerated corrosion and durability test to collect corrosion and material performance data that can be related to service life of military vehicles in highly corrosive environments. This test is based on tests developed by General Motors and has been found to accurately simulate 10 years of cosmetic corrosion and 3 years of crevice corrosion.

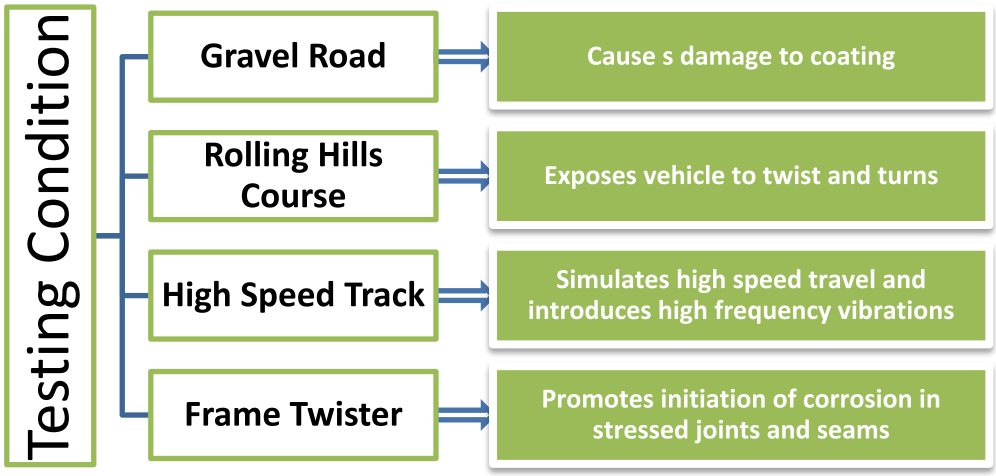


Figure 36: Durability test procedure.

This method combines accelerated corrosion tests and durability tests to introduce typical situations encountered over the service life of the vehicle. The procedure is outlined in Figure 36. The application portion of the test includes a grit trough, salt mist, and humidity chamber. The grit trough allows small particles to accumulate on surfaces, which increases time of wetness and introduces abrasive particles to the coatings. The salt mist applies a high concentration salt solution to the vehicle typical of roadways with deicers applied and the use of the high temperature and high humidity chamber is to increase the rate of corrosion (Ault, 1999).

While most corrosion tests show their high efficiency of saving costs on corrosion effect, researchers have experienced that the downside of those experiments is the required long time periods. For example, salt spray accelerated test methods requires 2000 hours of exposure and electrochemical measurements can take up to 10 weeks for results. Accelerated test methods similar to this have been proven to be very difficult to develop when the goal is to decrease the time of failure while preserving the failure mechanisms. Some discoveries have shown that corrosion resistance performance can be obtained through thermal cycling and monitoring low frequency impedance changes of coating systems. Bierwagen discovered that the use of thermal cycling paired with electrochemical impedance spectroscopy provides a faster, quantitative method to evaluate coating corrosion resistance, which leads to corrosion resistance results obtained within a week of testing (Bierwagen et al., 2000).

Recently, a new system called the wire beam electrode (WBE), which uses a multi-electrode technique, has been applied to corrosion studies. An electrochemically non-uniform metal surface occurs when a metal surface is exposed to an electrolyte causing localized defects in protective coatings and a polarization voltage across the surface. Galvanic corrosion current and corrosion potential are measured and analyzed to assess the distribution of corrosion rates with the wire beam electrode system (Tan, 1999, Jakab et al., 2008, Demo et al., 2009, Ayello et al., 2011, Weng, 2004, Kane et al., 2005).

Crevice corrosion has typically been studied using traditional methods involving weight loss measurements and inspection, which provide details on mechanisms and processes. However, the wire beam electrode system is able to assess instantaneous corrosion rates (Tan et al., 2001). Electrochemical noise resistance coupled with wire beam electrode methods offers some advantages for determining corrosion rates and patterns. The noise resistance is defined as the ratio of the standard deviations of the potential noise and the current measured noise. The noise resistance has been found to be equivalent to the polarization resistance, therefore being used to determine rates of corrosion (Tan, 2003). It was determined that the time-average noise resistances from stainless steel sensors provide a strong relationship with solution corrosivity. Furthermore, coupled multi-electrode array sensors also provide a strong correlation with solution corrosivity **(**Yang et al., 2005).

Evaluating anti-corrosion coatings often depends on electrochemical properties such as corrosion potential, DC resistance, AC impedance at room temperature, AC impedance as a function of temperature, current flowing through a coating at high potential, repetitive cathodic polarization, cathodic delamination, and current/time measurements. Properly collecting and analyzing these parameters can provide valuable coating performance information (Leidheiser 1991, Sun 2005, Davis et al., 2000, Dante et al., 2007).

Proactive Approaches to Deicer Corrosion Management

Current approaches available to manage the risk of deicer corrosion to equipment assets, including design considerations, materials selection, and maintenance strategies can greatly improve performance, reliability and service life of winter maintenance equipment while reducing overall costs related to corrosion impacts and extensive corrosion to equipment. A discussion comprising the methods and knowledge of corrosion management strategies observed from recent and past experiences is presented. For instance, it is well known that specific metals are more susceptible to corrosion than others, which makes choosing materials for desired applications an essential component of corrosion protection. Subsequently, information gained from survey responses and a maintenance operation site visit focused on specific maintenance practices to improve and maintain designs that will assist in the reduction of corrosion to equipment is presented.

A survey to gain insight on the current practices related to best practices or products used by various industries and agencies to protect their equipment or vehicles from the corrosive effects of chloride deicers was performed. The survey consisted of 15 multipart questions and was published online at https://www.surveymonkey.com/s/ZL77RPB. The survey was distributed to various professional forums, including NACE Corrosion Network, Corrosion Prevention Association (CPA), equipment engineers, Northern State DOTs, and relevant Linkedin groups. A total of 105 responses were received (30 from government agencies and 75 from private entities), among which 40 responses were complete and used for further analysis. The agency survey identified annual expenditures in the current practices of managing deicer-related metallic corrosion in the equipment fleet of responding agencies that report it as being a significant issue. While there are some responses from cities and counties, most responses came from state DOTs in the U.S. The average estimated cost of corrosion management in six areas is estimated as follows: training programs ($190,938), materials selection ($320,667), design improvements ($45,000), corrosion monitoring and testing ($10,000), proactive maintenance ($171,424), and reactive maintenance ($325,000). As such, the total cost of current corrosion management related to deicer exposure is estimated to be $1,063,029 per year. The coefficient of variance among the six cost items averaged 143%, which is attributed to the inherent diversity in the responding agencies' fleet size, level of deicer exposure and other environmental conditions, rules of practices in corrosion management, etc. Nonetheless, it is assumed that the average cost numbers reported here reflect the current practice by an "average agency" (e.g., a northern state DOT with an average fleet size asset) (Li et al., 2013).

The agency survey also identified the current risks of deicer corrosion to the equipment fleet of responding agencies that report it as being a significant issue, estimated under the current level of corrosion management. The deicer exposure leads to risks in six areas: an average of 17.3% depreciation in equipment value, an average of 8.5% increased equipment downtime, an average of 11.9% in reduced equipment reliability, an average of 17.3% in reduced equipment service life, an average of 19.6% in increased premature repair and replacement, and an average of 1.5% safety risk due to faulty parts on equipment (Li et al., 2013).

Materials Selection

Materials selection for corrosion-resistance is one critical aspect of the overall design process. Materials of construction should be economical yet provide adequate resistance to the specified service conditions and consider the likely corrosion mechanisms in the equipment/component's expected operational condition. Advancements in technology have allowed for various improvements in material selection to minimize corrosion. It is well known that corrosion resistance performance greatly varies among dissimilar types of metal, which needs to be taken into consideration when selecting materials for specific applications. For instance, in natural environments, unalloyed aluminum has superior corrosion resistance properties relative to carbon steel but poor mechanical strength. The Cambridge Material Selector (www.grantadesign.com) and DoD Corrosion website (www.corrdefense.org) provide useful information sources for materials selection. Metallurgists and corrosion engineers have been attempting to improve the aluminum mechanical behavior without losing corrosion resistance properties. If a high-strength alloy is needed, it is recommended to use exfoliation resistant tempers like T76 or 7xxx alloys with copper. Copper-free alloys and alloys with low noble impurities or alloying elements contain high pitting corrosion resistance. Alloys in the 1xxx, 2xxx, 3xxx, 5xxx, and 6xxx series contain the highest corrosion resistance properties (Reboul and Baroux 2011)**.** A study conducted by Uchida and Mochizuki found that the use of zinc coating on aluminum and steel sheet displayed effective anticorrosion performance. A direct relationship between corrosion and the amount of zinc coating on aluminum sheets was also observed (Uchida and Mochizuki 2000).

Payer suggested that a combination of environmental stresses can lead to the failure of automotive electronics, frequently initiated at the contact surfaces of connectors (Payer 1992). Therefore, resistance to chemical, thermal, and mechanical stresses are essential for connector reliability and corrosion protection of the connector and more resistant contact surfaces can be achieved via proper design, materials selection and the use of seals/grommets and lubricants.

The survey respondents were also surveyed for the corrosion-prone material seen in their agency's equipment fleet and the results are summarized in Table 19 (Li et al., 2013). From Table 19, it can be obtained that the cast irons have the most serious general or uniform corrosion (81.3%) followed by carbon steels (73.5%), composites (68.8%)

and magnesium alloys (68.2%). On the other hand, aluminum alloys and stainless steels have the most serious localized corrosion (50%) followed by metallic glass (43.8%), metallic coatings (40.0%) and magnesium alloys (36.4%).

Table 19: Common types of corrosion-prone material and their respective forms of corrosion seen in respondents' agency's vehicles/equipment caused by exposure to chloride deicers.

Materials	General or uniform corrosion	Localized corrosion	Response count (*)
Cast irons	81.3% (26)	21.9% (7)	32
Aluminum alloys	55.9% (19)	50.0% (17)	34
Magnesium alloys	68.2% (15)	36.4% (8)	22
Copper and copper alloys	67.9% (19)	35.7% (10)	28
Carbon steels	73.5% (25)	32.4% (11)	34
Stainless steels	50.0% (12)	50.0% (12)	24
Metallic coatings	64.0% (16)	40.0% (10)	25
Metallic glass	56.3% (9)	43.8% (7)	16
Composites	68.8% (11)	31.3% (5)	16

* Some respondents selected both forms of corrosion.

Design Improvements

Corrosion prevention and control begins with material selection, however the use of corrosion engineering principles in design can also have a significant impact. If an operating environment is considered to be corrosive, corrosion prevention designs of components need to be taken into consideration. For example, a design should be used to avoid locations where water may accumulate. Heat treatment process called Retrogression Re-Aging (RRA) is another approach to improve the corrosion resistant properties of designs. RRA treatment consists of a retrogression phase of heating at 195 °C for up to 40 minutes, quenching, and then heating at 120 °C for 24 hours, which is known as the re-aging phase. RRA has been tested by the Air Force Research Laboratory and was found to be successful for improving corrosion resistance of 7075-T6 alloy (Agarwala 2004).

Agencies should consider corrosion-resistance requirements at the stages of materials selection and design. Existing knowledge about the anti-corrosion performance of various materials and design configurations in various deicer-laden service environments should be utilized to refine the equipment purchasing specifications developed by the transportation agencies. For instance, the zinc coating on aluminum and steel substrates can provide effective anti-corrosion performance. Structures designed for resistance to atmospheric corrosion should always provide easy drainage from all exposed surfaces. Stress corrosion cracking (SCC) can be prevented by substituting a more resistant alloy, removing the tensile stress, or making the environment less aggressive. For example, in SCC of austenitic stainless steel by chlorides, substitution of ferritic or duplex stainless steels often alleviates the problem. The ferritic stainless steels may be subject to pitting, but the duplex grades are more resistant. Crevice corrosion can be minimized by proper design of welded joints and gaskets that minimize crevices. Welded joints are thus preferable to bolted and riveted joints; however, the welds must be properly designed and constructed to eliminate crevices. Gaskets must be properly sized to minimize crevices exposed to the corrosive solution and should not use absorbent or permeable material. Sealing compounds and inhibitive coatings on flange faces also provide a barrier from chloride deicing chemicals. Galvanic corrosion can be avoided by using the same type of metallic material for the same structure. If dissimilar alloys have to be used in electrical contact with each other, galvanic corrosion can be controlled by selection of alloys that are adjacent to each other in the galvanic series. In other unavoidable couples, the anode alloy should be larger in area compared to the cathode and both members of a galvanic couple should be coated to avoid any small anode area at coating defects. If feasible, dissimilar alloys should be electrically insulated from each other at their junction. Crevices between dissimilar alloys should be avoided, under which the corrosion is more serious than galvanic corrosion or crevice corrosion alone. Furthermore, configuration of structures should be as simple as possible. Design should allow maximum access for maintenance and repair painting. Box sections have poor access to coatings, collect water and debris, and maximize possibilities of corrosion. Edges and corners are difficult to coat uniformly, and thinly coated protrusions are susceptible to corrosion. The use of simple cylindrical structural members is preferred since they allow for ease and uniformity of paint application as well as convenient inspection (Aluminum Association, Inc. 2001).

Maintenance Practices

Winter maintenance agencies typically integrate a wide range of methods and procedures that may involve routine washing, reapplication of coatings, grit blasting, mechanical removal of rust, or the use of rust removers to improve the service life of equipment. Surface protection is a common successful corrosion preventative strategy, which is achieved in various methods. Surface treatments such as applying a coat of paint reduce the contact between the metal and deicing agents, thereby preventing corrosion. Palmer suggested that regular wash operations (coupled with the addition of environmentally acceptable corrosion inhibitors) and aftermarket rust-proofing (coating formulations able to displace moisture and penetrate corrosion product layers) can both be effective solutions in mitigating deicer corrosion to motor vehicles (Palmer 1992). Li et al. conducted some laboratory tests to assess the effectiveness of four anticorrosion coating products, four spray-on corrosion inhibitors, and six salt removers. Under the investigated conditions, it was determined that at least one coating (Rust Bullet™), one inhibitor (Krown™), and two salt removers (HoldTight™ and ChlorRid™) exhibited outstanding performance in reducing the corrosion effect of magnesium chloride solution to carbon steel (Li et al., 2013).

Winter maintenance agencies have reported various modifications of specific components to mitigate impacts of chloride deicers to equipment. In particular, WSDOT has been actively involved in extensive corrosion research and development projects as it has recognized the need to protect its equipment asset from deicer corrosion. WSDOT has made substantial progress towards effective corrosion prevention methodologies and has been very proactive with various corrosion mitigation approaches such as appropriate deicer and corrosion inhibitor selection, equipment modification techniques, and regular maintenance schedules.

Recent research and information collected from the WSDOT has identified various best practices focused on reducing impacts to equipment from roadway deicers. These specific techniques have been an integral part of effective reduction of corrosion rates on winter maintenance equipment and have allowed WSDOT to achieve the recommended 12-year service life for their equipment fleet.

- Use high-quality weather-proof terminations, high-quality primers and topcoats

- Position wiring to reduce damage to the outside casing of wires.
- Do not probe the wires to test for continuity.
- Use dielectric silicone for sealing damaged areas or connections.
- Open up closed areas and allow them to flush out easily.
- Use welds to close and seal off certain areas that are difficult to drain.
- Caulk welds prior to painting.
- Do not apply paint to the rubber seals around lights.
- Sealed hydraulic components.
- Sealed brake canisters.
- Install modified protective cover for battery.
- Eliminate junction boxes wherever possible.
- Install modified electrical junction boxes, which are mounted inside the cab and off the floor.
- Replace original oil pans with more resistant zinc oil pans.
- Replace radiators every two years.
- Specify self-healing undercoats and fender liners for chassis.

Some additional best practices collected from other agencies include: eliminating areas that solids and liquids may accumulate; specifying rust-proof brake shoes when rebuilding; specifying self-healing undercoats for chassis; specifying fender liners for chassis; using dielectric silicone for sealing damaged areas or connections; and avoiding any damage of wiring insulation. In addition, a general consensus of survey respondents was observed with respect to replacing certain corrosion-prone components with corrosion-resistant materials such as stainless steel or non-metallic wherever possible or be inspected and replaced on a regular basis. It has been reported by a survey respondent that stainless steel components last 25% to 100% longer than carbon steel.

Additionally, WSDOT has implemented the following best practices: consistent washing after application, regular rinsing and localized cleaning (followed by fast drying), using high-quality primers and topcoats in equipment specifications, using composite materials less susceptible to corrosion, and protecting new and replacement components prior to installation with wraps, covers, or shields.

A laboratory investigation performed by the authors confirmed that power-washing with the salt remover, *HoldTight* or similar products, significantly enhanced the anti-corrosion property of carbon steel and stainless steel against deicer corrosion. It is recommended to frequently wash equipment exposed to deicers to minimize the possibility of chloride penetration into crevices, coatings or the metal surface. The use of the salt remover *HoldTight* can significantly improve corrosion performance of carbon steel and stainless steel when subjected to 30% $MgCl_2$ solution (unpublished data). The appropriate application of salt removers implemented with high pressure washing would greatly improve proactive maintenance of equipment and help preserve the value of the equipment asset.

Additional laboratory testing following cyclic exposure methods confirmed that once active corrosion of metals has started, power-washing should be coupled with periodically applying a corrosion inhibitor such as *Krown T40* or *Rust Oleum* immediately after the equipment is washed clean and dried to effectively protect aluminum, stainless steel and carbon steel components against corrosion related to NaCl or $MgCl_2$ deicers. Other methods of aftermarket rust-proofing may include the application of post-assembly coatings (e.g., *Rust Bullet*). It was shown that applying a corrosion inhibitor reduced corrosion rates by at least 99% and similarly, a one-time application of a protective coating such as *Rust Bullet* reduced corrosion rates by at least 99.5% (Shi et al., 2013).

Sharman compared the efficiency of a newly developed biodegradable rust remover and mechanical rust remover and found that this approach creates an inexpensive method of removing rust and improving the quality of the surface of the steel. Moreover, after the surface was cleaned, coating adhesion greatly improved causing an increase in performance of the coating thus increasing the service life of the material (Sharman 2009). The rust remover offers a great alternative to grit blasting and mechanical removal of rust particularly in situations where grit blasting may be prohibited or unfeasible for safety and environmental reasons.

Figure 37 provides a detailed flow chart of corrosion prevention and control tasks, which can be adopted by maintenance agencies to ensure effective implementation of a corrosion management program (USD 2007).

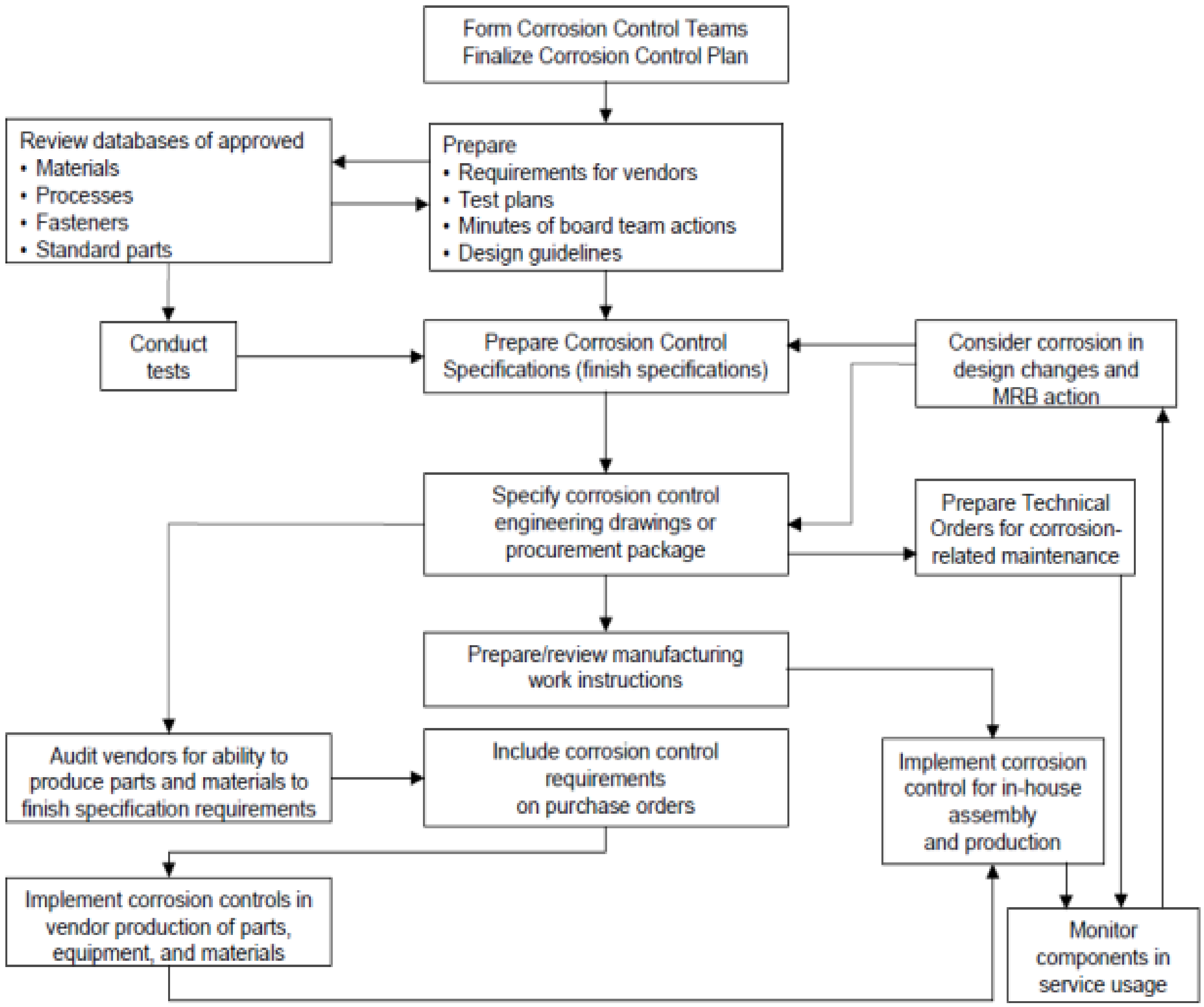


Figure 37: Flow of tasks for managing the corrosion of defense equipment assets (USD 2007).

Concluding Remarks

A general overview of the mechanisms of corrosion is reported in order to gain a better understanding of the corrosion process, which will enable effective improvements to existing practices. In addition, accurate test methods and procedures play a crucial role in determining mitigation strategies through research and development. Therefore, common test methods for determining effective corrosion mitigation strategies to protect equipment are explored along with specific proactive approaches focused on reducing the impacts of chloride deicers to winter maintenance equipment. Table 20 presents a summary of the identified best practices in managing the deicer-induced corrosion of metals on maintenance equipment.

The application of improving designs and implementing maintenance practices can combine to significantly reduce the harmful effects of corrosion and the associated costs. Research focused on understanding and characterizing corrosion mechanisms can provide valuable insight on the corrosion process, which can be integrated into developing accurate testing methods. New corrosion prevention techniques involving advancements in materials science and engineering can be developed by supplementing knowledge gained from mechanistic studies and improved corrosion testing methods.

Online corrosion monitoring provides valuable real time corrosion information, which can effectively reduce corrosion maintenance costs, offer alternative corrosion maintenance approaches, and improve safety standards. These systems are able to provide early detection and assessment of corrosion, while being utilized to estimate service life and assess performance of corrosion inhibitors. Although many test methods and online corrosion monitoring systems have been developed, the corrosion process is complicated and it is still necessary to explore new theories, methods and technologies to address the existing problems and bridge knowledge gaps.

Through research and development several approaches to achieve better corrosion resistance and increase savings such as improving designs, modifying practices and policies, refining corrosion modeling and prediction methods will subsequently advance technology and increase education. WSDOT has made significant advancements in materials design, which have been proven to effectively mitigate corrosion impacts to winter maintenance equipment caused by roadway deicers. It is recommended for winter maintenance operations in the snowy regions of North America to integrate these techniques into standard corrosion control protocol to protect maintenance equipment, reduce costs of corrosion caused by roadway deicers, and increase equipment service life.

Research is needed to optimize the use of best practices or products for corrosion protection of vehicles and equipment and to evaluate their long-term effectiveness. For instance, there is currently a lack of information on the cost-effectiveness of automated internal washing mechanisms and other effective washing techniques, relative to a low-volume high-pressure washing system. It is desirable to test the field performance of regular washing (with salt remover) and innovative anti-corrosion products. Research is also needed to identify, develop, and evaluate technologies to improve on-line assessments of the condition of key metallic components and their applied coatings so that maintenance of the metal or coating can be performed based on the corrosion condition. Finally, research is needed to develop best practice guidelines (e.g., a user's corrosion management guide) once laboratory and field studies are conducted to validate the best practices against deicer corrosion.

Table 20: Corrosion Management Best Practices.

Corrosion Management Best Practice	Highlights	Comments
Materials Selection	Recommended to use exfoliation resistant tempers such as T76 or 7xxx alloys with copper. Alloys in the 1xxx, 2xxx, 3xxx, 5xxx, and 6xxx series contain the highest corrosion resistance properties.	Increased corrosion resistance and increased service life. Cost savings due to minimized corrosion. Use composite materials wherever possible.
Design Improvements	Structures designed for resistance to atmospheric corrosion should provide easy drainage. Properly designed welded joints to eliminate crevices are preferable to bolted and riveted joints.	Design should allow maximum access for maintenance and repair painting. Use of Sealing compounds and inhibitive coatings can greatly reduce effects of corrosion.
Maintenance Practices	Methods and procedures that involve routine washing, reapplication of coatings, grit blasting, mechanical removal of rust, or the use of rust removers. Selection of appropriate deicer and corrosion inhibitor combinations, equipment modification techniques, and regular maintenance schedules.	Significantly improves the service life of equipment. Recommended to seal hydraulic, electrical, and brake components and remove junction boxes. Indicate high quality coatings and materials in equipment specifications. Record and maintain detailed documentation.

CHAPTER FIVE

5. WATER QUALITY IMPLICATIONS AND TOXICOLOGICAL EFFECTS OF CHLORIDE BASED DEICERS. PART III: MITIGATION MEASURES

Contribution of Authors and Co-Authors

Manuscript in Chapter 5

Author: Scott Jungwirth

Contributions: Collected and analyzed data and literature. Provided insights and wrote draft of manuscript.

Co-Author: Eric Strecker

Contributions: Provided field expertise and feedback on early drafts of manuscript.

Co-Author: Laura Fay

Contributions: Provided assistance, insights and feedback on early drafts of manuscript.

Co-Author: Dr. Xianming Shi

Contributions: Provided guidance, insights and feedback on early drafts of manuscript.

Manuscript Information Page

Scott Jungwirth; Eric Strecker; Laura Fay; Xianming Shi, PhD
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Introduction

This is the third in a three-part series of papers on understanding and mitigating the impacts of chloride based deicers on the environment. Part I summarizes current and previous research to develop a better understanding of the water quality implications and toxicological effects of chloride based deicers in the natural environment. Part II discusses common methods to quantify deicer toxicity in a laboratory or field setting and monitoring relevant parameters in the field. Part III summarizes the current practices and methods available to mitigate the water quality risks associated with chloride based deicers, as detailed in the following sections.

It is well known that anthropogenic sources of chloride to surface waters include industrial and municipal wastewaters, effluent wastewater from water softeners, road salt, agricultural runoff, and production water from oil and gas wells (Missouri DNR, 2013). In most locations, road salt application is the major contributor to chloride release into the environment. The most commonly used deicers containing chlorides are sodium chloride (NaCl), magnesium chloride ($MgCl_2$), or calcium chloride ($CaCl_2$), or a combination such as salt brine with $CaCl_2$ added at cold temperatures (Shi et al., 2013).

Chloride based deicers have been used for decades and have been the primary snow and ice control products used by roadway agencies (Fay and Shi, 2011). Due to their long-term and widespread use, the environmental impacts have been observed by a number of researchers (Hawkins, 1971; Roth and Wall, 1976; D'Itri, 1992; Paschka et al., 1999; Ramakrishna and Virarghavan, 2005; Levelton Consultants Limited, 2007; Shi et al., 2009). Figure 38 shows the movement of chloride based deicers through the environment. Chloride laden runoff from roads can splash or spray onto soil and plants, and flow off the road into soil and into surface and ground waters. Elevated chloride concentrations in waters associated with chloride laden runoff from roadways and maintenance yards have ranged from 10s of mg/L to 10,000s mg/L (MTO, 1997; Bowen and Hinton, 1998; Alberta Infrastructure, 2000; Shaw et al., 2012). Road salting has been found to significantly affect chloride content and salinity of groundwater in many locations (Pitt et al. 1994, 1996). Long-term studies have shown that chloride concentrations in groundwater are increasing, particularly in the North Eastern United States (NAS, 2005), but also in western areas where reclaimed water is used for irrigation. Current standards used by the Environmental Protection Agency (EPA) for chloride in surface waters are Chronic- four-day average concentration of dissolved chloride, associated with sodium, should not exceed 230 mg/L and the Acute one-hour average concentration should not exceed 860 mg/L, more than once every three years on the average [EPA 440/5-88-001)] (EPA, 1988).

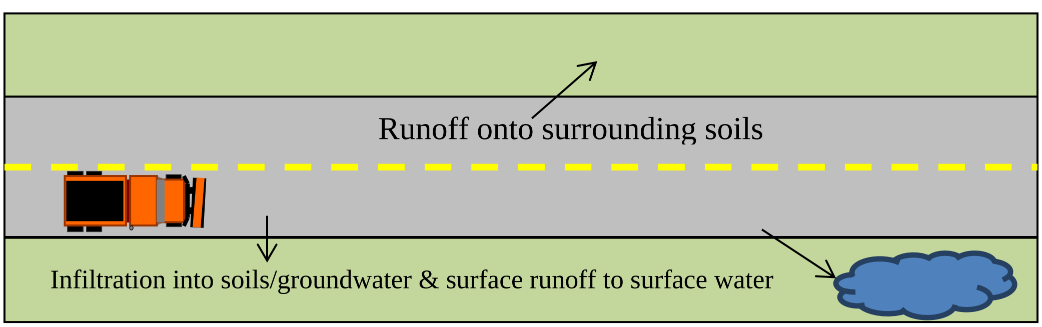

Figure 38: Movement of chloride based deicers through the environment.

When chloride concentrations in streams reach or exceed the acute and chronic standards, toxicity to aquatic species can result. In addition to toxicological impacts, elevated chloride concentrations can disrupt normal functions of surface water such as causing density stratification and late vertical mixing in waters.

Recent research has demonstrated the negative effects of road salts on constructed wetlands (Tromp et al., 2012). Additionally, road salts can also mobilize hazardous materials causing significant impacts to water sources. In a treatment system consisting of a detention basin and a vertical flow wetland heavy metals and poly-aromatic hydrocarbons were monitored, and high retention efficiencies above 60 percent were achieved for poly-aromatic hydrocarbons; however, during periods of high levels of road salt exposure, copper, cadmium, zinc and nickel concentrations increased at the effluent of the wetland, due to mobilization of these metals from contact with sodium chloride (Tromp et al., 2012).

Research Objectives

Two common approaches are used for reducing the impacts of chloride based deicers (Fay et al., 2013). The first approach focuses on reducing the amount of chloride based deicers introduced into the environment through techniques such as salt management plans, effective anti-icing practices, equipment calibration, effective use of weather information, staff training, and detailed monitoring and record keeping. The second approach consists of effective practices used to reduce the impacts of chloride based deicers after they have been introduced into the environment. This approach typically consists of treatment options such as phytoremediation or evaporation ponds. In addition, stormwater Best Management Practices (BMPs) can be employed to manage chlorides by regulating flow and conveyance of runoff often resulting in diversion and dilution. Common reactive strategies used to mitigate the impacts of chloride roadway deicers on the natural environment identified from literature review include: infiltration trenches and basins, detention/retention and evaporation ponds, wetlands and shallow marshes, vegetated swales and filter strips. Figure 39 shows an overview of the strategies used to reduce chloride based deicers in the environment. Note that there are other reactive strategies that can be used to mitigate environmental impacts of chloride roadway deicers but are not discussed in this synthesis, such as strategic use of salt-tolerant plants to buffer roadways and controlled release of highway runoff to mitigate spikes in deicer concentrations. Golub *et al.* (2008) discusses other effective practices aimed at removing salt from collected runoff, including: thermal distillation processes, multistage flash distillation, multiple effect distillation, vapor compression distillation, reverse osmosis, and electro dialysis. However, these practices are not covered in this synthesis due to high capital and maintenance costs.

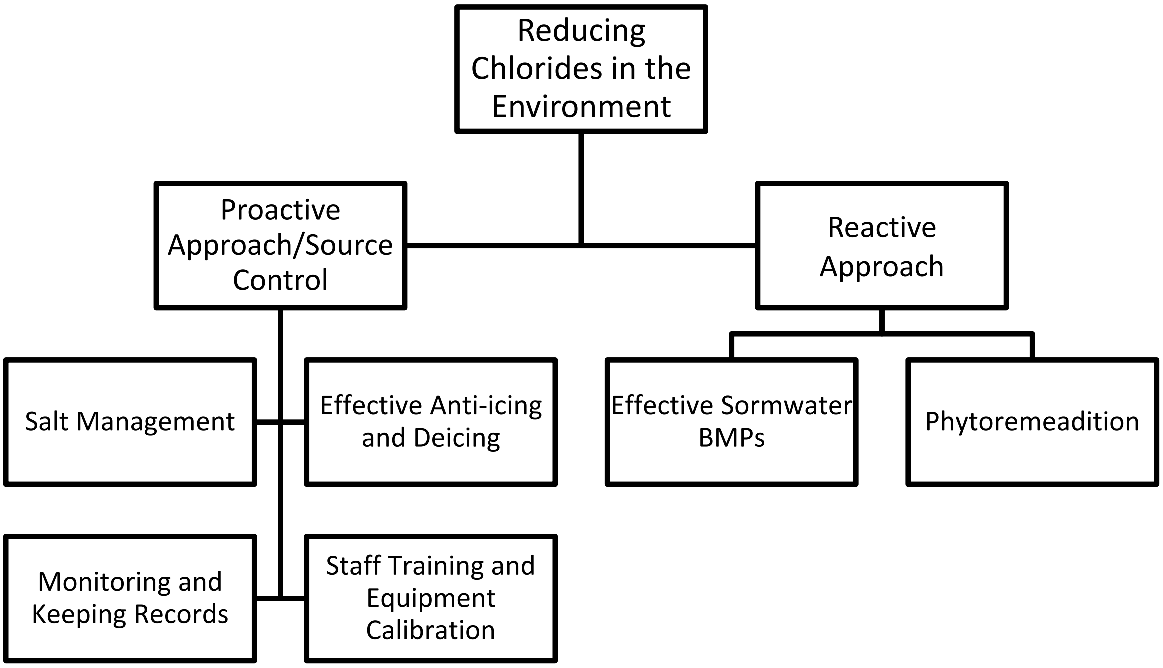

Figure 39: Overview of strategies to reduce chloride based deicers in the environment.

Knowledge of the interactions of the precipitation and the pollutants aids in selection of appropriate practices. Understanding the temporal evolution of such interactions can provide assistance in choosing appropriate best management practices (BMPs) for a given site (Oberts, 2003). Early in the spring thaw, when flow rates are lower, dissolved pollutants may be transported by lower volumes and lower velocities. At this stage, receiving waters may be more vulnerable to the impacts of these soluble pollutants. Later, suspended pollutants such as sand and chlorides may be carried by runoff with higher velocities and higher volumes that may reduce the efficiency of the reactive mitigation strategy.

Strategies for Reducing the Impacts of Chloride Based Deicers

To reduce the impacts of chloride based deicers, there are four potential management strategies including reducing the amount of chloride deicers applied (either through minimization and/or use of other control substances), treatment of runoff that includes deicers, mixing runoff to reduce concentration peaks and/or routing of deicing runoff away from sensitive receiving systems, either surface and/or groundwater systems.

Since chloride is a conservative constituent, it is very difficult to remove from the environment. Potential treatment options include reverse osmosis or membrane filter (with a remaining brine stream) or routing to an evaporation pond. However, storage issues to allow for evaporation are a major concern since deicing occurs during cold periods of the year. The use of reverse osmosis or membrane filters for stormwater runoff is cost-prohibitive. Therefore, the three most successful strategies are to minimize use and/or mix runoff volumes to reduce peak concentrations and/or route deicing containing runoff to less sensitive receiving waters. Source control via either minimization of the amount needed to meet deicing requirements and/or product substitution is likely the best option whenever possible. The other options are to use stormwater BMPs to mix larger volumes of stormwater to reduce within storm peak chloride concentrations and/or route the runoff away from sensitive receiving waters. This can be accomplished either via routing around a sensitive receiving system or infiltrating to groundwater when groundwater chloride or total dissolved solids (TDS) are of less concern.

Proactive Approaches to Reducing the Amount of Chloride Based Deicers

The following section discusses strategies that can be used to reduce deicer application rates and the amount of deicers applied through proactive approaches to winter maintenance operations. Using less chloride based deicer means less is going into the environment and that related toxic impacts are reduced, avoided, or further delayed. DOTs have demonstrated that proactive approaches such as anti-icing and salt management techniques can reduce the amount of chloride deicers applied. In recent years, winter maintenance practitioners have implemented new technologies, tools, and methods to reduce the amount of snow and ice control chemicals used.

While cost saving has been the primary driver, these practices also reduce chloride impacts to the environment (Fay et al., 2013). Such proactive measures by winter maintenance programs have effectively reduced salt use (Fay and Shi, 2012; Fay et al., 2013). The most successful approaches consist of use of alternative products, snow removal, anti-icing, pre-wetting, precision application and use of AVL and GPS technology, frequent and consistent staff training and equipment calibration, appropriate material storage, utilizing real time weather and pavement condition data, including programs like MDSS, and creating detailed maintenance records, all of which will be presented in this section.

Salt Management Plans

Salt management plans (SMP) provide maintenance agencies with a strategic tool to effectively implement salt management practices while providing safe, efficient, and cost-effective road management. The SMP apply to all winter maintenance staff and personnel (TAC, 2003a). Pioneered by Canadian transportation agencies, a SMP is generally agency-based and aims to follow the principles of safety, environmental protection, continual improvement, fiscal responsibility, efficient transportation systems, accountability, measurable progress, communication, and a knowledgeable and skilled workforce (TAC, 2003a; Venner, 2004). Fundamental components of a SMP may consist of a statement of policy and objectives, situational analysis, documentation, and proposed approaches to achieve goals or protect identified sensitive areas. The Transportation Association of Canada (TAC) recommends using general and broad guidelines developed at the federal level to act as a framework for further development of local guidelines, considering the amount of salts used, roadway systems, funding constraints, local weather conditions and variability in conditions across a country, state, province, county or municipality (TAC, 2003a, Venner, 2004). SMPs assess specific progress and identify areas for further improvement. Important components of a SMP include a statement of policy and objectives based on policy with guiding principles from a high-level organization, situational analysis – on road use, salt vulnerable areas, sand and salt storage sites, documentation, in which activities are recorded, monitored, audited and reported periodically to assess the progress and identify areas for further improvement and training and management review.

In order to implement a successful SMP, it is recommended that agencies provide detailed records and annual reports for each storm event and winter season. These records may contain valuable information such a salt usage and performance records, which can be analyzed to determine general trends or develop improved management strategies (MSHA, 2012). In addition, annual audits and inspections can identify specific areas of or for improvement. Procedure improvements and shifts in snow and ice management policy are sometimes documented in ice and snow policies or formal DOT levels of service (Venner, 2012).

Specific modifications to basic SMP guidelines can be implemented to address specific budgets, and climatic and road conditions. For instance, the City of Toronto, Canada utilizes electronic salt dispensers to control the salt flow and mixes sand into the salt when conditions permit (to reduce salt use) and DOTs in the US are increasingly turning to these technologies as well. Maryland, Michigan, Ohio, and many other DOTs use Automatic Vehicle Location (AVL) tracking systems to monitor past and present locations of winter roadway maintenance equipment and to improve efficiencies (Welsh, 2005; Venner 2011; Venner, 2012; MSHA, 2012).

Anti-icing, Deicing and Pre-wetting Practices.

Recently, transportation agencies have transitioned from deicing to utilizing anti-icing wherever possible (O'Keefe and Shi, 2005). Anti-icing is the application of material prior to a storm system to prevent the bonding of ice to the pavement. Deicing is the application of material after a storm system to break the ice-pavement bond. Anti-icing can lead to an improved level of service (LOS), reduced need for chemicals, abrasives or plowing, and associated cost savings and increased safety and mobility (Hossain et al., 1997; Kroeger and Sinhaa, 2004; Conger, 2005; O'Keefe and Shi, 2005; Ye et al., 2013). Caltrans has reported about a 50 percent material savings by shifting from application of solid rock salt to salt brine (liquid application) (personal communication, Dave Frame, Caltrans, April 5, 2012). Other DOTs have reported smaller, but consistent reductions in salt applications (Venner, 2012). More information on anti-icing is available in the FHWA anti-icing manual produced by Ketcham et al. (1996).

A recent study from Clear Roads synthesized the current practice of during-storm direct liquid applications (DLA) and identified the following benefits: reduced application rates, reduced loss of materials, faster time to reach bare lane, fast action/safer conditions, further prevention of ice-pavement bonding, accurate low application rates, and reduced corrosion effects (Peterson et al. 2010).

Pre-wetting, which is the use of chemicals to wet abrasives or solid deicers before application to quickly activate material for immediate ice melting performance, and reduce scatter and bounce, is also becoming more common (Venner, 2004). Pre-wetting has been shown to increase the performance of solid chemicals or abrasives and increase their longevity on the roadway surface, thus reducing the amount of material required by reducing the number of applications (Hossain et al., 1997). Additionally, pre-wetting is preferable to the application of dry salt to roadways, which may blow away or bounce off the road prior to actively melting snow and ice. In a recent case study, the use of brine to pre-wet salt resulted in a 15% reduction in product usage, as the pre-wet salt exhibited equivalent ice melting performance, better adherence to the road surface and less loss from bounce and scatter (personal communication, Peter Noehammer, City of Toronto, March 28, 2012). A Michigan DOT study has reported significant material loss of up to 30% occurs when using dry salt applications on dry pavement (Michigan DOT, 2012).

Another pre-wetting method known as slurry is the application of up to 30% liquid to solid product and has shown promising results (Fay et al., 2013). It is recommended to use 10 gal of liquid per 1 ton of dry material (Ketcham et al., 1996).

Precision Application and AVL/GPS Technology

The Washington State Department of Transportation (WSDOT) estimated that the use of precision controllers prevents over-application and saves up to 10% of material applications resulting in an approximate biennial savings of $1.2 million annually (Venner, 2012). Nova Scotia DOT & Public Facilities reported that calibrated application was saving $500,000 annually (Venner, 2012). Michigan DOT estimates savings of $3 million annually, or 10% of agency costs. Increasingly, these systems are also combined with Geographic Positioning System (GPS) and AVL systems (Venner, 2011; Ye et al., 2012). Half of WSDOT's fleet is equipped with AVL and automated data collection, eliminating the need for maintenance technicians to fill out paperwork on their activities for the day. This results in about 10,000 hours per year that maintenance employees are out plowing instead of filling out paperwork, equating to $350K/year in labor savings (Venner, 2012). In a national survey of DOTs' in 2011, Delaware, Idaho, Kentucky, Minnesota, Missouri, and North Carolina DOTs all reported using GPS/AVL to manage resources/materials usage and to optimize operations.

A new and emerging technology known as geo-fencing is currently being evaluated as a possible best management practices technique. Geo-fencing uses GPS software to set boundaries in specific locations along spreader routes. Within the boundaries, spreader applications are stopped or adjusted automatically to reduce or prevent the potential for overlap applications as several salt application vehicles travel through the common routes multiple times. In addition, geo-fencing can be utilized to inform or alert operators when they enter environmentally sensitive areas or areas of concern so critical adjustments can be made (Mass DOT, 2012). Such areas may include groundwater recharge areas, sources of drinking water, salt-sensitive vegetative communities, salt-sensitive wetlands and small ponds and lakes.

Equipment Calibration

Calibration of equipment ensures that equipment is operating optimally, and in the case of material spreaders, that the appropriate amount of material is being applied. Not calibrating equipment can result in over or under application, potentially leading to wasted product or hazardous driving conditions, respectively. A calibration policy is recommended as part of the facility management plan and should be reinforced in staff training (TAC, 2003, Fay et al., 2013). Timing of calibration is recommended to take place at least once per year prior to a winter season and when a piece of equipment is acquired or installed, or when material calculations indicate a significant discrepancy (Fay et al., 2013).

Calibration for all application methods – solid and liquid, and for each product type – sand, salt, salt brine, etc. should be completed routinely. Records of calibration results and proper calibration will allow for the most efficient use of equipment, and prevent waste or loss of product to the environment, potentially reducing impacts.

Weather Information,
Forecasting - RWIS & MDSS

Weather forecasts and real-time environmental monitoring, e.g., RWIS (Road Weather Information System) aid maintenance managers in developing effective and efficient treatment strategies, and allow for optimization of equipment and materials used. Accurate weather forecasts can be utilized to reduce application rates while providing the same, or better, level of service. Weather information may be gathered from a variety of sources such as free and public weather services, private-sector weather forecast services, RWIS, and decision support systems (e.g., MDSS), each providing distinct levels of detail. Near-real-time weather and road condition information and customized weather services are valuable to the success of proactive maintenance strategies (Strong and Shi, 2008; Ye et al., 2009a). Real-time data for air temperature, wind, type and amount of precipitation, as well as forecast weather conditions, pavement temperature, bridge temperature, and pavement conditions play a vital role in winter maintenance decision making process. It has been reported that accurate weather and road condition forecasts and information have enabled a reduction in chloride deicer usage (Fay et al., 2013).

In addition to RWIS, MDSS (Materials Decision Support System) is becoming a popular tool to provide accurate and reliable weather information to state agencies (Venner, 2004). MDSS is a powerful software application system, which processes RWIS data in order to develop accurate forecast information and assist maintenance personnel in the decision making process of determining roadway maintenance activities. MDSS systems provide real-time and post storm analysis to evaluate materials used, rate of application, and timing of application. The utilization of RWIS and MDSS can provide valuable information, which can assist roadway maintenance agencies in determining the most effective strategies aimed to reduce impacts and increase level of service (Mass DOT, 2012). A pavement condition and treatment data flow chart for MDSS is shown in Figure 40. The MDSS software uses collected weather, pavement, traffic, and environmental data to develop road weather forecasts and make suggestions on products, applications rates and frequency of repeat applications or snow removal based on defined rules of practices. After each treatment occurs, and the information is input into the system, updated treatment options are provided.

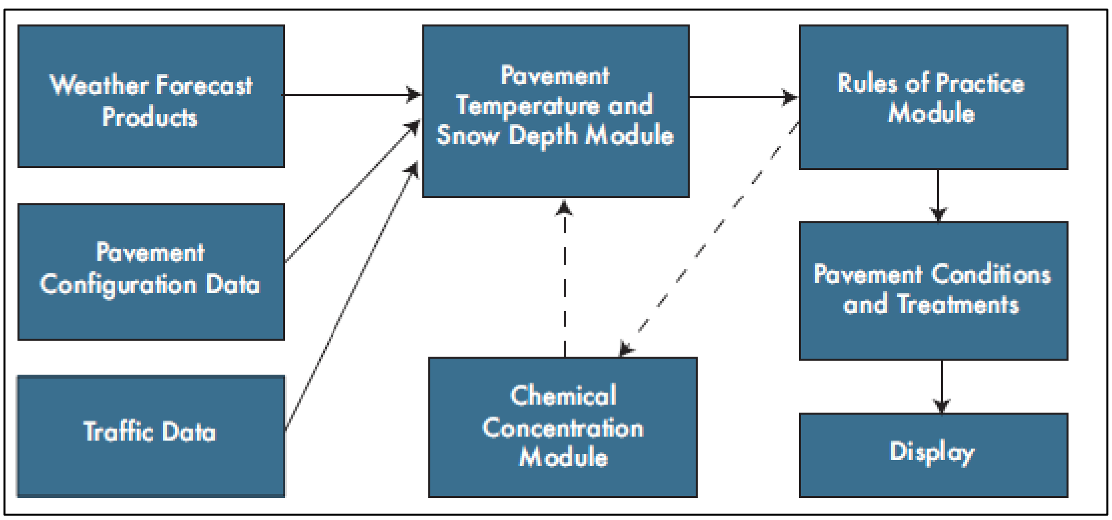

Figure 40: Typical MDSS pavement condition and treatment data flow. (NCAR)

Using MDSS, Indiana reported salt savings in one winter (2008-2009) of 228,470 tons ($12,108,910) and when normalized for winter conditions based on storm severity, total salt savings were 188,274 tons ($9,978,536) based on salt prices of $53/ton (McClellan et al., 2009). MDSS proved to be a strong management tool, for planning ahead of the storm. A cost-benefit analysis of MDSS implemented in New Hampshire, Minnesota, and Colorado identified benefits as reduced material use, improved safety and mobility, and significant cost savings (Ye et al., 2009b). The benefits were found to outweigh the costs associated with the technology in all three states, with benefit-cost ratios ranging from 1.33 to 8.67 due to varying conditions and uses of resources.

Cost/benefit studies associated with the use of weather information for winter highway maintenance found that winter maintenance costs decreased as the use of weather information increased or as accuracy improves (Ye et al., 2009a). Focusing forecasts on the road environment and investing in equipment with high accuracy ultimately provides more focused information and allows for the development of better winter maintenance strategies (Ye et al., 2009a).

Staff Training

Training of winter maintenance staff and personnel is of particular importance for the effective and efficient use of chloride roadway deicers. A comprehensive training program is recommended to demonstrate the purpose and value of new procedures, to address staff concerns and potential resistance to change, and to ensure needed competencies. Training can focus on techniques to use less deicer without compromising public safety or mobility of the traveling public, while still maintaining or exceeding the states defined level of service. Successful training programs are designed to identify the learning goals and have a logical progression to the lesson plan. Successful training programs have been shown to reduce deicer usage and improve winter maintenance operator practices (Eckman et al., 2011).

Learning goals such as LOS guidelines, principles of ice formation, chemistry of road salts, and environmental impacts of road salts need to be identified and addressed during training. To be most effective, it is recommended to hold annual training shortly before the onset of the snow and ice season. This helps to ensure current learning goals are taught, reinforced, and tested. In addition, many DOTs utilize statistical data to provide regular feedback to managers and operators, such as posting annual material or cost savings to reinforce the importance of training efforts. Operators should be encouraged to share information, experiment with new concepts, and challenge old ideas (TAC, 2003b).

A comprehensive training program is recommended to demonstrate the purpose and value of new procedures, to address resistance to change, and to ensure competency of personnel carrying out their duties. Training involves designing a training program to identify the learning goals, components and logical progression, and developing a lesson plan and determining the training methods such as in class, in field, or post-storm debriefing.

The important role of technology in staff training has been validated by agencies. Computer-based training (CBT) has been proven to be a powerful tool for staff training. A CBT has been developed under the leadership of AASHTO and for the winter maintenance staff in state and local governments. The course consists of several lessons containing a total of about forty units, covering a host of topics about winter roadway management.

Monitoring and Record Keeping

Monitoring environmental parameters and practicing effective record management of snow and ice control products and related procedures can aid in material saving, create a more effective working environment, increase efficiency, reduce person and equipment hours, and enable cost savings. Collected data helps DOTs report on point source and non-point source runoff from roadways or stockpiles. Monitoring chloride concentrations on and along roadways and in adjacent water bodies can provide an indication of potential impacts to stream biota. Furthermore, information from monitoring chloride concentrations in salt-vulnerable areas can inform selection of appropriate winter maintenance and mitigation strategies. A municipality in Canada implemented a monitoring approach that included maintenance agencies working with their local conservation authority to add chloride sensors to their stream monitoring network.

A quality assurance (QA) plan should be developed prior to sampling and analysis. The sampling design plan should discuss what types of samples are being collected, where they are being collected, the timing of sampling, and how the samples should be handled. The analysis protocol should discuss the test methods being used, the analysis methods for the data, and any relevant reporting parameters. The QA plans should be available, on site, reviewed prior to the initiation of sampling or analysis, and followed by trained staff (EPA, 2002).

Various important issues should be considered before initiating a water monitoring program such as frequency and location of samples, health and safety issues, and maintenance of sensors (TAC, 2003d).

Detailed Maintenance Records

Consider maintaining the following records - winter severity ratings, total number of events requiring road salt application during the winter season and how much material was applied, and where and when the material was applied, at a minimum. Transportation agencies should also consider keeping detailed records of the average chloride concentrations and frequency of sampling at each sampling location to determine various alternative strategies (Highway Deicing Task Force Report, 2007). Table 21 shows a list of recommended records and reports.

Table 21: Example list of records and reports maintained during the winter season (adapted from Northumberland, 2011)

Title	Description
Salt/Sand/Grit Inventory	Inventory record of salt materials including date, supplier, quantity, and storage. Brine production quality control and materials usage.
Road Patrol	Pavement temperature trends in daily logs, along with pavement conditions, weather conditions and winter treatment strategy (TAC, 2003). Total length of road on which salt is applied.
GPS Vehicle Report	Report generated by GPS unit installed on maintenance vehicles detailing date, time, speed, trip length, etc.
Dickey-John Spreader Controls	Continuous reporting of application of materials on roadways
Daily Activity Reports	Daily record of Operators activities performed through the shift.
Equipment	Inspection and repair records. State of calibration on equipment.
Weather	Temperatures, snow depths and durations during snow/ice storms with applied salt. Storm and overall winter severity ratings. Total number of events requiring road salt application during the winter season.

Reactive Approaches: Removing Chlorides from the Environment

Recently, increased chlorides in the environment associated with road salt have been identified as a major environmental concern, partly due to the nature in which chlorides move through the subsurface and the difficulties inherent in remediation. Traditional methods of removing chlorides from water such as reverse osmosis and membrane filtration are very expensive and require significant maintenance; they are not appropriate for transportation rights-of-way. Although effective chloride removal strategies are still being developed, some innovative approaches involve phytoremediation or capturing chlorides on filter media, such as concrete. Research focused on removing road salt related chlorides from the environment is presented.

Phytoremediation

Phytoremediation is the use of plants to aid in the removal of contaminants within soils, groundwater and surface waters. The main transport processes of phytoremediation consist of sorption and plant uptake, which are dependent upon the properties of the plants and contaminants involved. In order for removal of a conservative substance like chloride to be successful, the plants must be harvested and removed prior to plant die-off. It has been reported that plant uptake of Na^+ and Cl^- ions by a species known as Kochia scoparia accounted for approximately 36% or the observed change in salinity (MacNeill, 2011). Since phytoremediation is still increasing in popularity with limited available data, regulatory agencies have not yet widely accepted this technique. Nevertheless, recognition of phytoremediation as a cost-effective, long term remediation strategy for soils is increasing (Schnoor et al., 1995). Depending upon the selected plant systems, plant growth and continued treatment can be achieved for 25-50 years with hybrid poplar trees (Schnoor et al., 1995). In addition, results from a heavy metal contamination site suggest that significant cost savings can be accomplished with phytoremediation; traditional technologies are up to ten times more expensive (Garbisu and Alkorta, 2001). However, planting costs have been reported to be approximately $10,000 per acre, plus the cost of monitoring (Schnoor et al., 1995).

Phytoremediation has been utilized to remove a wide variety of contaminants from the environment. Successful treatment of a variety of hazardous waste contaminants such as organics, agricultural runoff, metals, landfill leachate, and chlorinated solvents has been achieved using phytoremediation techniques (Schnoor et al., 1995). However, phytoremediation has some associated limitations. Phytoremediation is most effective at sites with shallow subsurface contamination since treatment mechanisms are dependent on plant root depths, which are limited to 50 cm (~20 in) for herbaceous plants and 3 m (~10 ft) for trees (Pilon-Smits, 2005). In addition, phytoremediation may require longer treatment times compared to excavation or pump–and-treat systems due to the nature of biological systems. For this reason, phytoremediation techniques are commonly integrated with other treatment technologies. For example, soil with the highest concentrations of contaminants may be excavated and phytoremediation used as a polishing technique to remove the remaining pollutant (Pilon-Smits, 2005). Removal and appropriate disposal of plants used for phytoremediation may be required for long-term performance.

In Quebec, halophytes, plants able to grow in high salinity areas, were selected, harvested and used in ditches to remove salt from runoff water (Morteau et al., 2006). All of the plants accumulated salt throughout the study; Atriplex, also known as Saltbrush, accumulated the most salt by mass. The amount of salt taken up by the plants was dependent on plant morphology, species, and the concentration of salt exposure. Based on this research, it is recommended to calculate the size of the marsh, ditch, and filter bed according to annual field data of runoff flow rates and observed salt concentrations, grow plants in a greenhouse instead of transplanting from another field location and study invasion of other marsh plants, and evaluate the ecological and physiological tolerance of each plant species in a saline environment.

Finally, phytoremediation will likely be successful for treating soils and remaining salt laden pore waters. Typically, the large volumes of runoff and timing of the events as compared to active plant growth and activities limit the use of phytoremediation for runoff control in most cases, unless very large storage is possible.

Using Traditional Stormwater Structural BMPs to Manage Chlorides

Stormwater structural Best Management Practices (BMPs) are practices that include treatment and flow management for runoff water management. Since chlorides cannot be removed from runoff waters with traditional controls, management of chlorides often includes diversion into different receiving waters such as from surface water to groundwater or less sensitive receiving waters to reduce concentrations thus reducing impacts. In addition, considerable chloride concentrations are released throughout the year within urban watersheds; therefore, it is critical to implement reactive mitigation strategies to effectively manage chlorides associated with winter maintenance through controlled storage and release (Ostendorf, 2013).

This section focuses on BMPs that are designed to redirect and provide storage for chloride-laden runoff. The basic mechanisms for pollutant removal in traditional BMPs consist of gravity settling, infiltration of soluble nutrients through soil or filters, or biological and chemical processes (Turner-Fairbank Highway Research Center, 1999). The chloride anion is a known conservative pollutant, which makes it difficult to remove from water and soil (Environment Canada, 2001).

Structural BMPs have been shown to effectively capture and manage chlorides. Reactive mitigation strategies effectively manage runoff velocity and improve the quality of highway storm water runoff through dilution and controlled storage and release of chlorides (Fitch et. al 2004). Structural BMPs should be designed, sited, installed, and maintained properly. It is generally recommended to use BMPs in combination to enhance overall performance and increase service life.

Vegetation along roadsides can play a crucial role in the general management of runoff through chemical and biological processes. Salt-tolerant species, such as perennial rye-grass, show a high resistance to the toxic effects of salt and in areas with frequent applications of salts, should be considered in vegetated BMPs and landscaping strips. It is also recommended to consider a combination with fescue-grass at 70:30 when building new roads or reconstructing existing roads to enhance performance (Baltrenas and Kazlauskiene, 2009; Eppard et al., 1992).

<u>Storage and Release</u>

The first class of potential structural BMPs for improving the management of chloride laden runoff includes ponds and wetlands. The primary mechanism specific to chloride includes storage and subsequent mixing of runoff to reduce the peak concentrations. In addition, the mixing of base flows and runoff without chlorides in stored wet pools results in reduced concentrations.

<u>Detention, Retention, or Evaporation Ponds</u>

Dry and wet detention ponds are examples of structures that can be used to remove pollutants through sedimentation or settling. Dilution of chloride can take place in dry and wet detention ponds and peak concentrations can be decreased. Dry settling ponds hold runoff for a given period of time and release it at a controlled rate so that the pond remains dry between storm events (*Staples et al.,* 2004). Dry extended detention ponds provide a higher level of water treatment than dry settling ponds, since they are designed to hold runoff for longer time periods which allows more particles to settle out (Staples *et al.*, 2004). Wet ponds generally hold water year round and have higher sediment removal rates than dry ponds and offer effective pollutant removal through mechanisms such as settling, nutrient uptake by plants, and biochemical processes. Salt laden runoff can be captured in these ponds and then potentially be disposed of by reusing it to make brine according to local regulations. If the water can be evaporated, the remaining material can be removed or used for dust suppression on unpaved roads or in brine making operations (Fitch et al., 2004; Golub et al., 2008; Fay et al., 2013). It has been reported that DOTs have successfully used evaporation ponds to prevent chloride migration offsite (Fay et al., 2013). Figure 41 shows a schematic of a detention basin compared to a retention basin.

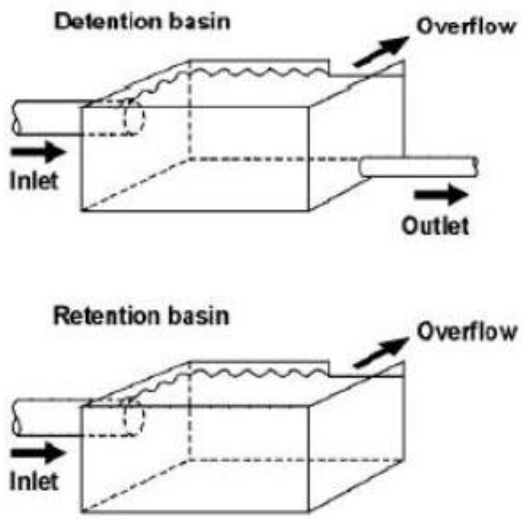

Figure 41: Comparison of a detention basin and a retention basin (TUHH).

An ongoing research project in France is measuring deicing salt storage in a detention pond originally installed to treat road water runoff and act as flow control (Remi et al., 2013). Continuous monitoring of salt and heavy metal concentrations of the influent (inlet) and effluent (outlet) of the detention pond is being conducted with the goal of evaluating the amount of road salts applied to roads, versus the amounts entering and leaving the detention pond. In addition, the monitoring of mobilization of heavy metals caused by the presence of deicing salts is performed. This information will be correlated with winter maintenance practices with respect to measured meteorological conditions to provide valuable information, which winter maintenance agencies will be able to use to determine effective chloride remediation strategies. It is projected that the result of this study may be that the pond will decrease chloride peak concentrations by dilution from baseflows from areas with less or no chloride application.

Li and Davis (2009) found that bioretention ponds in Massachusetts promoted the slow release of chlorides and removed many other TDSs from surface runoff. The reduced runoff volume from using the bioretention facility contributed to lower pollutant output and increased water quality. The effectiveness of a bioretention structures may increase in proportion to the depth and area of the structure (Li and Davis, 2009).

Wetlands and Shallow Marshes

Constructed wetlands utilize both physical and chemical processes such as adsorption, filtration, sedimentation, plant uptake, and decomposition to treat runoff (Staples et al., 2004). Stormwater wetlands are designed to store runoff, sustain plant life, and promote microbial growth, which contributes to the removal of pollutants. Grass infiltration areas can be utilized to reduce the initial chloride concentration in the runoff before it reaches the wetland to decrease harmful impacts to the wetland vegetation (NYSSMDM, 2010). Wetlands can provide storage for chloride laden runoff and promote the slow release of chlorides effectively reducing overall chloride concentrations in the effluent.

Infiltration

Infiltration of stormwater is a very effective stormwater management technique under many conditions. Infiltration systems treat runoff and reduce water volume by allowing water to infiltrate into the surrounding soil (Staples *et al.*, 2004). In areas where sand and gravel are applied infiltration practices may be challenging. Therefore, infiltration technologies require a pre-settling or pre-treatment to remove suspended solids such as sand and gravel that would clog the system and reduce the infiltration capacity. However, infiltration systems may have limited applications to treat chlorides in runoff since chloride is conservative and high amounts can cause groundwater concerns. The potential for long term accumulation of salts in groundwater is related to the characteristics of the aquifer and the loading of chloride-laden water compared to fresh water. Aquifers in confined or relatively closed basins are more susceptible to long term increases in salts.

Roadway runoff in cold climates have a high potential for contaminating groundwater since road salts are water soluble, not readily absorbed to soil particles, and can percolate into groundwater as infiltration occurs (Weiss et al. 2008; Pitt et al. 1994, 1996).

Infiltration Trenches

Infiltration trenches and basins treat runoff and reduce surface runoff water volume by allowing water to infiltrate into the surrounding soils and underlying groundwater systems (Staples et al., 2004). Infiltration trenches are excavated trenches filled with stone and lined with filter fabric where runoff is collected and allowed to percolate into the soil (Staples et al., 2004). Infiltration trenches reduce runoff volume and have moderate to high ability to remove some soluble pollutants from the runoff. Infiltration trenches require regular maintenance to ensure the inlet structure is functioning properly. Infiltration systems have been found to effectively remove fine silts, clays, and phosphorus in the Lake Tahoe region (TIRRS 2001). In Washington State, infiltration technologies including ponds, bio-infiltration ponds, trenches, vaults and drywells are the preferred methods for flow control and runoff treatment, offering the highest levels of pollutant removal (WSDOT, 2011). According to Golub et al. (2008), “the depth of ground water and soil type limits the use of this option.” The sensitivity of underlying groundwater to increased chloride loadings is also a critical factor that needs to be taken into consideration.

Infiltration Basins

Infiltration basins function similarly to infiltration trenches, but more closely resemble a dry pond (Staples et al., 2004). Infiltration basins hold runoff, which allows for longer infiltration times; however, infiltration basins can release runoff from larger storm events depending on the design. Design considerations such as infiltration rates and site selection play an important role in the effectiveness of an infiltration basin. Infiltration basins are not recommended in areas with compacted soil, high or shallow groundwater levels, areas with contaminated soils or groundwater, and steep slope areas. Where stormwater has high levels of sediment, failure may occur and expensive remediation or re-installation may be required. Use of dense vegetation with deep roots at the bottom of the basin can enhance infiltration capacity and reduce soil erosion.

Vegetated Swales and Filter Strips

Biofiltration is the use of closely grown vegetation to filter runoff. This is achieved by allowing water to flow through the vegetation, which decreases the runoff velocity and allows particles to settle (Staples et al., 2004). Biofiltration systems are generally open channels and are referred to as swales, filter strips or natural and engineered dispersion. These systems provide effective removal of pollutants through mechanisms such as adsorption, decomposition, ion exchange, filtration, and volatilization. Biofiltration is most effective when combined with other treatment options such as ponds, infiltration trenches, or wetlands (Watson, 1994). Vegetated swales can be used for snow storage and allow the melt water to infiltrate. Vegetated swales and filter strips require minimal maintenance (mainly mowing and sediment/debris removal), which helps to keep their life-cycle cost low.

Bioinfiltration swales can be dry, grassy or vegetated channels (Staples et al., 2004; WSDOT, 2011). Swales are generally located in naturally low topographic areas of uniform grade such as road ditches (Staples et al., 2004). They are also useful for runoff control on highway medians (Barr Engineering Company, 2001). Dry swales may have check dams to temporarily pond runoff to both increase the removal of suspended solids and reduce the runoff velocity. Wet swales vary from dry swales by having very impermeable soils, often located close to the water table (Staples et al., 2004). Wet swales improve water quality through mechanisms such as adsorption, sedimentation, and microbial assisted decomposition of pollutants (Barr Engineering Company, 2001). Bioinfiltration swales would be expected to have the same potential issues with groundwater and the infiltration systems discussed above.

Grass swales, with both pre-treatment grass filter strips and vegetated check dams were used to treat highway runoff and found to not remove chloride but store it, such that it accumulated during the winter and was then released throughout the year (Stagge et al., 2012). Pretreatment grass filter strips were found to serve as chloride reservoirs and when used in combination with bioswales, chloride effluent concentrations significantly increased. Chloride removal was determined to be from infiltration. During rain events of 3 cm (about 1 inch) or less, bioswales in combination with check dams were found to significantly reduce total volume and flow magnitudes (Davis et al., 2012). During larger storms, the bioswales reduced the fluctuation in flow.

Alternative Methods to Remove Chlorides

In addition to the more conventional approaches to remove chlorides associated with winter road way operations from the environment such as the use of phytoremediation, new and emerging technologies focus on capturing chloride in filter media such as dolomite, calcium, or concrete. This technology is in the very early stages of research and minimal data is available. The primary treatment mechanism involved in this new method is sorption of chloride to the filter media, which is dependent on the capacity of the filter media. Recycled concrete has been shown to make an effective sorption material for chlorides and is capable of increasing chloride penetration rates and chloride binding capacity, which would help increase chloride removal efficacy if correctly implemented (Villagrán-Zaccardi et al., 2008); however, more research is needed to determine effective application methods and materials. Given the mass of chlorides released during snow melt events, it is likely to be very challenging if not cost prohibitive to use media for chloride removal.

Concluding Remarks

Several approaches used to reduce the toxicity of chloride based deicers have been discussed. The first technique focuses on reducing the amount of chloride base deicers applied to highways. However, when chloride based deicers are introduced into the environment reactive strategies such as treatment of chloride laden runoff by mixing to promote dilution reduces peak chloride concentrations, and routing chloride laden runoff away from sensitive surface and groundwater offer effective options to ultimately reduce the impact of chloride based deicers.

The main proactive method of reducing chloride based deicer toxicity is source control by reducing the amount of chloride based deicers introduced into the environment using the minimum amount of chloride based deicer needed to achieve the prescribed level of service. It is recommended to implement multiple proactive salt management techniques to ensure high success. Techniques such as salt management plans, deicing, anti-icing and pre-wetting practices, equipment calibration, use of weather services and forecasting information, staff training, and monitoring and maintaining accurate records can be used by roadway maintenance agencies to reduce or minimize the amount of chloride based deicers used or lost during operation. Table 22 summarizes proactive methods that can be used to reduce the amount of chloride based deicer released into the environment.

Table 22: Summary of proactive chloride mitigation methods.

	Description	Purpose	Benefits	Reference
Salt Manageme nt Plan	Guidelines to provide maintenance agencies effective salt management practices.	Provide safe, efficient, and cost-effective road management.	Assesses specific progress and identifies areas for further improvement.	TAC 2003a
Staff Training	Comprehensive training programs to demonstrate the purpose and value of procedures.	Provide LOS guidelines, principles of ice formation, chemistry of road salts, and environmental impacts of road salts.	Successful training programs have been shown to reduce deicer usage and improve winter maintenance operator practices.	Eckman et al. 2011
Monitoring and Record Keeping	Record management of deicing products and related procedures.	Aid in assessing the extent of deicer impacts and the effectiveness of mitigation measures.	Improve the understanding of deicer migration and determine mitigation strategies.	Environmen t Canada, 2004 TAC, 2003d
Anti-icing, Deicing and Pre-wetting Practices	Techniques for various winter roadway conditions focused on reducing amount of chloride released into the environment.	Provides high levels of service with multiple strategic approaches depending on conditions.	Reduced application rates, reduced loss of materials, reduced costs, and faster post-storm cleanup.	Peterson *et al.* 2010
Geo-fencing	Sets boundaries in specific locations along spreader routes and in sensitive areas.	Alerts operators when they enter environmentally sensitive areas.	Reduces the potential of overlap applications.	Mass DOT, 2012
Weather Forecasting and RWIS	Utilizing accurate weather forecasts and road weather information to develop effective and efficient treatment strategies.	Obtain real time data to support winter maintenance decision making processes.	Reduce application rates while providing the same, or better, level of service.	Strong and Shi, 2008 Shi *et al.* 2007 Ye *et al.* 2009a

When implemented correctly, these proactive mitigation strategies have been shown to reduce the total amount of chloride based deicers introduced into the environment while ensuring a high level of service. Future research efforts and management need to focus on reducing loss of product in patrol yards, reducing roadway application rates and reducing the frequency of application of deicers, and appropriate snow disposal and subsequent waste water treatment (Environment Canada, 2001).

Once chloride based deicers have been applied, various reactive mitigation techniques can be used to minimize the toxicity of chloride in the environment. Phytoremediation has been shown to remove chlorides from runoff when sufficient time for the biological process to work is allowed and the plants that take up the chloride are harvested and removed. Phytoremediation is most effective at sites with shallow subsurface contamination and is recommended as a polishing technique for treating soils and remaining salt laden pore water. Traditional stormwater structural BMPs can be used to manage chloride concentrations in runoff by controlling storage, conveyance, and promoting dilution, which can reduce the potential toxicity of highway stormwater runoff. Ponds and wetlands can be an effective reactive mitigation strategy focused on the storage and release of captured runoff. In addition, detention, retention and evaporation ponds can reduce peak chloride concentrations through the mixing of chloride laden runoff with base flow or non-chloride runoff. Wetlands and shallow marshes also reduce peak chloride concentrations when sufficient storage capacity is available and phytoremediation is applied. Careful considerations need to be evaluated since chlorides from roadway salts can have negative effects on the performance of wetlands. Infiltration of stormwater is an effective stormwater management technique; however, chloride contamination of ground water is a concern. Infiltration trenches and basin can be used to reduce surface water volume, but the depth of groundwater and soil type may limit their use. Vegetated swales and filter strips utilize bioinfiltration to filter and reduce runoff velocity, and work best when combined with other treatments. Vegetated swales can be used for snow storage. Grass swales have been found to store chlorides from runoff and later re-release it acting as a chloride reservoir. Table 23 summarizes reactive mitigation strategies that have been shown to reduce chloride concentrations and minimize the impacts of chloride based deicers. The use of various proactive strategies combined with effective reactive strategies will ultimately reduce the environmental impacts related to chloride based deicers.

Limited data and research is available on the performance and effectiveness of structural BMPs and phytoremediation with respect to chloride contamination associated with winter maintenance. Therefore, this knowledge gap needs to be supplemented with more research focused on the treatment and management of chlorides associated with winter maintenance in the environment. In addition, more extensive research is needed with respect to water quality sampling to determine how downstream dilution affects the transport of chlorides. Furthermore, the development of a method for continuous monitoring of chloride concentrations in highly affected areas would be a beneficial asset to winter road way agencies to assist in salt management decision making. Research focused on a cost/benefit analysis and the identification of the environmental impacts of using non-chloride deicing alternatives needs to be explored.

Table 23: Summary of reactive mitigation strategies.

	Description	Cost and Benefits	Ref.
Phytoremediation	The use of plants to aid in the removal of contaminants within soils, groundwater and surface waters.	Planting costs of $10,000 per acre. Provides effective contaminant removal through plant uptake.	Schnoor et al., 1995
Detention or Evaporation Ponds	Ponds used for storage and controlled release of runoff.	Decrease peak concentrations and promote dilution of chlorides. Offer effective pollutant removal through settling, nutrient uptake by plants, and biochemical processes.	Staples *et al.*, 2004
Infiltration Trenches and Basins	Excavated zones filled with stone and lined with filter fabric where runoff is collected and allowed to percolate into the soil.	$4 - $9 per cubic foot of storage provided in 2003 US dollars. Efficient removal of pollutants, increases groundwater recharge and reduces runoff volume and flow rate.	Staples *et al.* 2004
Wetlands and Shallow Marshes	Treatment wetlands designed to utilize both physical and chemical processes to improve water quality.	$39,000 to $82,000 with maintenance costs ranging from $780 to $1,640 for a one acre wetland in 2007 Provides high pollutant removal performance and reduces soil erosion.	Staples *et al.* 2004 Charles River Watershed Association, 2008
Vegetated Swales and Filter Strips	Dry, grassy or vegetated channels used near impervious surfaces.	$0.50 per square foot for vegetated swales in 2004. Design life of 20-50 years. Treat runoff by reducing velocity and allowing particles to settle. Effective removal of pollutants.	Staples *et al.* 2004 University of Florida, 2008

6. CONCLUSION

Key Findings

In order to develop strategies to reduce the environmental impact of roadway deicers, the initial research phase reviewed the state of the art of chemicals used for snow and ice control and the findings were reported to gain a better understanding and identify knowledge gaps within the literature. In addition, the knowledge and trends discovered from the review of chemicals used for snow and ice control guided the research approach for the subsequent phases of research. This portion of research focused on developing locally sourced salt brine additives for winter maintenance from waste utilization in an effort to reduce the overall environmental footprint of roadway deicers. This was achieved by identifying a specific set of liquid deicers made from agricultural resources and evaluated the performance in terms of ice melting capacity and impacts to carbon steel and Portland cement concrete to quantify performance characteristics and understand which products offer the highest potential. In an effort to reduce salt usage, the use of commercially available by-products in deicers was explored. Five test methods were used to evaluate liquid deicers containing by-products that reduce environmental impacts, enhance performance, and reduce costs. Differential scanning calorimetry (DSC) and electrochemical impedance spectroscopy (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.

Development of new snow and ice control chemicals has been actively progressing over the past several years in order to increase performance and reduce environmental impacts associated with conventional materials. Considerable data gaps exist with respect to the quantification of deicer performance and environmental impacts for new and emerging products derived from agricultural sources. Consequently, this research identified various agricultural by-products and determined that they offer promising ice melting performance with reduced impacts to metals and can be effective alternatives to conventional chloride based deicers. Commercially available by-products were successfully used in the development of a high-performance anti-icer formulation, which resulted in decreased environmental impacts, lower corrosion impacts, and lower costs 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.

In addition to deicer performance evaluations, this work then focused on the impacts of deicers when released into the environment and various strategies to mitigate the environmental risks. Specifically, the detrimental effects of roadway deicers on winter maintenance equipment were recognized and strategies for protecting maintenance equipment and increase service life were explored. The mechanisms of corrosion were reported in order to gain a better understanding of the corrosion process, which will enable effective improvements to protect maintenance from the harmful effects of chloride roadway deicers. It was determined that proactive approaches such as the application of improving designs and implementing maintenance practices can combine to significantly reduce the harmful effects of corrosion and the associated costs while increasing service life of equipment fleet.

Several approaches used to reduce the toxicity of chloride based roadway deicers were examined. Chloride source control through the implementation of techniques such as salt management plans, staff training, and record management combined with effective treatment of chloride laden runoff by mixing to promote dilution can significantly decrease the harmful effects of chloride roadway deicers. It was determined that various proactive and reactive strategies such as effective winter maintenance practices and improved use of stormwater structural BMPs can combine to successfully reduce the overall environmental risk of chloride deicers. The key findings and knowledge gaps of this thesis are summarized in Table 24.

Future Research

In order to make effective decisions during winter maintenance operations, it is critical that agencies understand the performance characteristics and negative impacts of snow and ice control materials. Additional research is needed to fully understand the effects of using snow and ice control products derived from agricultural processes. Environmental impacts such as toxicity and effects on water, vegetation and soils need to be carefully evaluated in order to fully understand the long term use of agricultural based products. Future research focused on the treatment and management of chlorides associated with winter maintenance in the environment is needed along with extensive research with respect to water quality sampling to determine how downstream dilution affects the transport of chlorides through the environment.

Table 24: Summary of key findings and knowledge gaps.

	Key Findings	Knowledge Gaps
Chapter 2 Recent Developments	Use of agricultural products reduces salt usage and environmental risks. Liquid deicers reduce impacts to air quality, water quality, and roadside vegetation.	Limited exploration of local products. Long term use effects of agricultural products on the environment. Minimal environmental impact data.
Chapter 3 Developing Alternatives	Successfully developed liquid deicers from waste product. Effective alternatives reduce salt usage and environmental risk. Decrease winter maintenance costs.	
Chapter 4 Protecting Maintenance Equipment	Effective equipment maintenance practices and improved design combine to significantly reduce the harmful effects of corrosion and the associated costs. Online corrosion monitoring provides valuable real time corrosion information. Implement corrosion control protocol to protect maintenance equipment.	Lack of information on the cost-effectiveness of automated washing systems. Field performance of regular washing and innovative anti-corrosion products. Need to develop best practice guidelines.
Chapter 5 Mitigation Measures	Proactive strategies can significantly reduce environmental risks of chloride based deicers. Stormwater structural BMPs can be used to manage chloride concentrations by controlling storage and promoting dilution.	Limited data and research on the performance and effectiveness of structural BMPs related to chloride contamination associated with winter maintenance. How downstream dilution affects the transport of chlorides. Continuous chloride monitoring programs.

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