

Understanding the Effectiveness of Non-Chloride Liquid Agricultural By-Products and Solid Complex Chloride/Mineral Products

Western Transportation Institute



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16. Abstract (Limit: 250 words) Agriculturally derived products, or agro-based products, and complex chloride mineral (CCM) based products are increasingly employed in snow and ice control operations, either used alone or more commonly as additives or blended with traditional chloride-based products such as rock salt (solid sodium chloride) and salt brine (liquid sodium chloride). Past studies and manufacturers have claimed that agro-based or CCM based products provide benefits such as freezing point depression, prolong performance on the road surface, the ability to utilize UV light as an aid to ice prevention, and various environmental benefits. However, the measurement of the effectiveness of such products has been limited. To further investigate the role CCM and agro-based products may have in deicing and corrosion protection, a literature review and national survey were conducted to identify potential products, how they are typically used, performance characteristics, and pros and cons. Ten products were selected for extensive laboratory testing which investigated the products ability to lowering the freezing point of water and improve the ice melting capacity, weaken the ice bond to pavement, improve the product longevity on the road surface, prevent ice formation or refreeze prevention, and assess the influence of absorbance of sunlight on product performance. Results of the laboratory testing and literature review were used to develop a best practices manual. This report documents the work completed for each task of this project, as well as provides a presentation of the major findings.			
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Executive Summary

Agriculturally derived products, or agro-based products, and complex chloride mineral (CCM) based products are increasingly employed in snow and ice control operations, either used alone or more commonly as additives or blended with traditional chloride-based products such as rock salt (solid sodium chloride) and salt brine (liquid sodium chloride). Past studies and manufacturers have claimed that agro-based or CCM based products provide benefits such as freezing point depression, prolong performance on the road surface, the ability to utilize UV light as an aid to ice prevention, and various environmental benefits. However, the measurement of the effectiveness of such products has been limited to qualitative field observations and their specific role in snow and ice control is poorly understood. To better understand how agro-based and CCM products work, this study utilized a systematic laboratory investigation to better understand the chemical and or physical processes by measuring the degree to which products 1) Lower the freezing point of water and improve the ice melting capacity, 2) Weaken the ice bond to pavement, 3) Improve product longevity on the road surface, 4) Prevent ice formation, 5) Influence absorbance of sunlight on performance, and 6) Corrosion to carbon steel. Components of the study included a literature review, survey, laboratory investigation, and development of a best practices manual.

For the purpose of this study, two complex chlorides/minerals based products and eight agro-based deicers were identified for laboratory testing. Four agro-based deicers were prepared by mixing the vendor-provided “concentrates” with a 23.3 wt. % sodium chloride (NaCl) aqueous solution, at either 70:30 or 80:20 volume ratio, depending on the vendor specification. Additionally, four agro-based products were used, as received from the manufacturer for laboratory testing. The CCM based products were also used as received.

Literature review

The main composition of agro-based products includes desugared beet molasses, corn by-products, cheese brewing by-products, beer brewing by-products, succinate salts, urea, and starch. These products are either used alone or as additives with other winter maintenance chemicals to improve performance and/or to reduce corrosion and environmental impacts. The use of complex chlorides and naturally available mineral products (Ice Slicer®, QwikSalt®, DriRox Coarse Salt®, Natural Alternative Ice Melt®, etc.) are becoming increasingly employed for snow and ice control operations.

Recent studies have shown improved performance of agro-based products and naturally occurring chloride and non-chloride products in snow and ice control operations, along with reduced risk to highway infrastructure and environment. Yet, few studies have been performed to examine the modes of action by which these newly developed products help in improving performance and reducing negative impacts on highway infrastructure and the environment.

National Survey

Thirty one respondents representing 16 states participated in an online survey to document the current state of knowledge of non-chloride liquid agro by-products and solid CCM products primarily used for winter maintenance activities. The following information was gleaned from the survey responses:

- Some respondents prefer using non-chloride agro-based products at low temperatures (below 20°F).
- Longevity on the road surface (residual effects) was one of the stated observed benefits of using agro-based products by survey respondents.
- Improved performance at low temperatures and reduced material usage were common benefits observed by survey respondents when using CCM based products.
- Limited research has been conducted by survey respondents on agro-based and CCM based products.

Laboratory Results

Lowering the freezing point of water & improving the ice melting capacity

CCM based products did not significantly reduce the freezing point of water compared to NaCl and did not produce more ice melt than the NaCl at 25°F and 5°F. However, CCM based product produced more ice melt than the NaCl at 15°F

Liquid agro-based products blended with 23.3% salt brine significantly lowered the freezing point of water compared to NaCl and did not produce more ice melt than salt brine (NaCl, liquid) alone at 25°F, 15°F and 5°F. Agro-based products (as-received) significantly lowered the freezing point of water compared to NaCl and produced more ice melt than salt brine.

The addition of agro-based by-products acted as freezing point depressants (potentially serving as a cryoprotectants, preventing ice nucleation from occurring). In addition, agro-based products exhibit significantly lower characteristic temperature and lower enthalpy values. This suggests that the amount of thermal energy corresponding to the aqueous brine solution's liquid/solid phase transition is reduced by the addition of agro-based by-products; making the agro-based by-products mixed with brine more difficult to freeze than salt brine alone.

Weakening of ice bond to pavement

For CCM based products, the bond strength between ice and pavement is slightly reduced compared to NaCl at 25°F and 15°F.

For agro-based products, the bond strength between ice and pavement compared to salt brine (NaCl, liquid) was significantly reduced at 25°F, 15°F and 5°F when used as anti-icer. The addition of agro-based products to salt brine increased the overall viscosity of the products. The agro-based products with higher viscosity compared to salt brine would have much slower grain boundary penetration than the salt brine with lower viscosity. This may result in more product spread on the pavement surface resulting in reduction in bond strength between ice and pavement surface.

Improving the product longevity on the road surface

Agro-based products tend to stay on the road surface longer than salt brine. Longevity of the product on the road surface depends on the amount of product dissolved in to the snow before each cycle of plowing. Agro-based products tend to dissolve less in snow compared to salt brine when used as anti-icer.

Prevention of ice formation/refreeze prevention

Agro-based products tend to have better friction values during extreme cold snow events (around 5°F) and during repeated warm snow events (25°F and 15°F). Agro-based products act as ice crystal nucleation point inhibitors, delaying the formation of ice compared to salt brine.

Absorbance of sunlight

For CCM based products, at higher intensity sunlight, ice melting capacity was similar, irrespective of the product type at 15°F and 5°F. At medium intensities of sunlight, ice melting capacity of CCM based product is slightly higher than NaCl at 15°F and 5°F.

For agro-based products, at higher intensity sunlight, ice melting capacity was similar, irrespective of the product type at 15°F and 5°F. At lower temperatures, darker colored agro-based products had higher ice melting capacity than lighter color agro-based products and salt brine.

Best Practices Manual

A best practices manual was developed based on the results from the laboratory investigation. Components of the best practices manual include storage guidelines, material handling and loading, storage and mixing, brine production equipment, application methods and guidelines, anti-icing and direct liquid application, and identified issues with agro-based products.

Chapter 1: Introduction

More effective and efficient snow and ice control chemicals could result in significant economic, environmental, and social benefits. Approximately 70% of U.S. roads are located in snowy regions, with nearly 70% of the U.S. population living in these regions (FHWA, 2013). Deicing chemicals are commonly used for snow and ice control operations in these regions and they melt snow and ice by lowering the freezing point of water. The most common deicing 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).

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, Volkening, Gallaway, & Shi, 2008). It is used in either a solid or liquid form and is effective over a wide range of temperatures (Cuelho, Harwood, Akin, & Adams, 2010). In addition, 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, Minsk, Blackburn, & Fleege, 1996; Warrington and Phelan, 1998; Shi et al., 2009b). CaCl_2 and MgCl_2 , which exhibit better ice-melting performance than salt brine at cold temperatures, are used by many departments of transportation (DOTs) in a brine solution for anti-icing or to pre-wet rock salt (Baroga, 2005). Despite their performance in snow and ice control operations, the use of chloride based deicers has led to deteriorating effects on motor vehicles (Johnson, 2014), transportation infrastructure (Shi et al., 2009a, Shi, Liu, Mooney, Berry, Hubbard, & Nguyen, 2010) and the environment (Fay and Shi, 2012). Departments of Transportation have begun to use acetate-based deicers such as CMA and KAc due to their non-corrosive effects, benign impacts on surrounding soils and ecosystems, and minimized adverse health effects (Shi, Staples, & Stein, 2005). However, recent studies have found that acetate based deicers, especially CMA, can cause significant loss of material and a reduction in stiffness and strength of concrete (Santagata & Collepardi, 2000; Darwin, Browning, Gong, & Hughes, 2008). Acetate based products in general have been found to elevate biological oxygen demand (BOD) in adjacent waterways (Fay, Shi, Venner, & Strecker, 2014).

More recently, agro-based chemicals are used for anti-icing and deicing activities. These agro-based chemicals are either used alone or as additives blended with winter maintenance chemicals (Nixon & Williams, 2001). Agro-based products have emerged since the late 1990s, often produced through the fermentation and processing of beet juice, molasses, corn, and other agricultural products (Cheng & Guthrie, 1998; Albright, 2005). Recently, glucose/fructose and unrefined sugar have been mixed with sand (applied to road to improve traction) to prevent freezing and added to salt brine for anti-icing (Hallberg, Gustafsson, Johansson, & Thunqvist, 2007). Agro-based additives increase the cost of the winter maintenance product, but may provide enhanced ice-melting capacity, reduce the products corrosivity, and/or last longer than standard chemicals when applied on roads (Fischel, 2001; Kahl, 2004). Due to high cost, agro-

based products are rarely used alone. Instead they are frequently mixed with other common deicers or anti-icers, in part to lower their freezing point and inhibit their corrosiveness (Nixon & Williams, 2001).

A considerable amount of research has been carried out in the recent years to study the improved performance of agro-based products and their benefits on the highway infrastructure and the environment. Taylor Verkade, Gopalaakrishnan, Wadhwa, & Kim (2010) evaluated the brines made of glycerol, NaCl, MgCl₂, and commercial deicers, individually and in combination, and concluded that the blend of 80% glycerol with 20% NaCl showed the greatest promise in terms of laboratory performance and low negative impacts (Taylor et al., 2010). Janke and Johnson Jr. (1999a) developed an environmentally friendly deicer from a by-product of a wet milling process of corn called steepwater. The deicer formulation is noncorrosive, inexpensive, water soluble, and readily available in large quantities. Tests have shown that corrosion inhibition is achieved with the addition of these steepwater solubles to chloride salts (Janke and Johnson Jr, 1999b). Despite the identified advantages, there are concerns over the toxicity to the aquatic ecosystems, high cost, quality control issues (Fischel, 2001), and possible attraction by wildlife (per the discussions on the Snow-Ice List Serve).

In addition to agro-based deicers, another class of deicers features the unique synergy of complex chlorides and mineral products (CCM). For instance, AquaSalina™ is a product consisting of natural brine and corrosion inhibitor which is produced from natural resources instead of fresh water, thus preserving valuable water resources and has been recently approved by the Pacific Northwest Snowfighters (PNS). AquaSalina™ claims to enhance the performance of rock salt and to feature higher ice melting capacity and colder effective temperatures than salt brine.

They are various commercially available products such as liquid sugar beet and corn by-products (Ice Bite®, GeoMelt®, IceBan®, Ice B'Gone®, etc) and mined and evaporated solid salt products with naturally occurring chloride and non-chloride constituents (Ice Slicer®, QwikSalt®, DriRox Coarse Salt®, Natural Alternative Ice Melt®, etc.).

Despite the recent studies showing improved performance of agro-based products and naturally occurring chloride and non-chloride products in snow and ice control operations and reduced impacts to highway infrastructure and the environment, little research has been done to study the mechanisms behind these benefits. Many studies have analyzed agro-based and CCM products either in comparison with non-agro based products or individually assessing the products ice melting capacity, corrosivity, and environmental impacts. No studies have been found which examine the properties of such products and or verified the chemical or physical processes by which the products are of value in snow and ice control operations, specifically at reducing impacts to highway infrastructure and the environment.

With this context, a systematic laboratory investigation was performed to understand the chemical or physical processes behind the effectiveness of agro-based and CCM based products in the following categories:

- Lowering the freezing point of water and improving the ice melting capacity
- Weakening the ice bond to pavement
- Improving product longevity on the road surface
- Prevention of ice formation
- Absorbance of sunlight
- Corrosion to carbon steel

:

Chapter 2: Literature Review

Existing Agro-based Products and Solid Complex Chloride/Mineral Products

This section is devoted to summarizing relevant literature regarding the existing agro-based and solid complex chloride/mineral products. Further, the main composition of each newly developed anti-icing/deicing product is presented with its potential advantages and disadvantages. Note the much of early laboratory work characterizing these products has been conducted by industry, likely due to interest and available funding. Where available information from peer reviewed third party testing is also presented.

As agro-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 impacts, and reducing corrosiveness. The most common commercially available agro-based liquid deicers are GEOMELT®, Magic Minus Zero™ and Magic Salt™, Icenator™, Bare Ground™, Caliber M1000™, IceBan®, and Ice Bite®.

- GEOMELT is made from a derivative of sugar beets and has been approved by PNS.
- Magic Minus Zero is a noncorrosive anti-icer composed of a mixture of MgCl₂ and a by-product of a distilling process.
- Magic Salt is a rock salt treated with liquid Magic Minus Zero.
- Icenator is a noncorrosive liquid deicer made from corn by-products, and has been known to increase the surface friction of asphalt when dry.
- Bare Ground is a corn based liquid deicer/anti-icer combined with MgCl₂.
- Caliber M1000 is composed of 30% MgCl₂ 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).
- IceBan® is prepared from the organic by-products in the processing of alcohol, cheese, or corn.
- Ice Bite® is an anti-icing fluid that has been approved by PNS and is reportedly effective at low temperatures (Road Solutions, Inc). Ice Bite® is made from an agricultural product and is usually mixed with salt brines to reduce corrosion and improve ice melting at lower temperatures.

Recent developments in agro-based deicers have been explored and multiple patents have been produced as shown in Table 1. 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.

Another 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% CaCl₂, 7-8% NaCl, 2-3% MgCl₂, and 1% potassium chloride. AquaSalina™ is produced from natural resources instead of fresh water, thus preserving valuable water resources and has been recently approved by PNS. AquaSalina™ has claimed to enhance the performance of rock salt and to feature higher ice melting capacity and have a colder effective temperature 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 products. A commonly used approach to address these issues has been the use of waste products, such as bio-derived components, in snow and ice control products to reduce environmental impacts and costs while minimizing corrosive effects.

Table 1: Patents for deicing agents made from agricultural products (Taylor et al., 2010).

Product Name	Reference	U.S. 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 & Wood, 2007)	7208101
Corn wet-milling by-products	(Janke & Johnson Jr, 1999a)	5965058
Cheese brewing by-products	(Janke & Johnson Jr, 1999b)	5919394
Beer brewing by-products	(Johnson & Pratt, 1999)	5922240
Urea	(Kerti, Kardos, & Kalman., 2001)	6319422
Particulate plant material	(Koefod, 2000)	6156227
Monohydric and polyhydric alcohols	(Haslim, Lockyear,& Zuk., 1998)	5772912
Alkalinally reduced sugars	(Montgomery & Yang, 2003b)	6605232
Succinate salts	(Berglund, Alizadeh, & Dunuwila, 2001)	6287480
Alkali metal acetate	(Dietl & Stankowiak, 2005)	6955770
Calcium chloride and urea	(Ossian & Steinhauser, 1997)	5683619
Non-chloride based liquid deicer	(Seo, 2007)	7276179
GEOMELT®	Road Solutions, Inc., 2007	-
Magic Minus Zero™ and Magic Salt™	MagicSalt.info, 2007	-
Icinator Liquid Deicer	eHealth Solutions, 2005	-
Bare Ground Solution	Bare Ground Systems, 2003	-
Caliber M1000	Glacial Technologies, 2008	-

Additives such as Boost® are proprietary formulas, but utilize organics such as sugar or alcohol to suppress the freezing point of salt brine. The use of CaCl₂ 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, 2014). These additives can be costly, but may be necessary in cold climates to produce a solution with a lower freezing point (similar to MgCl₂). The anti-icers available on the market are faced with growing concerns over their corrosivity to metals (chlorides), impact on concrete and asphalt (MgCl₂ and acetates), and toxicity to the aquatic resources (chlorides, acetates, glycols, and agro-based products). Agencies are continually searching for alternative snow and ice control products 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 MgCl₂ at reasonable costs.

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 (Pachauri & He, 2006, Thompson & He, 2006). Crude glycerol is inexpensive at \$0.02 per gallon. The addition of succinate salts, derived from succinic acids, and glycerol to salt brine can enhance anti-icing performance at cold temperatures to the level comparable to MgCl₂ or KAc 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 not been used as highway anti-icers or deicers. 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 potassium succinate (KSc) (50 % by weight) 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, sponsored by DNP Green Technology, Inc., New York (DNP), 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 O₂/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 DNP fermentation-based biotechnology has facilitated a significant cost reduction in the production of succinate salts. While the fermentation-derived succinate salts have shown great potential for airport runway applications, they have not been used as highway anti-icers or deicers. For highway applications, a different set of priorities exist for anti-icing products and new research efforts are needed to develop commercially viable formulations consisting of agro-based succinate salts, rock salt and other additives in order to develop cost-effective formulations addressing the needs of winter highway operations (Berglund, Dunuwila, & Alizadeh, 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 CMA, which can also be

produced from products of the fermentation process. Mathews (1994) has proposed a procedure for the practice of utilizing fermentation products to create road deicer products. 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 (James, Klyosov, Monovoukas, & Philippidis, 2000).

Chemical deicing fluids for airplanes 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 as 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 (LD50) 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.

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). Janke & Johnson Jr. (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 steepwater solubles to chloride salts (Janke & Johnson Jr., 1997).

Table 2: Typical composition of steepwater (Janke & Johnson Jr, 1997)

ITEM	DRYBASIS (No Moisture)	CONDENSED (48% solids/52% Moisture)
Crude Protein	33%	16%
Crude Fat	0.20%	0.10%
Acid Detergent	0.66%	0.32%
Fiber		
Phosphorus	2.31%	1.12%
Calcium	0.02%	0.01%
Sulfur	0.56%	0.27%
Potassium	2.74%	1.32%
Magnesium	1.08%	0.52%
Sodium	0.13%	0.06%
Iron	145 ppm	70 ppm
Aluminum	22 ppm	10 ppm
Manganese	34 ppm	17 ppm
Copper	8 ppm	4 ppm
Zinc	140 ppm	68 ppm
Total Ash	27%	5.4 - 21.68%

Similarly, Kharshan, Gillette, Furman, Kean, & Austin, (2012) demonstrated the successful increased corrosion protection of carbon steel using corn extracts (Kharshan et al., 2012). Table 2 displays the typical composition of steepwater. It is suggested that an amount of 20 to 60 gallons per lane mile of the steepwater deicer be applied to effectively clear snow and ice from roadways. When applied to roadways, the steepwater 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 steepwater 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 steepwater demonstrated higher melting performance than the salt, sand mixture with respect to both duration and strength. In addition, the steepwater 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 & Johnson Jr., 1997). A proposed 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 has a freezing point around -14.8°F (-26°C) (Montgomery & Yang, 2003). Furthermore, corrosion testing resulted in little effect on mild steel as shown in Table 3. Mild steel bolts were immersed in various concentrations of steepwater and showed no oxidation after four months. Moreover, mild steel bolts were sprayed with various concentrations of steepwater and showed no signs of

oxidation after four months; rather the mild steel bolts appeared to be sealed with a protective coating (Janke & Johnson Jr., 1997).

Table 3: Corrosion results (Janke and Johnson Jr, 1997)

MATERIAL	CORROSION (mils per year -MPY)
Mild Steel	0.5
Stainless Steel	None detectable
Aluminum	None detectable

Another proposed deicer is made from a fermentation by-product of processing cheese known as whey (Janke & Johnson Jr., 1998a). 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% soluble 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 5% by weight chloride salts compared to a solution of 5% salts. Also, the whey composition can be used as an anti-icer, applied to the roadway prior to the accumulation of snow and ice. Tests have shown that the whey based 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 & Johnson Jr., 1998a).

Janke & Johnson Jr. (1998b) proposed an additional noncorrosive, environmentally safe deicer composition made from condensed solubles acquired from the processing of wine. The wine by-product deicer has a low freezing point of -20°F (Janke & Johnson Jr., 1998b). Although the deicer composition presented by Janke and Johnson Jr., (1998b) offers viable alternative deicers to chloride salts, some negative characteristics were reported. 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 in residential areas.

Bloomer (2000) proposed developing a deicer formulation made from a waste product of processing sugar beet molasses. Sugar beets are processed to remove the sugar and produce commercial grade sugar. Syrup is formed and then heated to separate crystals that become commercial grade sugar from liquor, which is the desugared sugar beet molasses. Currently, this waste product, the desugared sugar beet molasses, is used as animal feed. The composition of

desugared sugar beet molasses is shown in Table 4. 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 $\frac{1}{4}$ -1 inch thick are shown in Table 5. 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 $MgCl_2$ 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 $CaCl_2$ showed no corrosion after three months (Bloomer, 2000).

Table 4: Composition of desugared sugar beet molasses (Bloomer, 2000)

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

Table 5: 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.

A study of a similar molasses based product performed by Petkuviene and Paliulis (2009) show comparable results. The corrosion inhibition of Safecote, an organic substance based on molasses, was tested and found to be an effective corrosion inhibitor. Immersion and spray testing coupled with mass loss measurements were performed on a variety of metals. Safecote exhibited good performance test results after 100 days as shown in Figure 1.

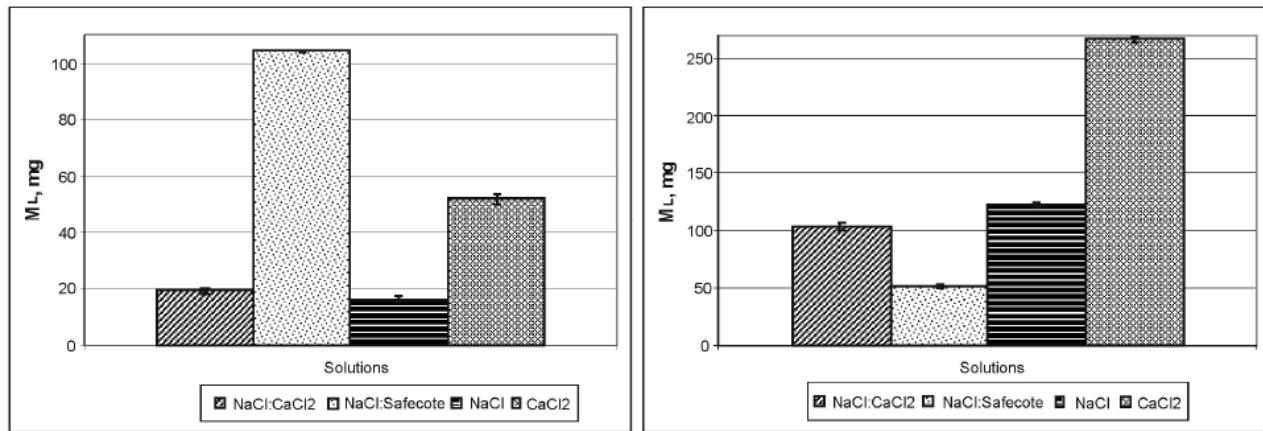


Figure 1: Carbon steel mass loss by immersion method on left and spray on right (Petkuviene & Paliulis, 2009).

Although Janke and Johnson Jr. (1998a, b) and Bloomer (2000) use materials that are naturally occurring and are considered renewable resources, it is believed that they contain hundreds of components and are very inconsistent with variable properties depending on source and batch. In addition, these materials have undesirable elements with high organic content, which causes biological degradation and high biological oxygen demand.

In this context, Hartley and Wood (2001) proposed a new synergistic approach for developing an effective deicer in which a low molecular weight carbohydrate is integrated with an inorganic freezing point depressant. Specifically, polysaccharides derived from agricultural based products such as corn, wheat, barley, oats, sugar cane, or sugar beets are added to chloride salts. A series of filtration mechanisms is used to isolate the active components in brewer's condensed solubles such that the low molecular weight carbohydrates can be utilized. Carbohydrate composition varies greatly, therefore, an evaluation of simple sugars, disaccharides, and polysaccharides to determine a relationship between freezing point and molecular weight is needed. The results are shown in Table 6 and Table 7. In addition, the effect of chloride salt content on freezing point of the deicing solution was evaluated and the results are shown in Table 8. Corrosion results shown in Table 9 were obtained following test method SHRP H205.7 Test Method for Evaluation of Corrosive Effects of Deicing Chemical on Metals and suggest corrosion inhibition was observed due to the carbohydrate additive (Hartley & Wood, 2001). Additionally, Hartley and Wood (2006) proposed a deicer composition, with improved viscosity characteristics, derived from brewers condensed solubles. This composition contains a mixture of carbohydrates and chloride salts to maintain a high level of performance (Hartley & Wood, 2006).

Table 6: Freezing point test results for simple carbohydrates (Hartley & Wood, 2001)

<u>SIMPLE CARBOHYDRATES</u>					
Carbohydrate		% Concentration	Freezing Point		
Type	Name	of Carbohydrate	° F.	° C.	
Control	MgCl ₂ (15%)	Nil	-4.7	-20.4	
Sugar	Fructose	25.0	-8.9	-22.7	
Sugar	Fructose	50.0	-18.2	-27.9	
Sugar	Fructose	75.0	-31.9	-35.5	
Sugar	Glucose	30.0	-11.4	-24.1	
Sugar	Glucose	65.0	-37.3	-38.5	
Disaccharide	Maltose	25.0	-8.3	-22.4	
Disaccharide	Lactose	25.0	-11.7	-24.3	

Table 7: Freezing point test results for complex carbohydrates (Hartley & Wood, 2001)

<u>COMPLEX CARBOHYDRATES</u>					
Carbohydrate		% Concentration	Freezing Point		
	of Carbohydrate		° F.	° C.	Comments
Control	MgCl ₂ (15%)	Nil	-4.7	-20.4	
Corn syrup-high maltose		30	-5.6	-20.9	Contains glucose, maltose and maltotrisose
Corn syrup-high maltose		65	-19.1	-28.4	
Corn syrup solids DE20		25.0	-9.9	-23.3	Average Mol. Wt. 3746
Corn syrup solids DE44		25.0	-11.6	-24.2	Average Mol. Wt. 1120
Corn syrup solids DE44		50.0	-21.3	-29.6	
Corn syrup solids DE44		65.0	-27.0	-32.8	

Table 8: Freezing point test results (Hartley & Wood, 2001)

Chloride Salt	% salt by weight	% Carbohydrate by weight	Freezing Point	
			° F.	° C.
MgCl ₂	22.7	18.0	Less than -47	Less than -43.9
MgCl ₂	15.0	25.5	-22	-30
CaCl ₂	29.6	18.6	Less than -47	Less than -43.9
CaCl ₂	17.5	4.1	-5.4	-20.8
CaCl ₂	15.0	4.1	-0.6	-18.1

Table 9: Corrosion test results (Hartley & Wood, 2001)

% Chloride Salt	%	Corrosion Rate (mils per year)		
		One Week	Three weeks	Six weeks
15% NaCl	Nil	5.97	4.66	5.48
15% MgCl ₂	Nil	2.58	1.93	1.73
15% MgCl ₂	4.1	0.89	0.61	0.40

To achieve improved corrosion inhibition, high concentrations of carbohydrates are required which affects the ice melting capacity and increases biological oxygen demand. The major constituents in most agricultural byproducts are sugars, thus Koefod (2010) 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% NaCl solution with various inhibitors during this cyclic immersion test. Test results are shown in Table 10 and Table 11. It was determined that this alternative approach yields effective corrosion inhibitors at lower costs and concentrations (Koefod, 2010).

Table 10: Corrosion test results (Koefod, 2010)

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 11: Corrosion test results (Koefod, 2010)

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

All of these newly developed agro-based deicing salts have shown great potential for anti-icing and deicing applications. 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.

Evaluation of Agro-Based and Solid Complex Chloride/Mineral Deicers

This section is devoted to synthesizing the existing methods for the evaluation of the effectiveness of the agro-based and solid chloride/mineral (CCM) products. 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. Existing evaluation methods mainly focus on testing the ice melting capacity, ice penetration, ice bonding, and thermal properties of agro-based and solid chloride/mineral products.

A three step process for evaluating deicers proposed by Nixon, Kochumman, Qiu, Qiu, and Xiong (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 & Williams, 2001).

Evaluation of liquid deicer performance has been the focus of many research projects in recent years. Shi et al. (2009b) 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 2 shows the eutectic curves for the most commonly used liquid deicers including MgCl₂, NaCl, CaCl₂, and KAc with solution concentrations (Ketcham et al., 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 (Ketcham et al., 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, 2011; Shi et al., 2011a).

Acetates are also a promising alternate deicers and exhibit high performance in lab and field studies. Fay et al., (2008) reported that CMA melted ice longer than chloride based deicers. 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 (Perchanok, Manning, & Armstrong, 1991; Wyant, 1998). Furthermore, 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 MgCl₂ (Fischel, 2001).

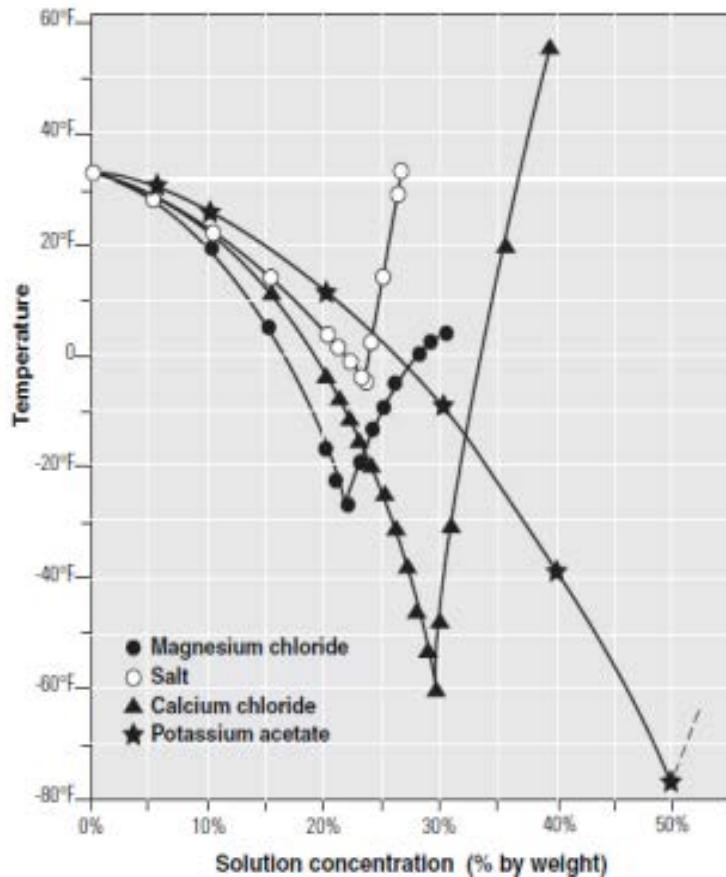


Figure 2: Eutectic curves of four common chemical solutions (Ketcham et al., 1996).

Fischel (2001) compared the eutectic temperatures and effective temperatures of selected liquid deicers at their specific solution concentrations. The results are summarized in Table 12, which shows that Caliber M1000, KAc, and CaCl₂ have low eutectic and effective temperatures, whereas CMA has higher eutectic and effective temperatures. MgCl₂, KAc, and CaCl₂ 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.

Table 12: Eutectic and effective temperatures of selected deicers.

Deicer	Concentration	Eutectic/Effective Temperature (°F)	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

Additional laboratory testing of Caliber deicing products was performed by Bytnar (2009). Ice penetration tests and ice melting capacity tests were able to demonstrate 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 3. Figure 4 shows a comparison of ice melting capacities at various temperatures for three Caliber products, 30% CaCl₂ and 30% MgCl₂. Caliber M1000 had great ice melting performance with ice melting capacities greater than or equal to 30% MgCl₂. Furthermore, corrosion testing following the PNS test method demonstrated Caliber M1000 had minimal corrosion impacts with significantly lower percent corrosion than salt and MgCl₂ as shown in Figure 5 (Bytnar, 2009)

In recent years anti-icing compounds developed from agricultural by-products have been produced 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 (Fischel, 2001; Kahl, 2004; Shi et al., 2011a). It was reported that adding beet juice to salt brine would help the salt stay on the pavement longer and thus improve the overall performance

of the brine. A formulated chloride based liquid deicer/anti-icer “GeoMelt S30” has been used in Southern Ontario, Canada (Soudki, Jeffs, & Safiuddin, 2011). It contains an organic additive derived from desugared beet juice (GeoMelt 55 concentrate) that is blended with NaCl brine. The use of GeoMelt was as effective as other deicers at lower application rates and it adhered 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% MgCl₂. Fischel (2001) has compared the effectiveness of Ice Ban to magnesium chloride based deicers, and Ice Ban was reported to have faster melting effects at lower temperatures than the MgCl₂ solutions. A more consistent, longer lasting residual effect was observed when compared to MgCl₂ (Fischel, 2001). Controlled field trials conducted in New York State 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, 1999)

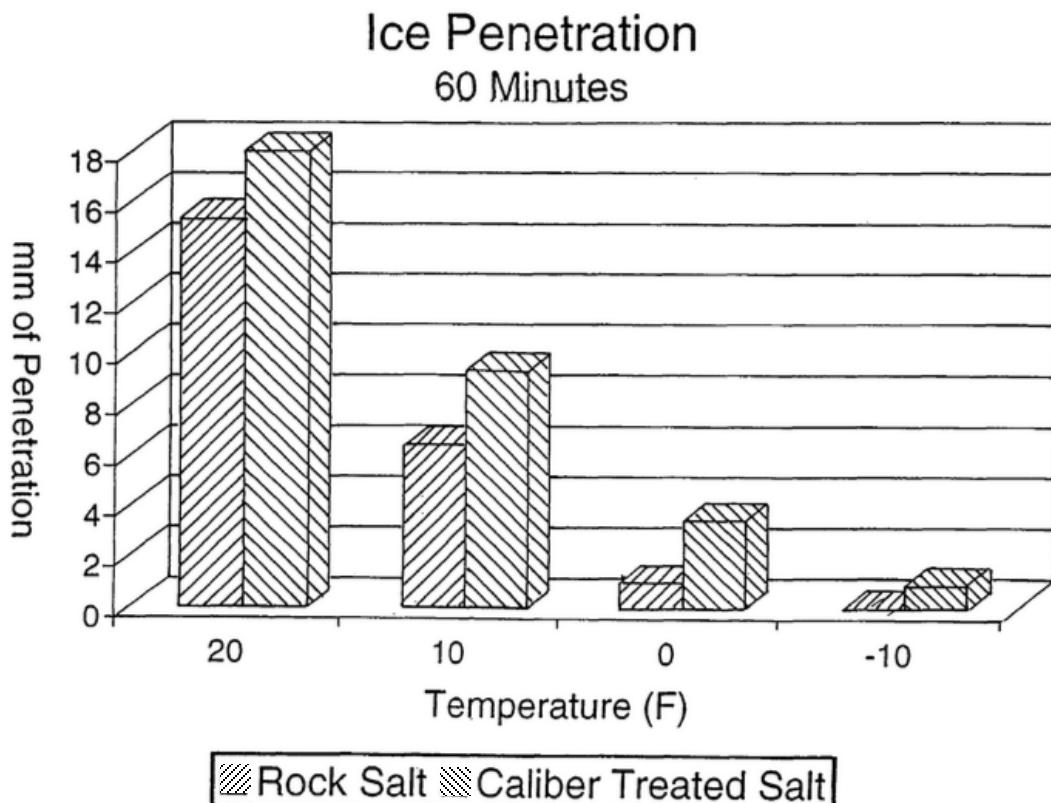


Figure 3: Ice penetration results of various deicers at different temperatures. (Bytnar, 2009).

Melting Capacities

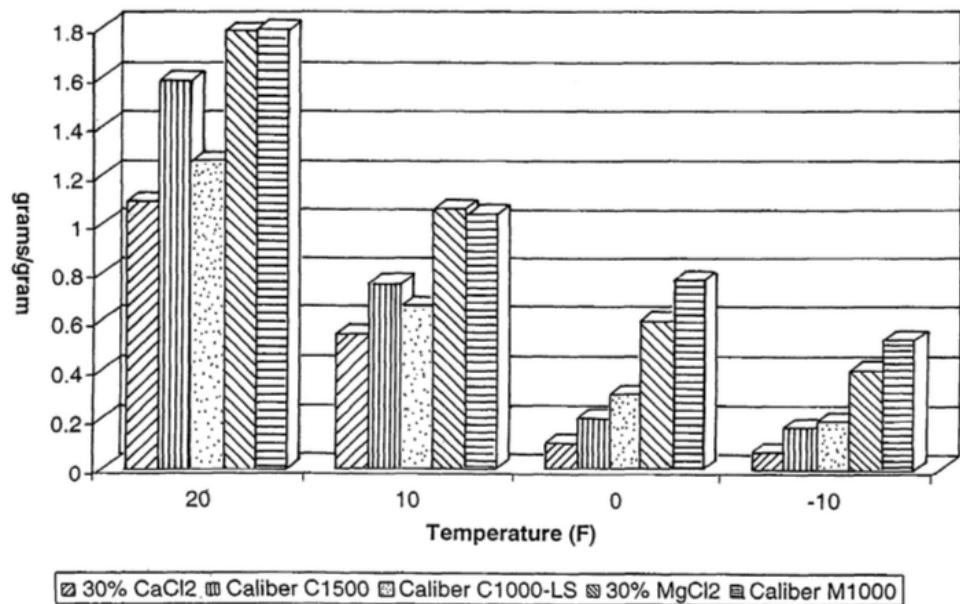


Figure 4: Ice melting capacity results of various deicers at various temperatures (Bytnar, 2009)

Corrosion Comparison

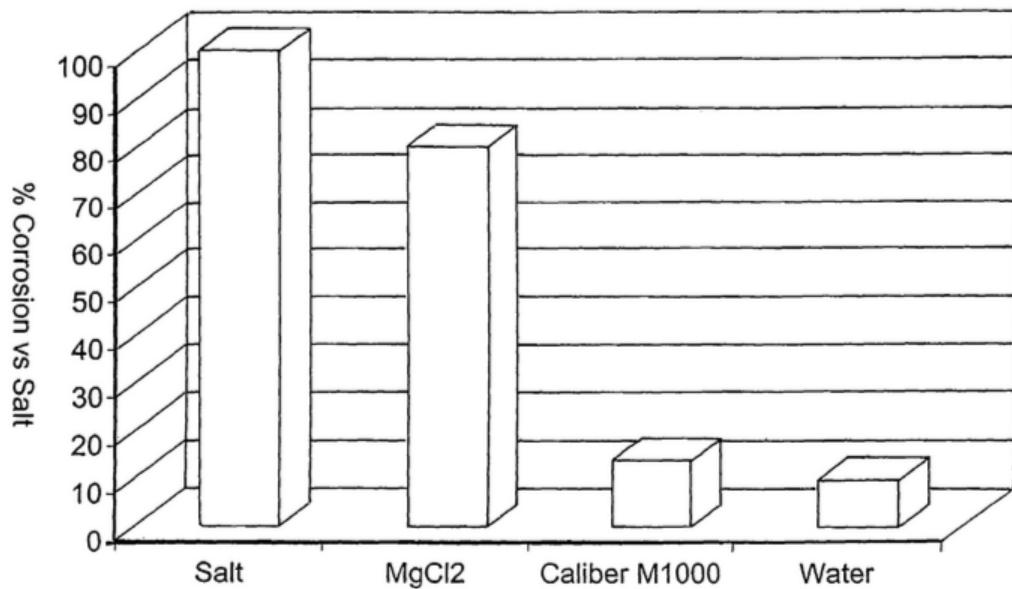


Figure 5: Corrosion results from PNS test method of various deicers (Bytnar, 2009)

Many commercial airports have transitioned from using urea and propylene glycol, which cause high BOD and COD in the adjacent environment, to using organic salts such as KAc 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 pavement surface. However, acetate and formate deicers are highly corrosive to galvanized steel (Shi, 2008; Shi et al., 2009c). Therefore, advancement is needed to develop less corrosive, highly effective, and environmentally safe deicers. Battelle has been able to successfully modify the transesterification process in the production of biodiesel 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 13 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 6 and Figure 7 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 8 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 13: Deicing fluid composition from biodiesel by-product (Chauhan et al., 2009)

RDF# (RDF Name)	30307	32207	32107	32607	111907 (RDF 6-12)	31708A (RDF J)
Additives						
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

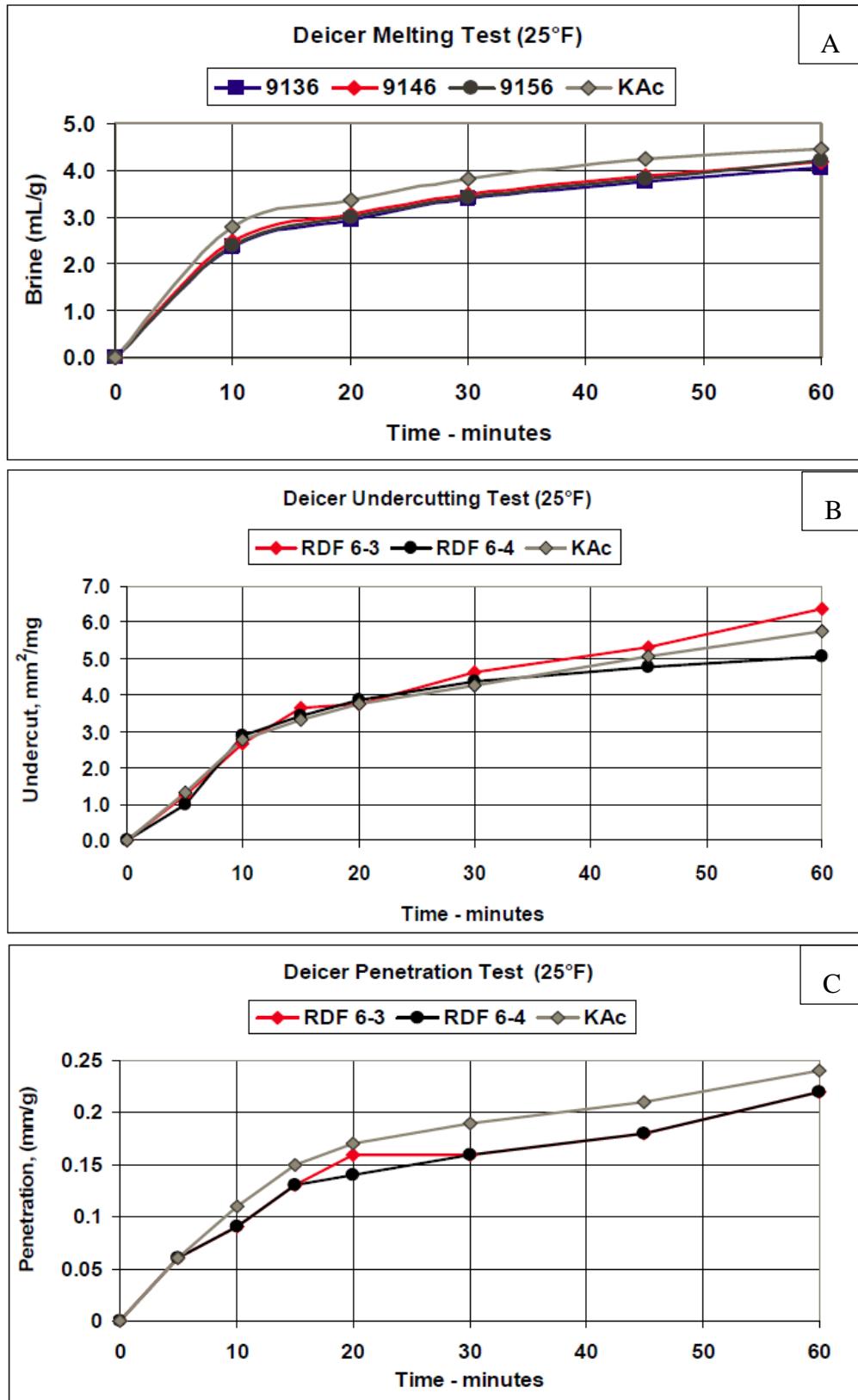


Figure 6: Ice melting performance at 25°F A) Ice Melting, B) Ice Undercutting, and C) Ice penetration (Chauhan et al., 2009).

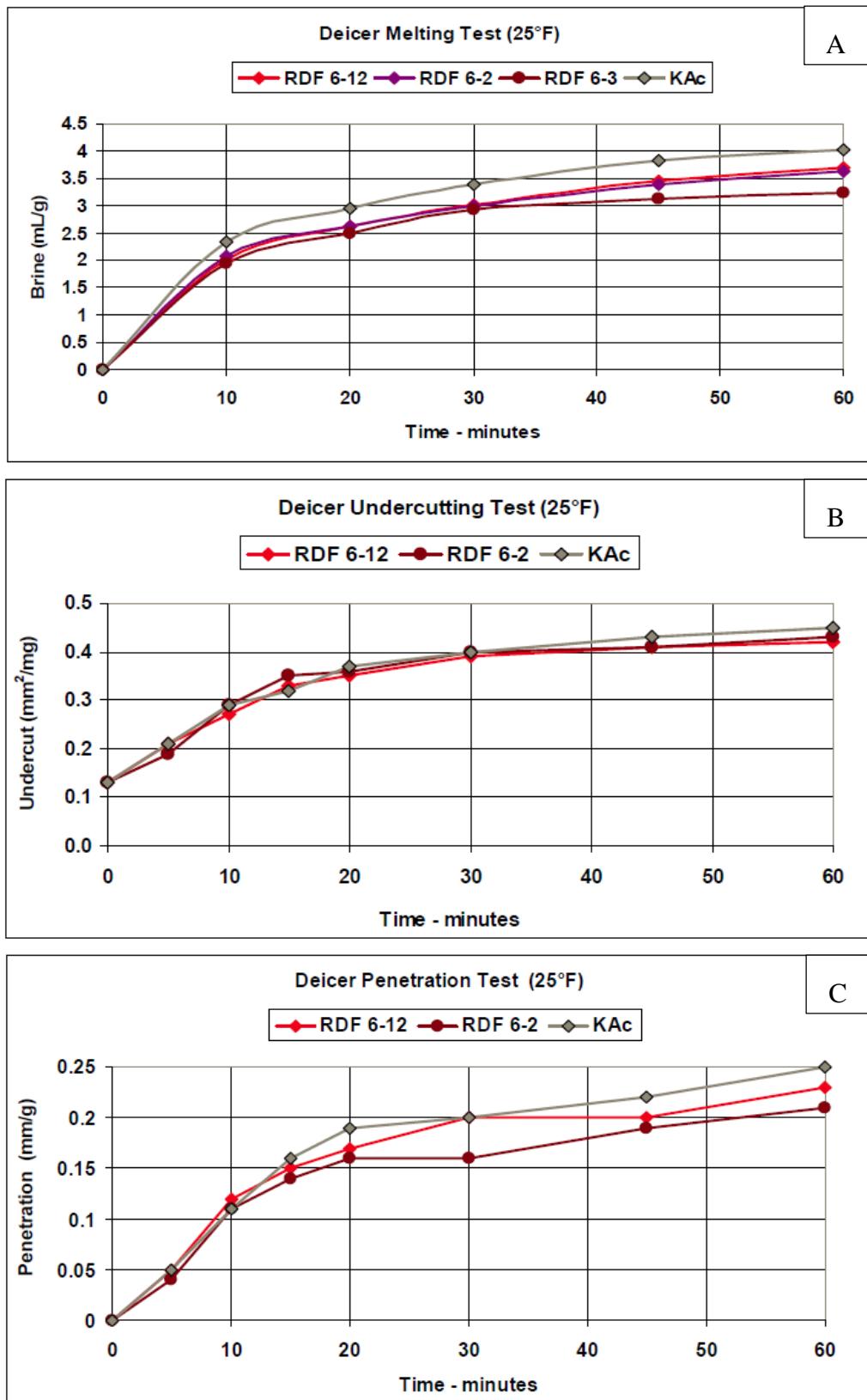


Figure 7: Ice melting performance at 25°F A) Ice Melting, B) Ice Undercutting, and C) Ice penetration (Chauhan et al., 2009)

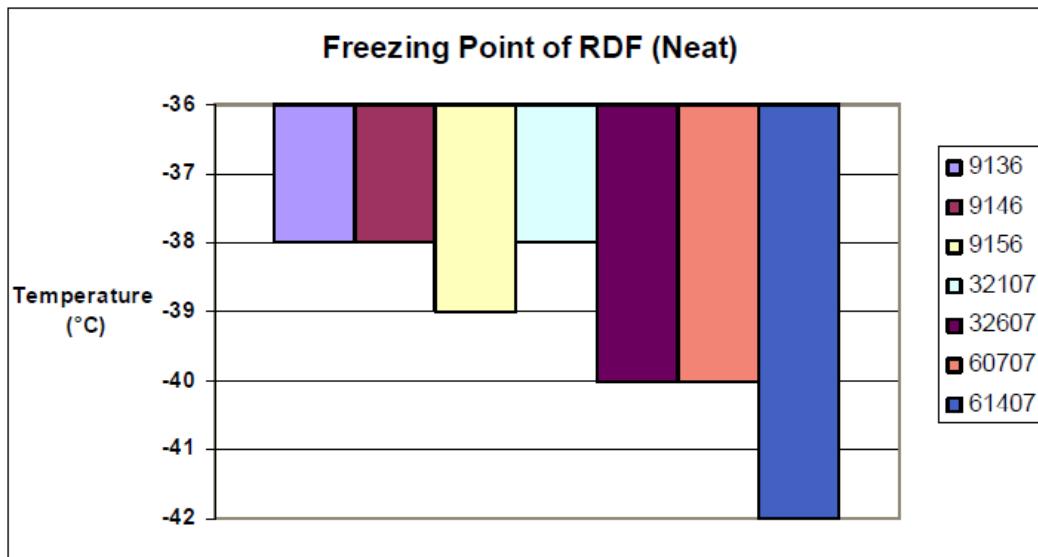


Figure 8: Freezing points of various deicers (Chauhan et al., 2009)

A study by Fay and Shi (2011) examined the performance properties of commonly used deicers at various temperatures. Figure 9 displays the results from the SHRP H205.1 and H205.2 ice melting capacity test methods, corresponding to 60 minutes after application of deicers. This demonstrates the variations in ice melting capacity with deicers and temperature. Solid deicers show increased ice melting performance at temperatures around 32°F (0°C), whereas, liquid deicers show improved performance at colder temperatures. Sodium chloride rock salt has the best overall performance. 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 10.

Additionally, Figure 10 shows that the liquid deicers outperformed the solid deicers (Fay & Shi, 2011). This study was able to demonstrate a wide range of performance among commonly used deicers and show some of the challenges faced in the development of new deicers.

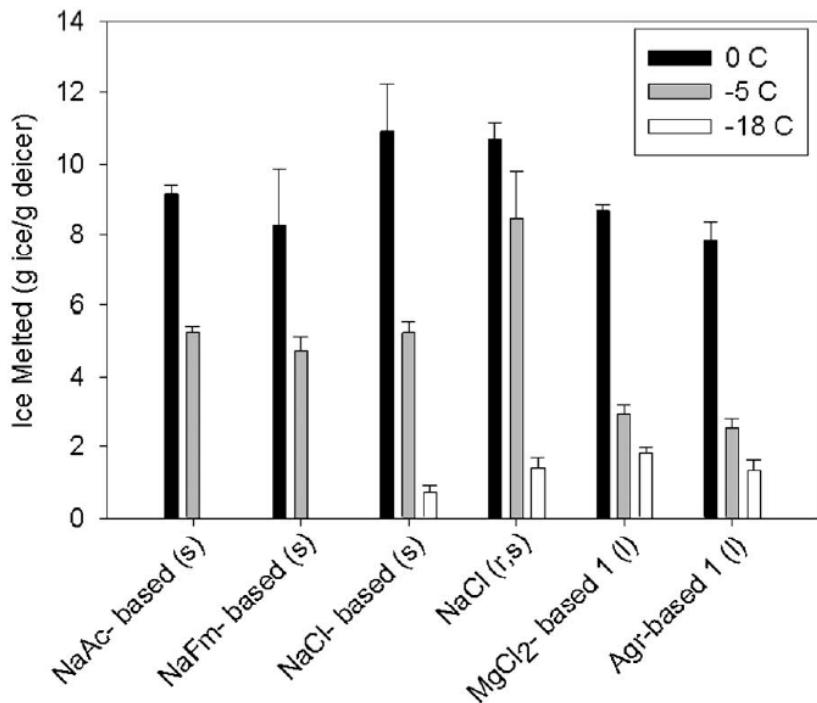


Figure 9: Data from SHRP ice melting capacity test after 60 minutes exposure to deicers at 32°F (0°C), 23°F(-5°C), and -0.4°F (-18°C) (Fay & Shi, 2011)

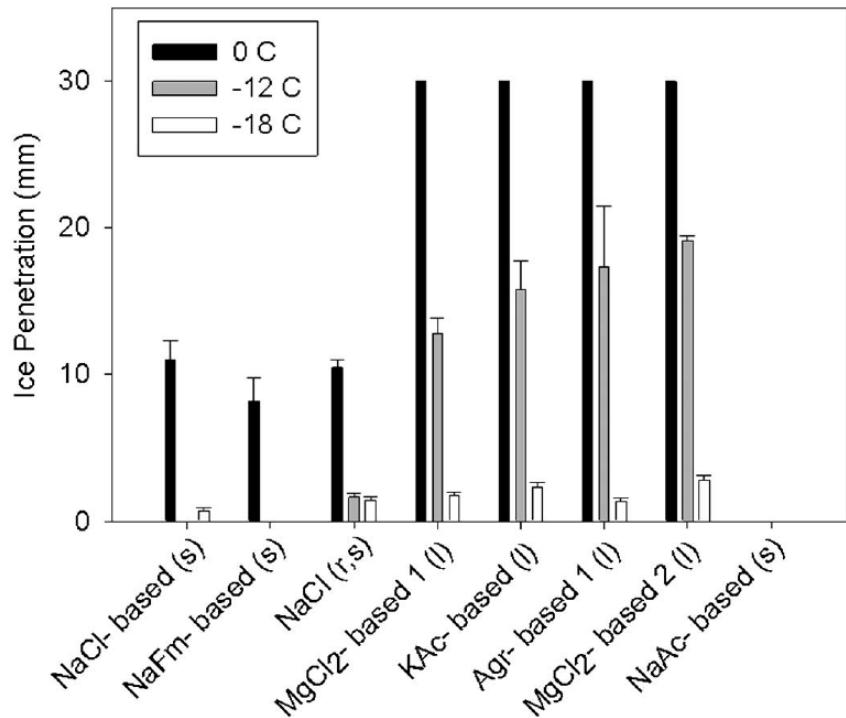


Figure 10: Results from SHRP ice penetration test after 60 minutes exposure to deicers at 32°F (0°C), 23°F(-5°C), and -0.4°F (-18°C) (Fay & Shi, 2011)

Modes of Action for Chemical Anti-icing or Deicing

This section is devoted to studying the mechanisms by which chemical anti-icers and deicers work to lower the freezing point of water, improve product longevity on the road, utilize sunlight and UV radiation to improve performance, prevent ice formation, improve ice melting capacity, prevent refreeze, and weaken the ice bond to pavement. In addition, this section summarizes how inhibitors present in the chemicals reduce the corrosiveness of metals.

Lowering the freezing point of water

Freezing point is the temperature at which an aqueous solution changes from a liquid state to solid state. Lowering the freezing point of a product is frequently done for a variety of purposes, including to reduce the freezing point of an aqueous solution so that ice cannot be formed or to melt formed ice. Generally, the composition of freezing point lowering products are dependent on the molar freezing point lowering effect, the number of ionic species which are made available, and the degree to which the composition can be dispersed in the liquid phase in which the formation of ice is to be precluded and/or ice is to be melted.

A eutectic curve (Figure 11) illustrates the freezing point temperature of an aqueous deicer solution as a function of deicer concentration. As such, solid products will have to be made into solutions first before their eutectic curves can be obtained. The test method standardized by ASTM International for automotive coolants (ASTM Standard D1177-12, 2012) is generally used to establish the eutectic curves for deicer products. The freezing point is determined as the intersection of the cooling curve and the freezing curve.

Phase Diagram for Salt

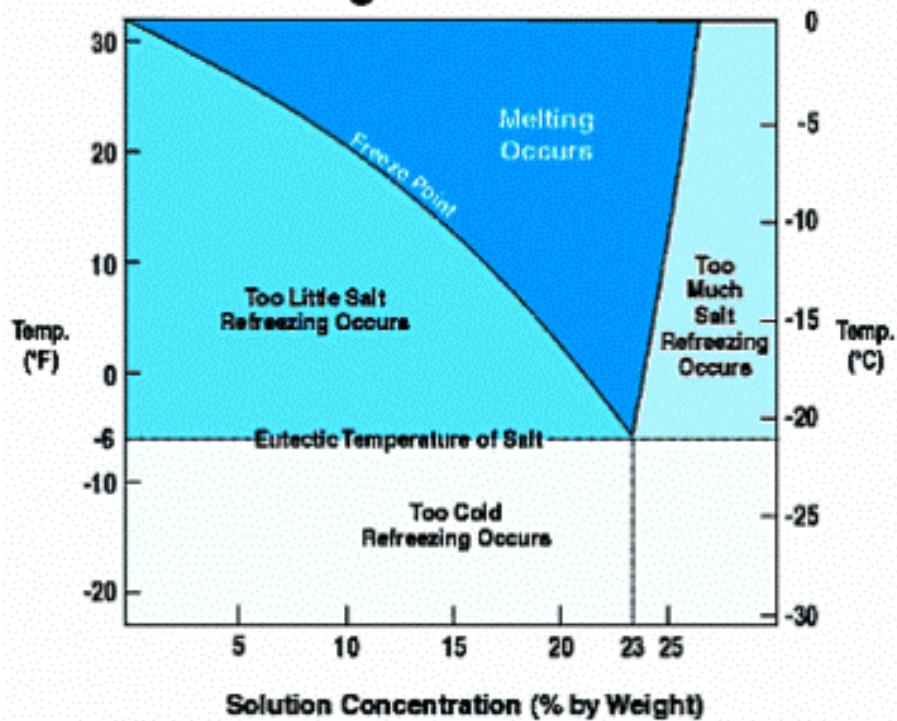


Figure 11: The phase diagram of sodium chloride (NaCl) in water featuring its eutectic curve

Note that eutectic curves do not provide reliable indication of a product's effective temperature, as the latter is affected by many factors in the roadway environment (pavement type and condition, intensity of precipitation, traffic volume, and solar radiation, among others). As shown in Figure 11, the lowest freezing point, eutectic temperature, for NaCl is -6°F (-21°C) at a concentration of 23.3% by weight of solution. Yet according to field experience, the effective temperature for NaCl is typically around 15°F (-9.4°C), which corresponds to a more diluted NaCl concentration (about 12% in Figure 11) and a stage where ice crystals started to form in the solution. The eutectic values will not only characterize the basic thermodynamic properties of such alternative products and their common blends, but also help test some modes of actions. Specifically, the results obtained will reveal whether the addition of select agricultural or mineral products into traditional deicers would lower their freezing point at a given concentration

Improving the product longevity on the road

Liquids are best suited for providing the longer residual effect than solid deicers as traffic will disperse dry materials (Kahl, 2004). Once applied, the chemical residuals of liquid deicing agents will remain on the surface and work for the next storm event. Residual effects of liquid deicers help reduce labor and costs by using less deicer, sand, and salt. It is of great importance to study

the longevity of liquid deicers and inhibitors on pavement surfaces to optimize material use and reapplication rates and timing. A series of papers have been published to investigate the factors affecting longevity of deicers and to develop equations to estimate the residual decay.

Ketcham et al. (1996) has determined that factors affecting longevity of deicers include “traffic volumes, speed, vehicle types, length of time since application, dispensing rate, road conditions, and weather, as well as whether the salt has dried out and could have been trafficked or blown away” (Ketcham et al., 1996; Kahl, 2004). Hunt, Mitchell, and Richardson (2004) evaluated the field persistence of anti-icing brine residuals on various pavements in Ohio. A brine residual decay equation was provided as a function of time or traffic for the various pavements chosen in the study such as three Asphalt cement (AC) and two Portland cement concrete (PCC) pavements. The factors affecting residual concentrations on the pavement are application method, pavement porosity, and surface roughness. The field studies yielded residual decay equations that provide an estimate of brine residual as a function of time or traffic for the various pavements investigated in the study.

Utilization of sunlight and UV radiation to improve performance

The reflection, absorption, and transmission of sunlight on the snow and ice and pavement surface play a key role in melting the snow and ice. Similarly, the presence of deicing chemicals may affect sunlight absorption and retention capacity to melt snow and ice. Darker colored deicing chemicals may have significant advantage compared to light colored deicing chemicals because they will absorb more heat from the sun. In addition, retention of heat from sunlight is directly related to albedo (reflectivity of sunlight) of the treated pavement surface, which is affected by the color of the deicer as well as other characteristics of the deicer, such as its chemical composition and gradation. White snow has a high albedo value because it reflects a lot of sunlight.

A study conducted by Gerbino-Bevins (2011) with deicing chemicals, liquid salt brine, beet juice, and blends of these two products. In the testing blended ratios of 50/50 mix of beet juice and salt brine and 15/85 mix of beet juice were used along with salt brine, solid road salt, and solid pink salt. The 50/50 mix of beet juice and salt brine had the darkest color of all the products tested. The experiment was conducted in clear sky with sunlight at 20°F. The result showed that the 50/50 mix of beet juice and salt brine melted the largest area. While, a similar experiment conducted in the shaded area did not show any significant difference in melting area between all the deicing chemicals. This suggests that darker color of the 50/50 mix of beet juice and salt brine may lead to great melting (Gerbino-Bevins, 2011). The results of the study highlight the importance of sunlight absorption and retention capacity of deicers in melting the snow and ice.

Prevention of ice formation, improving the ice melting capacity and preventing refreeze

The aforementioned mechanisms (lowering the freezing point of water, improving the product longevity on the road, and utilization of sunlight to improve performance) all contribute to the performance of the anti-icing or deicing products and help prevent the formation of ice, improve the ice melting capacity, and prevent refreeze. However, there is little information in the published domain devoted to the specific mechanism underlying these processes.

In general, ice formation is prevented when deicer molecules interfere with water molecules which make it harder for them to lock together and crystalize into ice. This results in a lower of the freezing point of water. Koefod and Tremblay (2013) found that high molecular weight organic polymer additives strongly inhibit the onset of rime ice formation and a modified Water Spray Endurance Test (WSET) was used to assess the rime ice growth rates. The ice melting capacity of deicers depends on their concentration of dissolved particles, not on their chemical composition. The more deicer that dissolves, the larger the drop in freezing point, resulting in increased ice melting capacity. As the concentration of dissolved chemicals began to dilute, the mechanism of refreeze begins. Refreeze of deicing products may be enhanced by the hygroscopic nature of some products. All these characteristics should be examined when determining the effectiveness of anit-icing and de-icing products.

Weakening of ice bond to pavement

Weakening the bond between snow and ice and the pavement aids in removal of snow and ice either by plowing or allowing the traffic to break-up the ice. The weakening mechanism between the ice and pavement with deicing products is related to brine fraction (Klein-Paste and Wåhlin, 2013) and the presence of deicing product between grain boundaries (Wåhlin, Leisinger, & Klein-Paste, 2014). Further, the amount of deicing product required to initiate weakening the bond is very low compared to the amount of deicing or anit-icing products used to melt ice (Klein-Paste & Wåhlin, 2013; Wåhlin et al., 2014).

Recently, Wåhlin et al. (2014) conducted a study to understand the mechanism behind the weakening of compacted snow by the application of NaCl. With the application of a small amount of NaCl, the compacted snow hardness dropped to 60% and with an increase in NaCl solution, the hardness saturated to one-fifth of dry snow. Wåhlin et al. (2014) concluded that there are two probable and simultaneous mechanism for this weakening effect such as “the lower ice–solution interfacial energy, compared to the ice–vapor interfacial energy, would reduce the work needed to separate the grains from each other and the NaCl solution forms a low dihedral angle with ice allowing it to penetrate grain boundaries and replace solid ice–ice bonds with liquid.”

The Klein-Paste and Wåhlin (2013) study found that weakening of ice is directly related to the brine fraction irrespective of deicing chemical or direction of heat flow. At higher deicer concentrations, the brine is more of an interconnected brine network rather than individual brine

pockets. The estimated brine requirement to weaken the ice is such that the weakened ice breaks itself with the traffic load (Klein-Paste & Wåhlin, 2013). The results emphasize the importance of applying lower concentrations of deicing chemicals on snow and ice, but over a larger area so that the deicing chemicals can attack more grain boundaries.

Reducing the corrosiveness to metals

Corrosion research is concentrated 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 the International Organization for Standardization (ISO), are “compounds that when present in a corrosive system at a sufficient concentration, decrease the corrosion rate of metals without significantly changing the concentration of any of the corrosive reagents” (Li, 2014). 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 has focused 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 phosphates, 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. In addition, organic compounds were also commonly used as corrosion inhibitors.

In this context, a new development in corrosion inhibitors is 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 (Koefod, 2000). An investigation performed by Kharshan et al. (2012) has demonstrated the potential of using corn derived by-products produced from ethanol production as effective corrosion inhibitors (Kharshan et al., 2012). The result from this study demonstrates the potential of agro-based deicers as a corrosion inhibitor.

Corrosion and Infrastructure Impacts

This section briefly discusses various impacts to highway infrastructure caused by anti-icing and deicing products. 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, 2014). 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., 2009 a, c). However, the corrosion of metals is a function of humidity, dissolved oxygen levels, debris, and type of metal (Jones & Jeffrey, 1992). Fischel (2001) reported corrosion test results for various metals as shown in Table 14. CaCl₂ and NaCl were considered the most corrosive and CMA was the least corrosive.

Table 14: Corrosion test results from various studies (adapted from Fischel, 2001).

Ranking	HITEC(1998) (flat steel)	McCrumb, 1992 (bridge steel- laboratory testing)	McCrumb, 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

Environmental Impacts of Deicers

This section briefly discusses environmental impacts caused by anti-icing and deicing products. Extended use and increased applications of chemical deicers for winter maintenance has resulted in increased concentrations of deicer constituents in the environment.

Water quality, air quality, soil, and terrestrial and aquatic flora and fauna can be negatively affected by the continued use of deicing products. However, the degree of impact depends on various factors and can be attributed to the types of products being used (Ramakrishna & Viraraghavan, 2005). Winter maintenance agencies are becoming 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 at the time of application, due to traffic, or be transported by wind and end up on the surrounding environment (Blomqvist, 1998; Environmental Protection Agency, 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, 2014). Liquid deicers can also reduce the need for applying abrasives and solid salts, therefore reducing the amount of product that can potentially reach the near road environment, and reducing impacts to air quality, roadside vegetation, and aquatic biota (CDOT, 2014). Chloride based deicers pose a significant risk to the environment and can cause elevated chloride concentrations in surface and ground water.

Table 15: 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 temp	Effective at low temp	Effective at low temp	Effective at low temp	Not effective at low temp	Effective at low temp	Effective at low temp
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.

Table 15 provides a summary of the potential environmental effects, corrosion, cost, and performance of common deicers developed by Fischel (2001). Every deicer product has the potential to cause negative impacts to the environment. In some cases, the common alternative

deicers such as CMA, MgCl₂ and CaCl₂ are believed to be less detrimental to the environment than conventional NaCl. For example, MgCl₂ 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 at low concentrations. CMA is a more corrosion resistant deicer but may result in decreased dissolved oxygen in receiving waters (Kelting & Laxson, 2010).

Chapter 3: Methodology

Online Survey

An online survey was used to capture the experience of winter maintenance practitioners with respect to currently used non-chloride liquid agricultural by-products and solid complex chloride/mineral products. The purpose of this survey was to gather information from winter maintenance professionals at state, provincial, and local transportation agencies on their experience with these products, challenges faced using the products, and lessons learned from the use of these products in winter maintenance operations.

Respondents were asked 16 questions to gather information on the effectiveness of the ten selected products. In addition, respondents were given opportunities to provide information about ‘other’ products that were not in the list. The survey was distributed in July 2014 among Clear Roads member states, APWA, and the Snow and Ice Listserv. The survey was open for responses for two months, closing in September 2014. A total of 31 responses were received from 16 US states. No vendors participated in the survey. The survey questionnaire and responses may be found in Appendix A.

Deicing and Anti-icing Product Description

Two complex chlorides/minerals (CCM) based products and eight agro-based deicers were identified by the research team and project panel for laboratory testing. Four agro-based deicers were prepared by mixing the vendor-provided concentrates with a 23.3 wt. % NaCl aqueous solution, at either 70:30 or 80:20 volume ratio, depending on the vendor specification. Additionally, four agro-based products were used as received from the manufacturer for laboratory testing purposes. The selected CCM based products were used as received. Depending on the specific test, a rock salt (white pellets from North American Salt Company, Overland Park, Kansas) or reagent grade NaCl powder were used as controls. For illustrative purposes, the products are divided in to three categories as shown below.

Category A: In this category, solid complex chlorides/minerals (CCM) based products were used as-received for testing purposes.

Product A1 - *Ice Slicer*®;
Product A2 - *Thawrox*®

Category B: In this category, the liquid agro-based deicers were prepared by mixing the vendor-provided concentrates with a 23.3 weight % NaCl aqueous solution, at either 70:30 or 80:20 volume ratio, depending on the vendor specification.

Product B1 - *Beet 55*®;
Product B2 - *BoostTM SB*;
Product B3 - *Snow Melt*®;
Product B4 - *Geomelt*® 55

Category C: In this category, the liquid agro-based deicers were used as-received from the manufacturer for testing.

Product C1 - *ApogeeTM*;
Product C2 - *BoostTM CCB*;
Product C3 - *Ice Ban® 305*;
Product C4 - *ThermaPoint IB 7/93*

Ice Slicer®, Geomelt® 55, Apogee™, and ThermaPoint IB 7/93 were selected by the project panel for additional laboratory testing to further understand the functional mechanism of the products. Additional laboratory testing for the selected products included the SHRP ice melting test at 5°F, weakening of ice bond to pavement at 15°F and 5°F, product longevity test at 15°F and 5°F, prevention of ice formation at 15°F and 5°F, and absorbance of sunlight at 15°F and 5°F.

Laboratory Test Methods

The following test methods were used to characterize each of the above mentioned deicers and anti-icers. Additional laboratory testing of Ice Slicer®, Geomelt® 55, Apogee™, and ThermaPoint IB 7/93 products was completed to further elucidate the mechanism behind the performance of the product.

Eutectic Curves

A eutectic curve illustrates the freezing point temperature of an aqueous solution as a function of concentration. As such, solid products were made into solutions first before their eutectic curves were obtained. To establish eutectic curves for deicer products, the test method standardized by ASTM International for automotive coolants was adopted (ASTM D1177–07). The test apparatus consisted of a plastic flask with deicer solution (100 mL), a stirrer made up of stainless steel operated by wiper motor (60 to 80 stokes per min), and a thermostat coupled with a data logger to measure temperature every second. The whole setup was placed in a state-of-the-art temperature-regulated environmental chamber as shown in Figure 12. The temperature of the environmental chamber was reduced until the deicer solution froze or became supercooled. Figure 13 shows the real-time monitoring of temperature data, using LoggerNet software, and the observed freezing point. According to the standard test protocol, “the freezing point is taken at the intersection of projections of the cooling curve and the freezing curve. If the solution supercools, the freezing point is the maximum temperature reached after supercooling” (ASTM D1177–07).

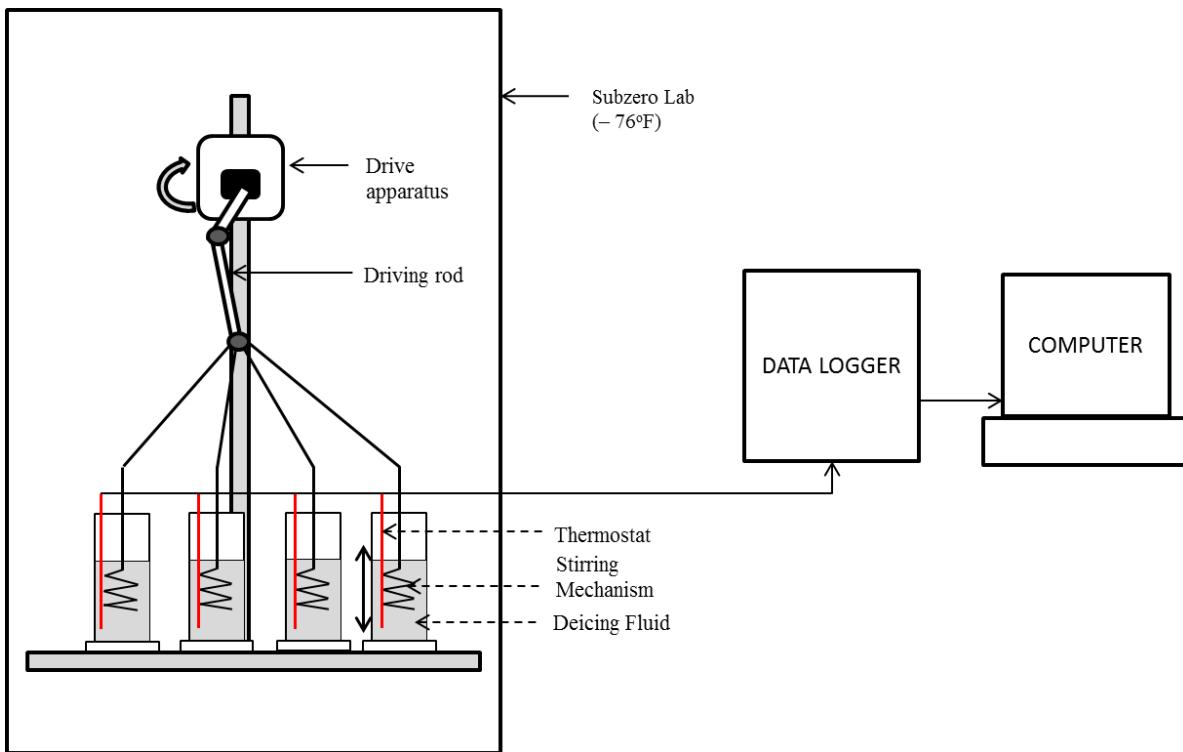


Figure 12: Setup of Freezing Point measuring apparatus.

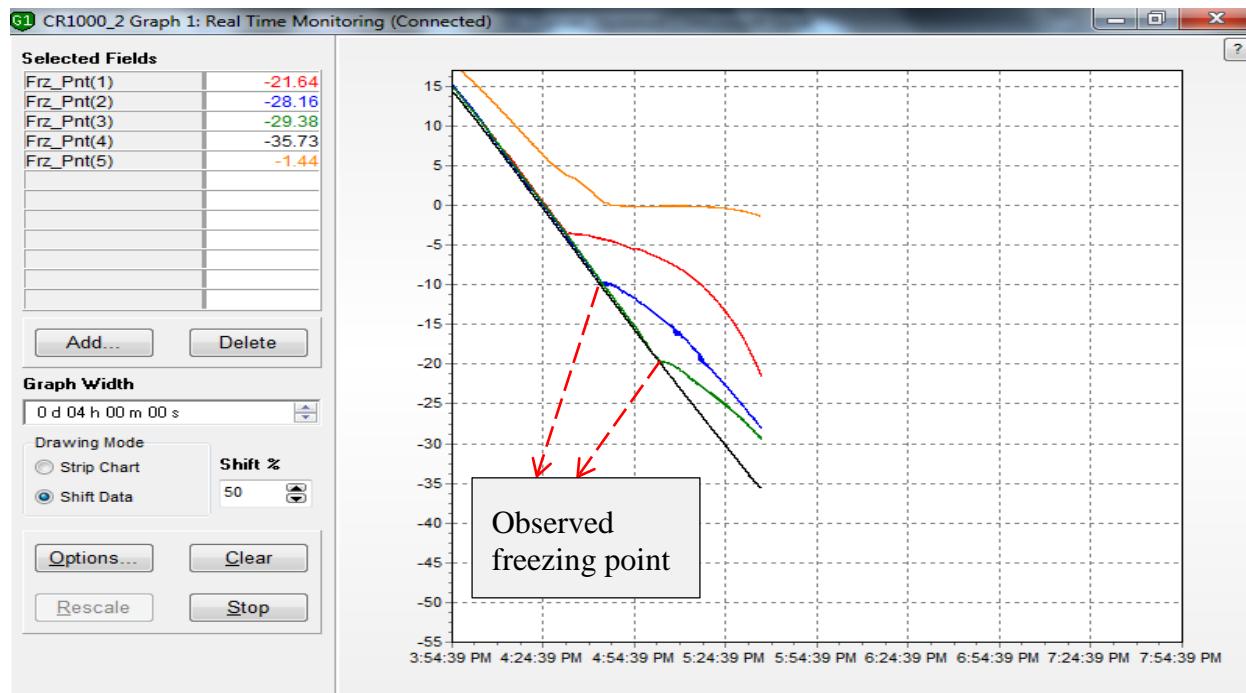


Figure 13: Realtime Monitoring of temperature data using LoggerNet Software.

As shown in Figure 11, at the eutectic point there exists equilibrium between ice, salt, and a solution with a specific concentration. This specific concentration is called the eutectic concentration and the temperature at which this equilibrium is found is called the eutectic temperature. Above the eutectic concentration the excess deicing chemical crystallizes out due to the saturation of liquid as shown in Figure 14B. In other words, the freezing point of the solution decreases with increasing concentration up to the eutectic concentration (Koefod 2009). As shown in Figure 11, the lowest freezing point, eutectic temperature, for NaCl is -6°F (-21°C) at a concentration of 23.3% by weight of solution.

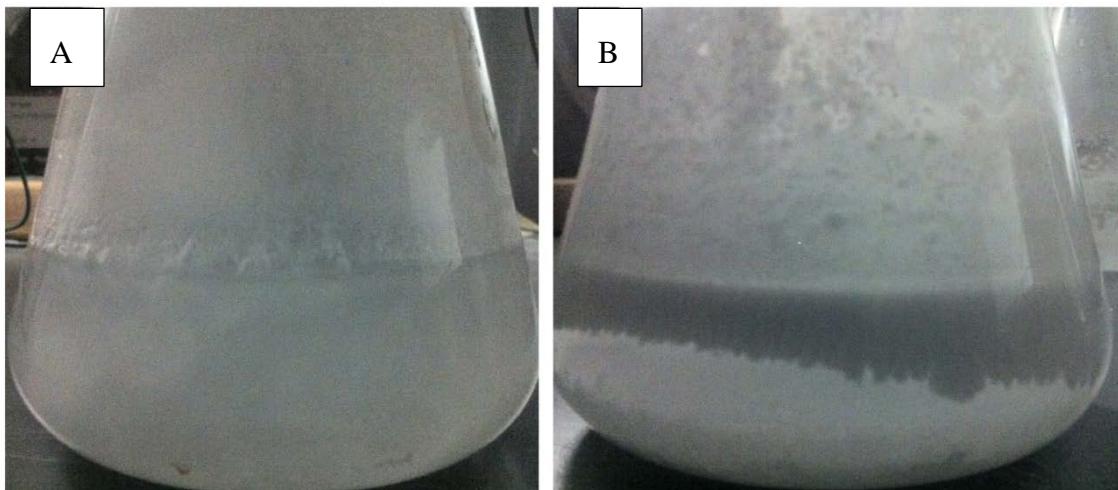


Figure 14: Freezing point observed for NaCl: A) 10% by weight of NaCl – below eutectic concentration (ice + solution), B) 27% by weight of NaCl - above eutectic concentration (solution + solid salt)

To develop eutectic curves for the liquid and solid based products, one of the three methods was used to prepare concentrations for testing.

- For category A products, concentrations were made by calculating weight percent.
- For category B products, the starting solution was an alternative to 23.3% NaCl, by replacing 20% or 30% of the 23.3% NaCl brine with agro-based concentrate, depending on the vendor specification.
- For category C products, the as-received agro-based product was used at the starting solution, assuming it was equivalent to a 23.3% solution.

The additional test solutions were made by dilution. This was designed to mimic the scenario that occurs on the pavement after the application of the liquid deicer. Reagent grade NaCl (Fisher Scientific) was used as a control for both solid and liquid deicers.

Modified SHRP Ice Melting Test

Modified SHRP ice melting tests were conducted in a Plexiglas chamber in a 12 ft. \times 14 ft. temperature-regulated environmental chamber using de-ionized water (Akin and Shi, 2012). The

tests were conducted at 15°F (-9°C) and 25°F (-4°C), respectively, with triplicate samples tested for each combination of deicer type and temperature. For testing solid deicers, 4.170±0.005 g of deicer was evenly applied over the ice sample. For liquid deicers, 3.8 mL of deicer is applied evenly over the ice surface with a syringe. After 10, 20, 30, 45, and 60 minutes, the liquid volume was removed and volumetrically measured with a calibrated syringe. Solid rock salt and 23.3% by weight of liquid salt brine was used as the control for CCM and agro-based deicers, respectively.

DSC Measurements

The differential scanning calorimetry (DSC) thermogram was obtained for each deicer to quantify its thermal properties, using a Q200 apparatus (TA Instruments, Salt Lake City, Utah). Solid deicers were made into 23.3 wt.% aqueous solutions first. Subsequently, these aqueous solutions and the liquid deicers were further diluted by de-ionized water, at 1:2 volume ratio. Approximately 10- μ L of sample were pipetted into an aluminum sample pan and hermetically sealed for DSC measurements. The DSC measures the amount of thermal energy that flows into a deicer sample during the solid to liquid phase transition. The thermograms were measured in the temperature range of 77 to -76°F (25 to -60°C) with a cooling/heating rate of 3.6°F (2°C) per minute. The first peak at the warmer end of the heating cycle thermogram was used to derive the characteristic temperature of the liquid tested (T_c), which indicates the effective temperature below which ice crystals start to form in the solution. In field practice, the effective temperature is the lowest temperature limit at which the material remains effective within 15-20 minutes of application and is the lowest temperature a deicer should be used to achieve effective ice melting (Ohio DOT 2011, Shi et al. 2011). The enthalpy of fusion (H , integrated surface area of the characteristic peak) is another parameter derived from the DSC thermogram (Akin & Shi 2012).

Corrosion to Carbon Steel

This work employed two different types of corrosion test methods, one of which was a gravimetric method and the other was an electrochemical method. For both tests, solid deicers and liquid deicers were made into their corresponding test solution, assuming a 3:100 dilution ratio by weight and by volume, respectively. The gravimetric method followed the NACE Standard TM0169-95 as modified by the PNS Association (Shi et al. 2011), but used de-ionized water in place of distilled water. Three replicate 1.38"×0.56"×0.11" ASTM F436, Type 1 TSI® steel washers, with a Rockwell Hardness of C 38–45, were used in each test solution and in the control solutions (de-ionized water and a 3% NaCl aqueous solution) for testing. The average cross-section loss result in MPY (milli-inch per year) was translated into a percentage, or percent corrosion rate (PCR, with no units), in terms of the 72-hour average corrosivity of the deicer solution relative to salt brine (NaCl) control.

The electrochemical test method, which is another tool used to assess the corrosivity of a deicing product, was established to allow rapid determination of corrosion rate of metals and to reveal

information pertinent to the corrosion and inhibition mechanisms. Corrosion of the CCM and agro-based deicers to ASTM A36 mild steel coupons were measured using a Gamry Instruments® Potentiostat and a conventional three-electrode system. The steel coupon, a platinum mesh, and a saturated calomel electrode (SCE) were employed as the working electrode, counter electrode, and reference electrode, respectively. At 24 hours of continuous immersion, the potentiodynamic polarization curve of three to five steel specimens in each diluted deicer was taken. The current-potential plot of the steel in deicer solution was measured as an external potential signal (DC perturbation) was applied within ± 150 mV range of its open circuit potential at a sweeping rate of 0.2 mV/s. The resulting polarization curve, potential (E , in mV) as a function of the log of current density (i , in $\mu\text{A}/\text{cm}^2$), was then used to derive the corrosion potential (E_{corr}) of the steel in the specific solution. From this, the instantaneous corrosion rate in terms of corrosion current density (i_{corr}) was derived. These parameters were taken from the point where the anodic current density (i_a) equals the cathodic current density (i_c) on the working electrode (i.e., mild steel).

Friction performance and weakening of ice bond to pavement

The lab tests were conducted at the Subzero Science and Engineering Research Facility (Subzero Lab) at Montana State University. Snow was made in the lab using a constructed system with a cold-temperature chute with high humidity. Snow crystals form on string and drop into a tray. Snow is collected from the tray and stored in a cooler in the cold labs to maintain temperature and humidity, until used in the lab tests (Figure 15). The snow was aged at least 4 days prior to use to ensure consistency in morphology of grain structure and proper temperature equilibration. Tests were conducted with dry snow with a loose density of 0.3 g/cm^3



Figure 15: Snow making process and snow storage at the subzero lab

Non-permeable asphalt pavement was used to study the friction performance and weakening of the ice bond to pavement of both solid and liquid type products. The pavement samples were 19

x 9 x 1 inches. For the lab testing, the solid products were used as deicers (products were applied on top of the compacted snow) and liquid products were used as anti-icers (products were applied on the pavement surface prior to snow being added). The solid products were applied at a rate of 350 lbs./lane mile (l-m) and liquid products were applied at a rate of 40 gal/l-m. For the selected pavement sample, the amounts of solid and liquid product used were 2.97 g and 2.83 mL, respectively. In order to equally distribute the solid and liquid product, the pavement sample was divided into 36 segments of 2 x 2 inch squares as shown in Figure 16. For each 2 x 2 inch segment, approximately 0.093 grams of solid product and 0.078 mL of liquid product were applied. Prior to weighing, solid products were sieved to approximately 4.75mm grain size. The liquid products were applied on the pavement sample using a pipette as shown in Figure 17.

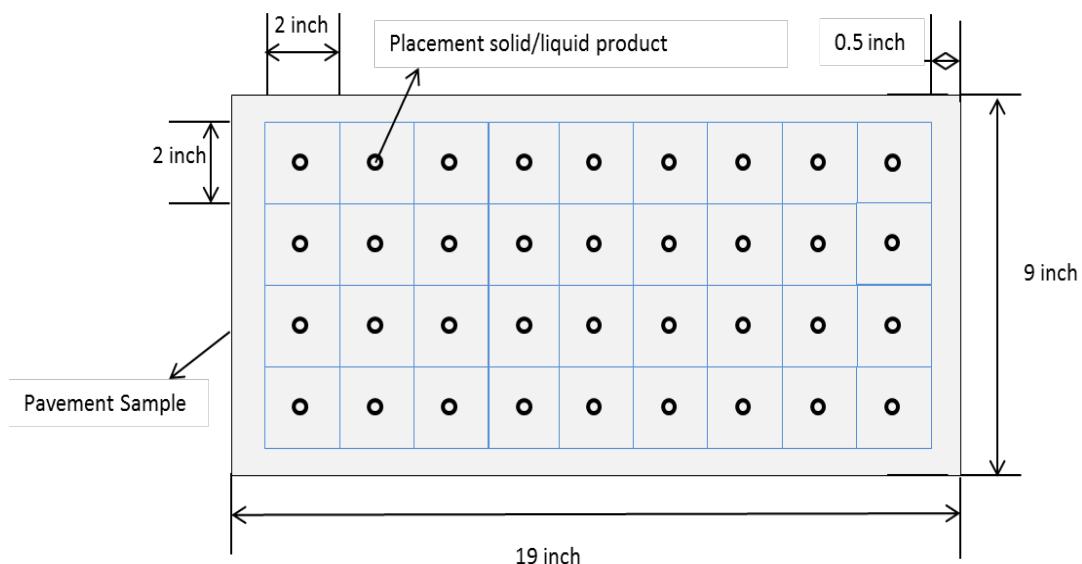


Figure 16: Pavement sample with locations for solid and liquid product application

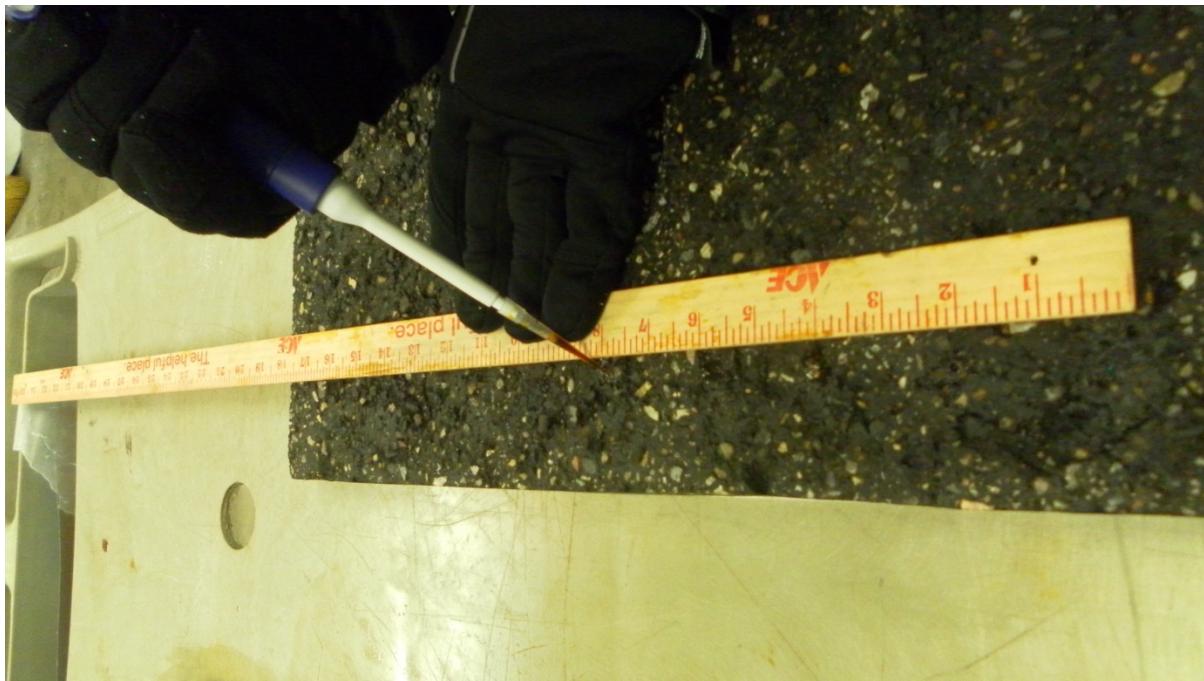


Figure 17: Application of liquid product on pavement sample using a pipette

The snow was sieved to 1mm snow grain size and 800 grams of sieved snow was applied on the pavement sample (Figure 18A). The applied snow was then compacted at 60 psi for approximately 5 minutes using a custom built compactor (Figure 18B). After compaction, the snow on the pavement surface was approximately $\frac{1}{2}$ inch thick. Figure 19C shows the pavement after compaction with liquid product applied as an anti-icer to the pavement surface.

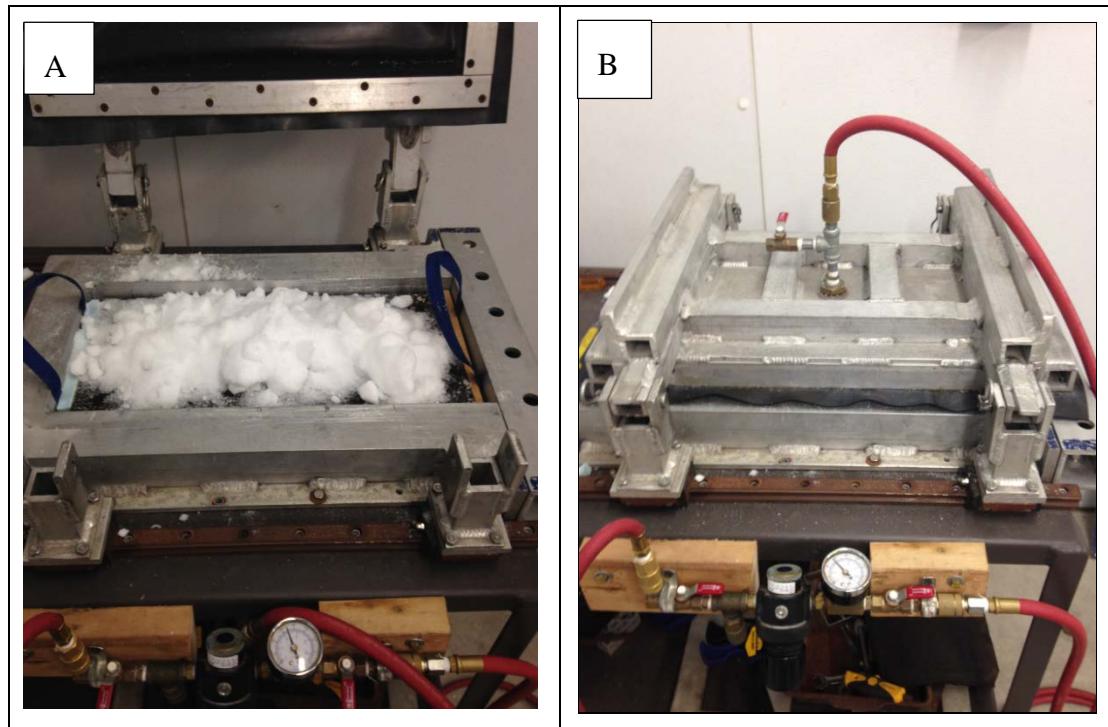


Figure 18: The snow compaction process. A) Sieved snow distributed on the pavement, B) Compaction performed at 60 psi, and C) Pavement after compaction with liquid product applied as anti-icer.

To simulate vehicle traffic, the pavement samples were trafficked using a custom built automated trafficking machine (Figure 19A). The load on the tire was set to approximately 630 lbs. and

samples were trafficked for 500 passes, equivalent to 500 passes of a single tire on the pavement sample. Figure 20B shows the pavement sample undergoing the automated trafficking.

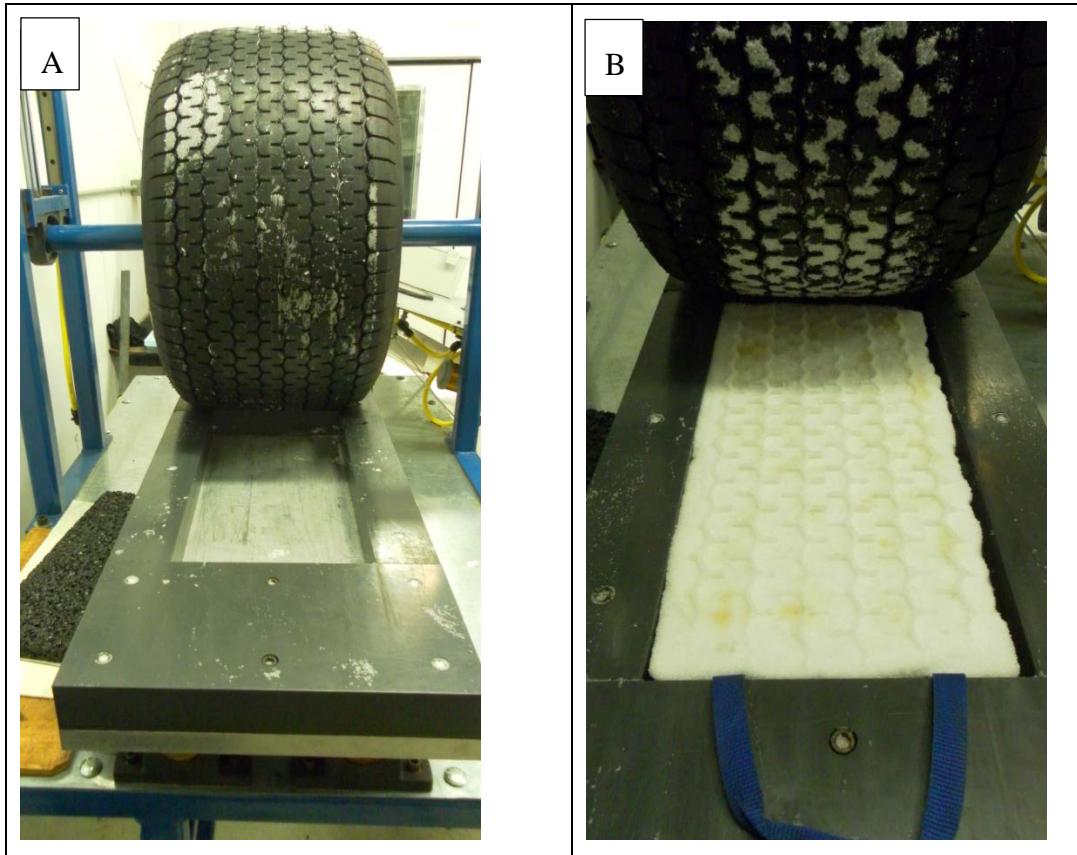


Figure 19: The trafficking process **A)** Custom-Built trafficking machine, and **B)** Pavement sample going through the trafficking

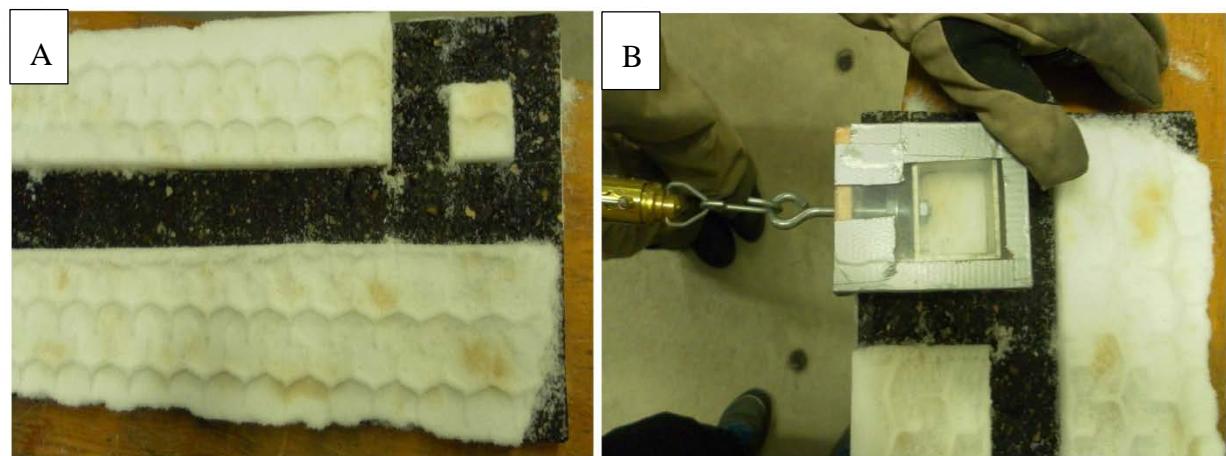


Figure 20: Measurement of shear force **A)** Snow cut to 2 x 2 inch segment, and **B)** Hollow aluminum box used to plow the snow with a spring scale to measure horizontal shear force.



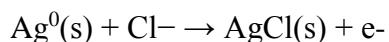
Figure 21: Friction tester measuring the friction after the plow

To investigate how solid and liquid products weaken the bond between ice and pavement, the shear force required to plow the snow from the pavement surface was measured. The snow on the trafficked pavement was cut to 2 x 2 inch segment and was pulled horizontally using a 2 x 2 inch hollow aluminum box (Figure 20). The shear force required to plow the snow from the pavement surface was measured with a spring scale. Friction was measured using a steel tester with a ¼-inch thick neoprene rubber (durometer rating of 30A) with a 2 x 2 inch contact surface. The apparatus was pulled across the pavement surface and the force needed to overcome static friction was measured with a spring scale (Figure 21). Shear force and friction were measured at six to ten locations on each pavement sample with 2 replicated pavement samples for each product type.

For experiments to measure the product longevity on the road surface, pavement samples were treated with selected liquid agro-based product at 40 gal/l-m, 800 g of snow (or ½ inch) was added to the pavement surface and compacted (60 psi for 5 minutes), and trafficked for 250 passes with load on the tire set to 630 lbs. Additionally, after measuring the bond strength and plowing the snow off the pavement sample, an additional 800 g (or 1/2 inch) of snow was added to the pavement surface without adding more product followed by compaction and trafficking. This process is repeated at 250 passes, 500 passes, and 750 passes of simulated traffic and compaction. The bond strength and friction coefficient was measured after each cycle (250, 500, and 750 passes). Additionally, snow samples were collected after each cycle to measure the amount of liquid agro-based product residual in the snow sample after each cycle of compacting, trafficking, and plowing.

Chloride Concentration

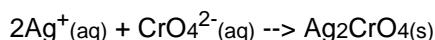
To measure the chloride concentration, a custom-made chloride ion-selective sensor was used to measure the chloride concentration in deicer samples (Fay and Shi, 2011). The Cl⁻ concentration was obtained by measuring the electrochemical potential (E) of a calibrated silver/silver chloride (Ag/AgCl) electrode (relative to a reference electrode). The chloride sensor functions as a redox electrode and the reaction is between the silver metal (Ag) and its salt — silver chloride (AgCl):



The silver sensor was fabricated by electroplating AgCl on the surface of a clean silver wire, which entails the use of a Princeton Applied Research Potentiostat/Galvanostat Model 263A to apply a series of galvanostatic steps to the wire immersed in a 1.0 M potassium chloride (KCl) solution. Once cleaned with de-ionized water, the fabricated sensor was stored in 1.0 M KCl solution. Before using plated silver wire for measurements, the sensor was calibrated by sequentially immersing it in at least five standard solutions with known Cl⁻ concentration. On each testing day, a chloride concentration standard curve was established for the sensor for each deicer type. There was a very strong linear correlation between the E of the sensor and logarithm of molar concentration of Cl⁻. If R-square of the linear regression was lower than 0.9, the calibration process was repeated. If the problem continued, then the chloride sensor was re-fabricated. A saturated calomel electrode (SCE) was used as the reference electrode and each E reading was recorded after a few minutes to allow the readings to stabilize. Subsequently, the sensor's response (E) to any deicer sample was compared against the standard curve to derive its Cl⁻ concentration.

Mohr's titration method

In order to measure the chloride concentration of each deicer, Mohr's titration method was used. In this method, chloride ion concentration of a deicer was determined by titration with silver nitrate (Korkmaz, 2015). Potassium chromate was used as indicator. The silver nitrate is added slowly to the deicer containing the indicator. When all the chloride ions have reacted, any excess silver nitrate added will react with chromate ions to form a red-brown precipitate of silver chromate.



The amount of silver nitrate added to the deicer was used to calculate the chloride concentration for each deicer. In some cases, deicers were diluted before the titration procedure with triplicate samples tested for each deicer.

UV-vis

The goal of UV-vis test was to measure the amount of liquid agro-based product residual left on the pavement after each cycle of compacting, trafficking and plowing. As explained in the previous section, snow samples were collected after each cycle of compacting, trafficking, and

plowing. The UV-vis test provides an estimated concentration of the liquid anti-icing product that was applied to the pavement sample, but then incorporated into the snow during the compaction and trafficking process.

UV-vis measures the absorbance of a liquid sample. In this test, UV-vis was conducted to measure the absorbance data in full spectrum (190 to 400 nm) for each snow sample containing liquid agro-based products. The characteristic peak facilitates the estimation of concentration of liquid product in the snow. For example, absorbance values were collected for product C3 as shown in Figure 22. It can be noted that the absorbance peak decreases with the reduction in product concentration. For the melted snow sample (containing liquid agro-based product), the change in the peak provides an estimate of the amount of liquid product in snow between each cycle of compacting, trafficking, and plowing.

The samples were tested using a ‘SPECTR MAX PLUX 384’ instrument and analyzed using SOFTMAX PRO. The absorbance was determined and characteristic peak was plotted for each sample.

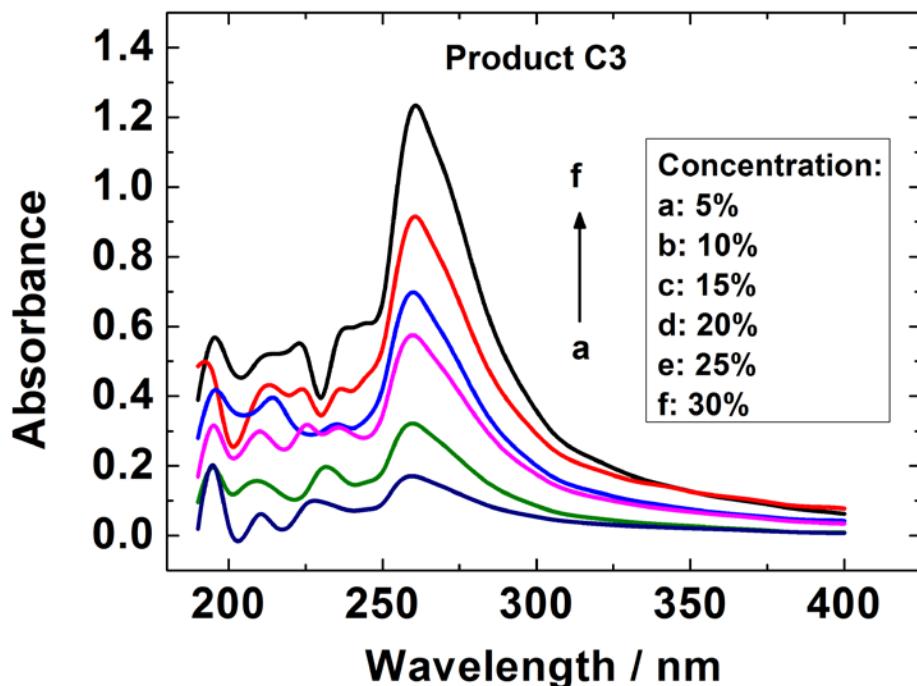


Figure 22: UV-spectra of the solutions containing Product C3 with different concentrations

Absorbance of sunlight

In order to measure the absorbance of sunlight, a SolarConstant 4000 solar simulation system was used to provide sunlight. The SolarConstant 4000 solar simulation system was placed on the

top of the temperature environmental chamber such that the sunlight covers the chamber. The intensity of solar radiation received ranged from 500 – 750 W/m² (based on the specific location in the temperature controlled environmental chamber). It should be noted that the intensity of sunlight on a clear and sunny day ranges from 500 – 1000 W/m² depending on the altitude.

In order to measure the ice melting capacity in the presence of sunlight, modified SHRP ice melting tests were conducted at 15°F and 5°F respectively, with triplicate samples tested for each combination of deicer type and temperature. For testing solid deicers, 4.170±0.005 g of deicer was evenly applied over the ice sample. For liquid deicers, 3.8 mL of deicer is applied evenly over the ice surface with a syringe. After 10, 20, 30, 45, and 60 minutes, the liquid volume was removed and volumetrically measured with a calibrated syringe. Solid rock salt and 23.3% by weight of liquid salt brine was used as the control for CCM and agro-based deicers, respectively. In order to randomize the intensity of solar radiation, plexiglas replicates of each deicer were placed in three varying locations within the environmental chamber such that they receive low, middle, and high ranges of exposure, 500 – 750 W/m².

Chapter 4: Results

Summary of Survey Results

Thirty one respondents participated in an online survey to document the current state of knowledge of non-chloride liquid agricultural by-products and solid complex chloride/mineral products primarily used for winter maintenance activities. Survey responses were from DOT (32%), County (29%), and City (19%) winter maintenance professionals, a university (3.2%), a program manager, and a technical assistant. The respondents represent a total of 16 states within the United States (Figure 23).

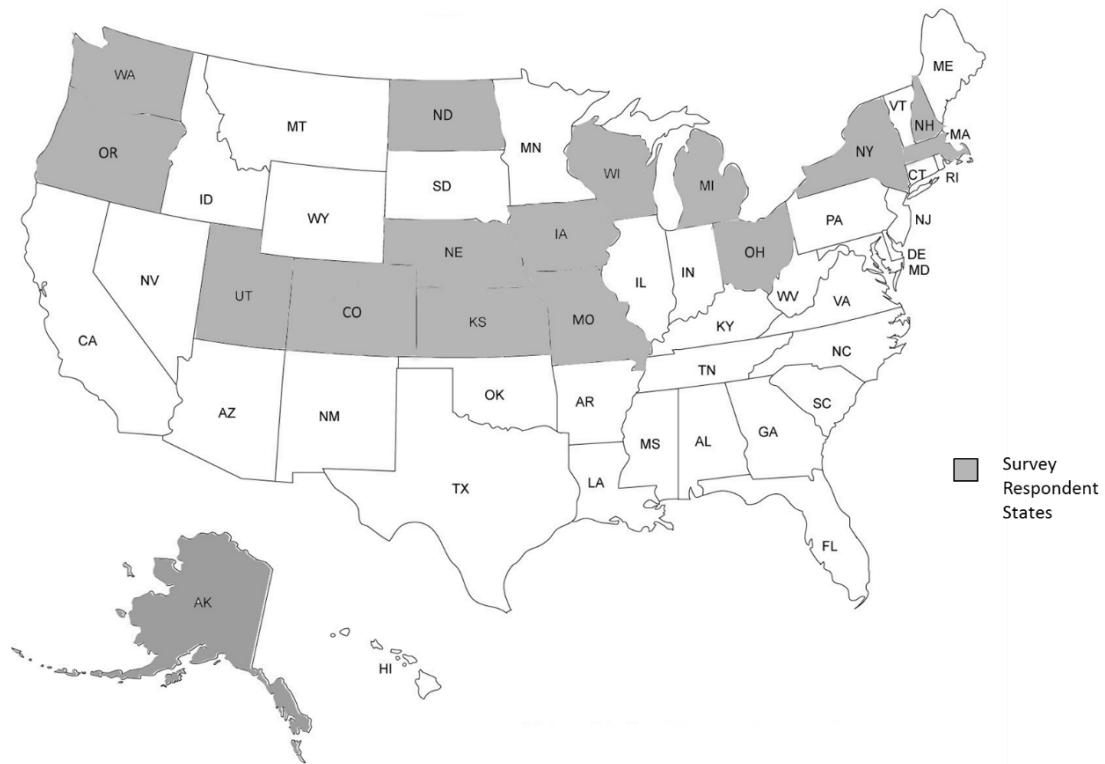


Figure 23: States that responded to the survey.

The following section provides a summary of the survey results. Detailed results of the survey including individual responses are provided in Appendix A.

Non-chloride liquid agricultural by-products

Of the selected non-chloride liquid agriculture by-products currently used by the survey respondents GeoMelt® 55 (about 40%) and Beet 55® (about 20%) were stated as being most commonly used. Additionally, Boost™ CCB and Snow Melt® were listed as being used by approximately 7% of the respondents. Other non-chloride liquid agriculture by-products (excluding selected products) that were listed as currently used by the survey respondents include Ice B'Gone, *Caliber*® M2000, and Magic Minus Zero®. It should be noted that a low

percentage of survey respondents stated that they use non-chloride liquid agriculture by-products, this may reflect the limited use of these products or may be an artifact of a low response rate for the survey (n=31). In general, respondents who use the above selected products such as GeoMelt® 55, Beet 55®, Boost™ CCB, and Snow Melt® found it either very effective or effective for winter maintenance operations and are use the products more frequently for anti-icing (38.5%) and pre-wetting (38.5%).

The estimated annual usage of the non-chloride liquid agriculture by-products ranges from 2,600 to 35,000 gallons for cities and counties and 200 to 800,000 gallons for state DOTs. Typically, non-chloride liquid agriculture by-products were used as additives with salt brine with blending ratios of 70/30 or 80/20 for brine/products. However, some agencies blended some percentage of CaCl₂ or MgCl₂ along with salt brine for non-chloride liquid agriculture by-products. For instance, Waukesha County (Wisconsin) uses blending ratio of 85/10/5 for salt brine/GeoMelt®55/CaCl₂ and Ashland County (Wisconsin) uses blending ratio of 85/10/5 to 75/15/10 for salt brine/GeoMelt®55/MgCl₂. Typical application rates of product ranges from 10 – 100 gallons per lane mile (gal/l-m). However, one respondent commented that high application rates on bridge decks can lead to slimy conditions (Wisconsin, Oneida County). For pre-wetting, respondents typically mixed these products with salt at 4 - 14 gallons/ton. Typical temperature ranges reported for using non-chloride liquid agriculture by-products for were from 0 to 34°F. Some respondents noted that they prefer using them for temperatures below 20°F.

The non-chloride liquid agricultural by-products were used by 60% of respondents for over five years, and by 23% of respondents for one to three years. Most agencies (75% of respondents) stated that these products are used as a part of their standard practices and policies, while 25% of respondents stated that they are using these products on a trial basis. The top priority for selecting non-chloride liquid agricultural by-products were “Improved performance” (n=11), “Reduced environmental damage” (n=6), “Cost saving” (n=6), and “Reduced highway infrastructure damage” (n=2). Observed changes by respondents from the use of non-chloride liquid agricultural by-products were “Improved performance” (n=11), “Cost saving” (n=6), “Reduced highway infrastructure damage” (n=2), and “Reduced environmental damage” (n=2).

The top five primary benefits of using non-chloride liquid agricultural by-products rated by respondents are as follows:

1. “Improving the product longevity on the road” (19%),
2. “Improving the ice melting capacity” (15.5%),
3. “Weakening of ice bond to pavement” (15.5%),
4. “Lowering the freezing point of water” (13.8%),
5. “Prevention of ice formation” (13.8%).

However, very little research has been completed by responding agencies to determine the mechanism behind the effectiveness of non-chloride liquid agricultural by-products.

Solid Complex Chloride/Mineral Products

Of the selected solid complex chloride/mineral products, Ice Slicer® and Thawrox® were used by 25% and 16.7% of the respondents, respectively. Other products used by the respondents include ClearLane®, Fire Rock, Rapid Thaw, Dri-Rox, and Solar Qwicksalt. The respondents who use Ice Slicer® found it either very effective or effective, and respondents who use Thawrox® found it either effective or somewhat effective. Survey respondents stated that the solid complex chloride/mineral products are most commonly used for de-icing purposes (45.8%).

The estimated annual usage of solid complex chloride/mineral products by survey respondents ranges from 163 - 85,000 tons. The typical temperature ranges reported by survey respondents for use of these products ranged from 0 to 34°F. Typical application rates used by survey respondents ranged from 150 - 250 pounds per lane mile (lbs/l-m).

The majority of responding agencies had used these products for more than five years, with around 27% of respondents using new types of solid complex chloride/mineral products in the past three years. More than half, 63%, of respondents used these products as a part of their standard practices and policies, while 36% were using these products on a trial basis. Improved performance was the primary reason for 36.4% of respondents choosing to use solid complex chloride/mineral products, followed by “Reduced highway infrastructure damage” and “Reduced environmental damage” both noted by 22.7% of respondents. Observed benefits of using complex chloride/mineral products by respondents included improved performance as the primary observed benefit, followed by cost savings. Some agencies observed a reduction in the volume of the material used when using solid complex chloride/mineral products compared to NaCl (Kansas DOT and Utah DOT).

The top five primary benefits for using solid complex chloride/mineral products listed by respondents include:

1. “Lowering the freezing point of water” (20.7%),
2. “Prevention of ice formation” (17.2%),
3. “Improving the product longevity on the road” (13.8%),
4. “Preventing refreeze” (13.8%),
5. “Weakening of ice bond to pavement” (13.8%).

Similar to non-chloride liquid agricultural by-products very little research has been completed by survey respondents to understand the mechanism behind the effectiveness of solid complex chloride/mineral products.

Laboratory Results

The ten products selected for testing have been broken up into three categories as explained below.

Category A: solid complex chlorides/minerals (CCM) based products were used as-received for testing purposes.

Product A1 - *Ice Slicer®*;
Product A2 - *Thawrox®*

Category B: Liquid agro-based deicers were prepared by mixing the vendor-provided concentrates with a 23.3 wt. % NaCl aqueous solution, at either 70:30 or 80:20 volume ratio, depending on the vendor specification.

Product B1 - *Beet 55®*;
Product B2 - *BoostTM SB*;
Product B3 - *Snow Melt®*;
Product B4 - *Geomelt® 55*

Category C: Liquid agro-based deicers were used as-received from the manufacturer for testing purposes.

Product C1 - *ApogeeTM*;
Product C2 - *BoostTM CCB*;
Product C3 - *Ice Ban® 305*;
Product C4 - *ThermaPoint IB 7/93*

Lowering the Freezing Point of Water/Improving the Ice Melting Capacity

Eutectic Curves

Figure 24, Figure 25 and Figure 26 illustrate the eutectic curves developed for category A Solid Complex Chloride/mineral products (CCM) and category B and C agro-based deicers. The experimental results in Figure 24 reveal that CCM based deicers did not show significant benefits in depressing the freezing point of water compared to the NaCl control. However, Figure 25 reveals that agro-based additives in place of 23.3% NaCl brine at 20% or 30% volume ratio significantly depress the freezing point compared to a NaCl control. Similarly, Figure 26 shows that as-received agro-based products significantly reduced the freezing point of water compared to a NaCl control.

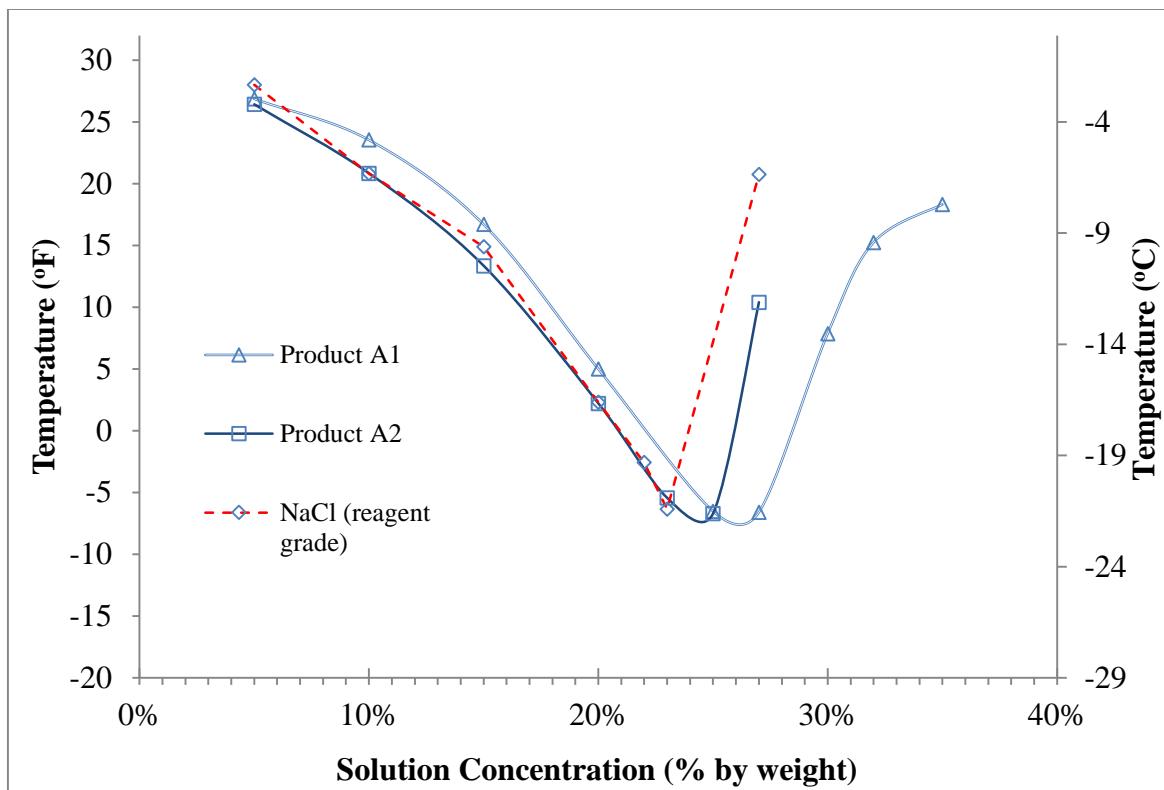


Figure 24: Eutectic curve for CCM based product – Category A

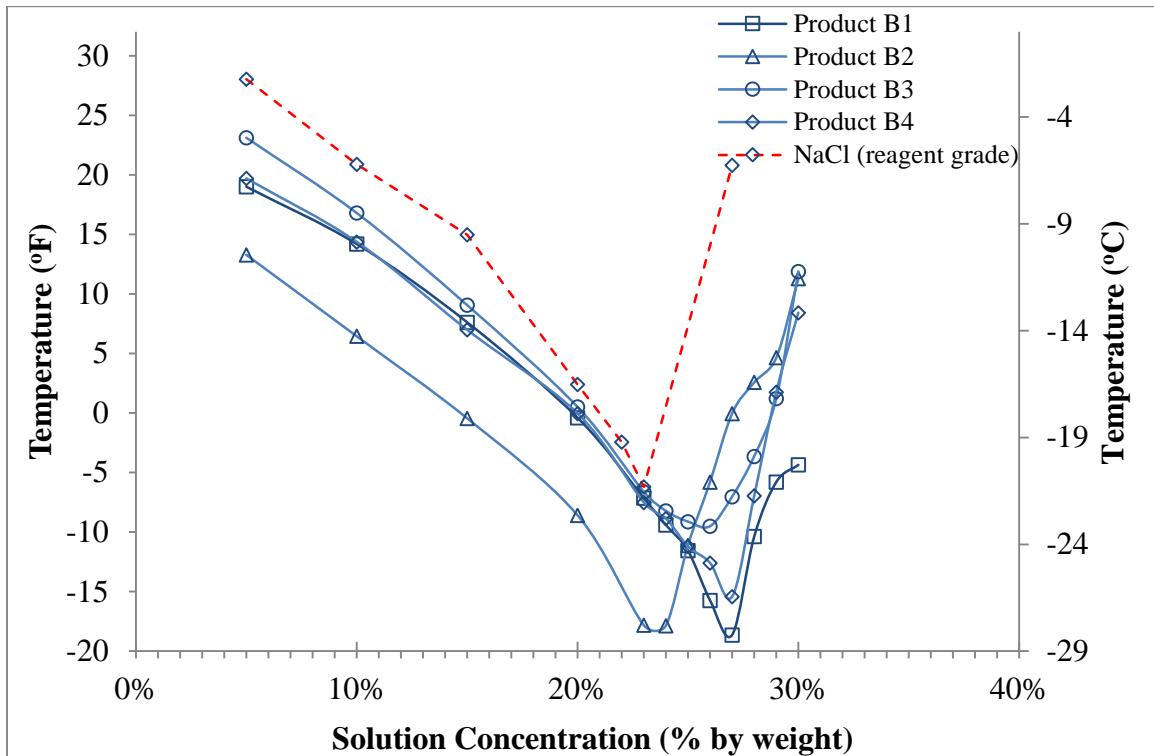


Figure 25: Eutectic curve for agro-based product - Category B

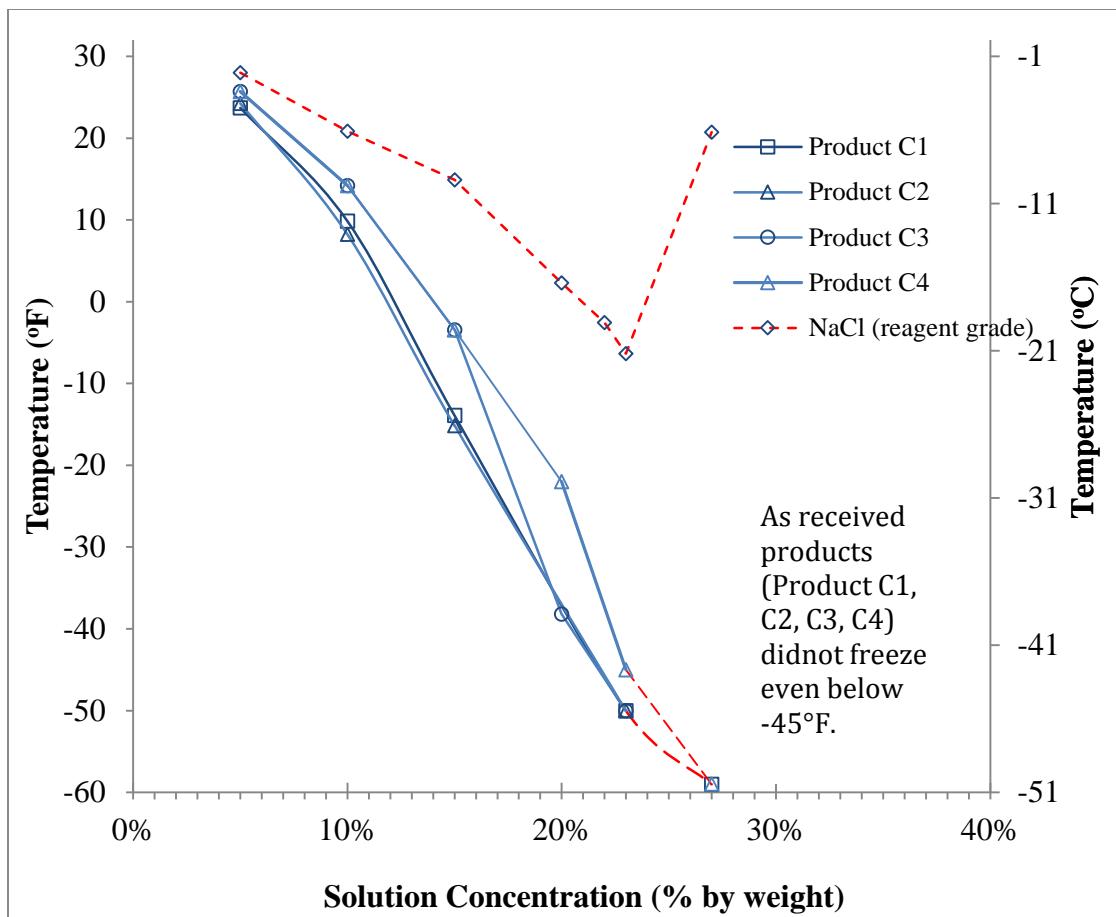


Figure 26: Eutectic curve for agro-based product – Category C

In Figure 24, the lowest freezing point of CCM 1 and CCM 2 are -6.6°F and -6.7°F at a concentration of 27% and 25% by weight of solution, similar to the freezing point of 23% NaCl brine (-6°F). Figure 25 shows that the measured freezing point of agro-based products ranges between -18.4°F and -9.52°F, i.e., significantly lower than the freezing point of 23% NaCl brine - 6°F. Noticeably, as-received agro-based products did not freeze at temperatures even below -45°F (Figure 26). These findings are consistent with the previous findings that agro-based products act as a freezing point depressants (Bloomer, 2000, Michigan DOT, 2014).

Improving the Ice Melting Capacity

Figure 27 and Figure 28 show the average ice melt per gram of CCM or per mL of agro-based deicer at 25°F and 15°F, respectively. Ice melting tests at 5°F were only conducted for products A1, B4, C1, and C4 and are results are in Table 16.

At 60 min, all the unit ice melt values were higher than 1 g/g for solid deicers and higher than 1 mL/mL for liquid deicers, confirming that the deicers used were effective and did not refreeze at 15°F or higher (warmer) temperatures. CCM based deicers produced more ice melt than the agro-based deicers, regardless of the testing temperature (note the y-axis in Figure 27A has a

different scale). This is reasonable considering that the melting power of liquid deicers had been diluted by the water in them. All liquid deicers achieved most of their melting potential within 10 to 20 minutes of application. In contrast, all solid deicers needed sufficient time (more than 60 minutes) to achieve full melting potential which is consistent with the previous findings (Shi et al., 2013).

It can be noted that CCM based deicers, category A products, produced a slightly higher volume of ice melt at 15°F relative to rock salt, but the differences were not always statistically significant. The improved melting capacity diminished at 25°F. At 25°F and after 60 min, CCM 1, CCM 2, and rock salt featured a melt rate of 7.15, 7.23, and 6.99 mL/g, respectively. At 15°F and after 60 minutes, CCM 1, CCM 2, and rock salt featured a melt rate of 4.46, 4.16, and 3.55 mL/g, respectively. However, the volume of ice melt diminished at 5°F for Product A1 when compared to rock salt.

For agro-based additives, in place of 23.3% NaCl brine at 20% or 30% volume ratio (category B), the volume of ice melt revealed mixed results when compared with the control at 25°F and 15°F temperatures. For instance, product B1 produced slightly more ice melt and product B2 produced slightly less ice melt than the salt brine at 25° F and 15° F. However, there is no significant difference between category B agro-based products and salt brine in terms of ice melting capacity at 5°F, 15°F and 25° F. These results suggest that the agro-based additives may act as ‘cryoprotectants,’ which tend to inhibit freezing without melting the ice (Koefod, 2010).

In contrast, agro-based products which were used as-received (category C) produced significantly more ice melt than salt brine at 5° F, 15° F, and 25°F. At 25°F and after 60 minutes, products C1, C2, C3, C4, and rock salt featured a melt rate of 4.48, 3.85, 2.96, 3.18 and 2.64 mL/mL, respectively. At 15°F and after 60 min, product C1, C2, C3, C4, and rock salt featured a melt rate of 2.81, 3.11, 2.50, 2.39 and 1.55 mL/mL, respectively. The increase in ice melting of agro-based product (category C) when compared to salt brine is likely due to the presence of MgCl₂, CaCl₂ and other chlorides in category C products.

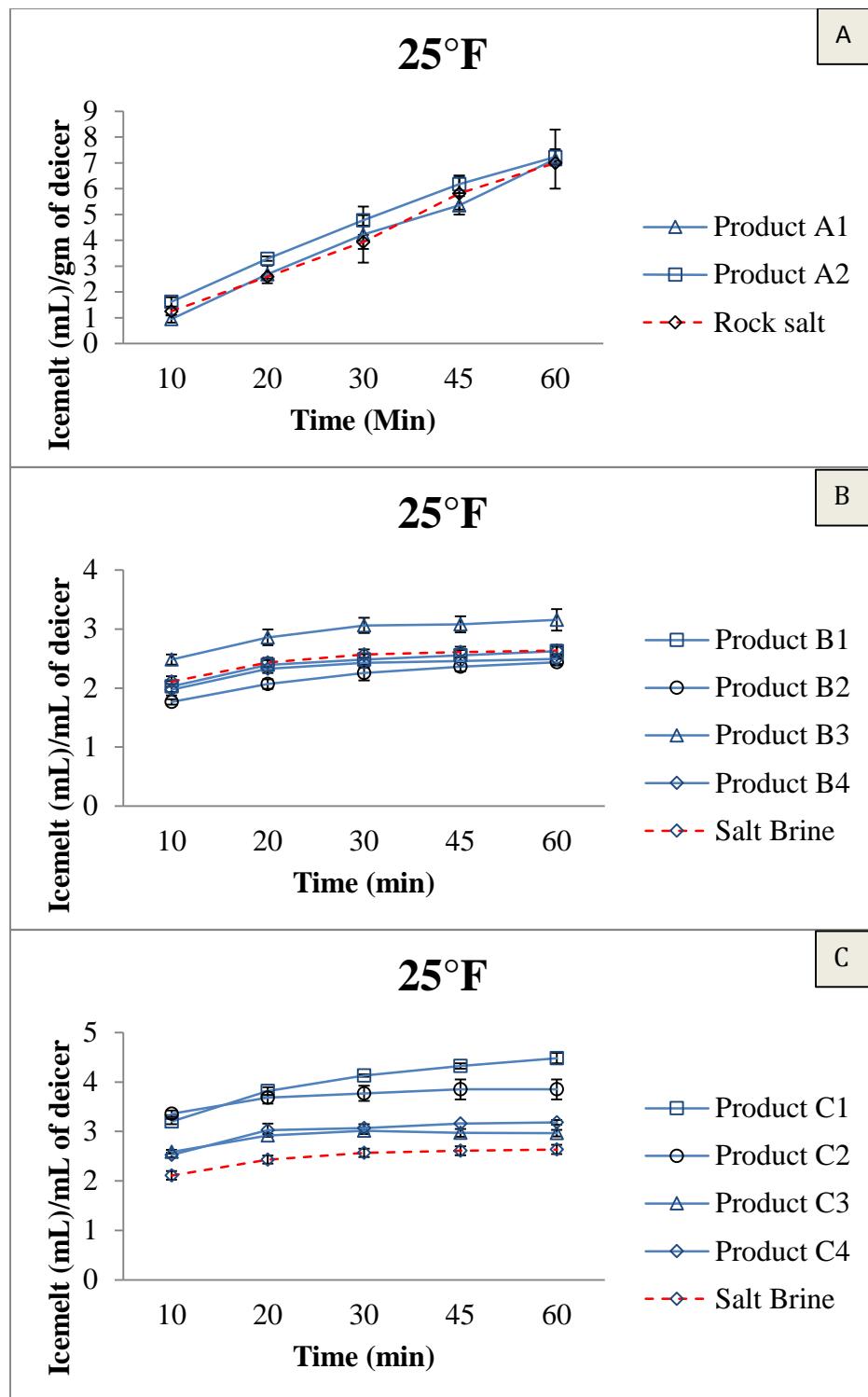


Figure 27: Temporal evolution of deicer performance measured using the Modified SHRP Ice Melting Test at 25°F, A) CCM based product – Category A, B) agro-based product - Category B, and C) agro-based product - Category C

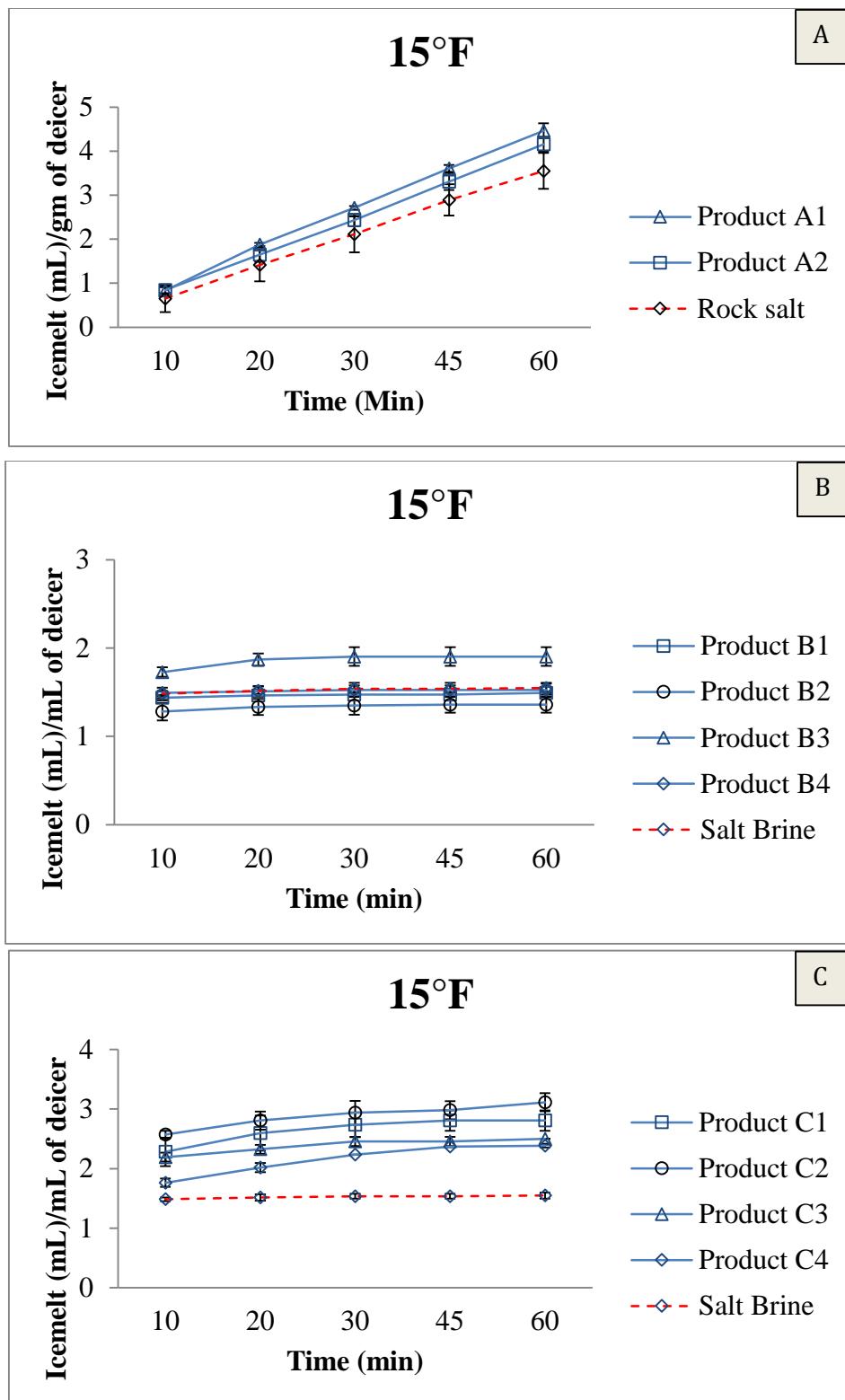


Figure 28: Temporal evolution of deicer performance measured using the Modified SHRP Ice Melting Test at 15°F, A) CCM based product – Category A, B) agro-based product - Category B, and C) agro-based product - Category C

Table 16: Comparisons between thermal property parameters obtained from DSC thermograms and eutectic parameters and ice melting capacities

Product	Original State	Characteristic Temperature Peak		Enthalpy of fusion (J/g)		Eutectic Curve		Ice Melt		
		Average (°F)	COV	Average	COV	Eutectic Temperature °F	Eutectic Concentration (wt.%)	60 min @ 25°F	60 min @ 15°F	60 min @ 5°F
								(ml/g for solid, ml/ml for liquid)		
Product A1	Solid	28	20%	162.2	8%	-6.61	27%	7.15	4.46	1.53
Product A2	Solid	22.9	1%	89.4	4%	-6.70	25%	7.23	4.16	-
Product B1	Liquid	24.8	3%	138.7	3%	-18.64	27%	2.62	1.49	-
Product B2	Liquid	30.4	42%	156.1	7%	-17.86	24%	2.44	1.36	-
Product B3	Liquid	25.4	4%	136.1	6%	-9.52	26%	3.16	1.90	-
Product B4	Liquid	28.1	23%	176.1	4%	-15.43	27%	2.49	1.53	1.14
Product C1	Liquid	16.2	2%	120.9	6%	< 45	as-received	4.48	2.81	1.58
Product C2	Liquid	6.1	6%	124.6	4%	< 45	As Received	3.85	3.11	-
Product C3	Liquid	8.9	4%	161.1	10%	< 45	As Received	2.96	2.50	-
Product C4	Liquid	6.4	5%	131.5	6%	< 45	As Received	3.18	2.39	1.58
NaCl (reagent)	Solid	23.5	2%	197.7	3%	-6.34	23%	-	3.90	-
Rock salt	Solid	-	-	-	-	-	-	6.99	3.55	1.72
Salt Brine (Rock 23.3 wt%)	Liquid	-	-	-	-	-	-	2.64	1.55	1.10

DSC Thermograms

Table 16 presents the characteristic temperature and enthalpy of fusion of the CCM (category A) and agro-based deicers (category B and C), both derived from the DSC thermograms. The results indicate that CCM (category A) and agro-based deicers (category B only) do not exhibit significantly lower characteristic temperatures than reagent-grade NaCl. The T_c of agro-based deicers (category B only) ranges between 30°F and 25°F, which is consistent with a previous study which found the T_c of one agriculturally based product to be 23°F (Fay et al., 2008). However, agro-based products which were used as-received (category C) exhibit significantly lower characteristic temperature than reagent-grade NaCl. Note that for some of the products tested the coefficient of variance (COV) was higher (at or close to 10%), highlighting the challenge of obtaining consistent and uniform results. The enthalpy of fusion, H , ranges from 89 J/g to 176 J/g, for CCM and agro-based deicers, all of which are lower than that of reagent grade NaCl (197 J/g). This suggests that the amount of thermal energy corresponding to the aqueous brine solution's liquid/solid phase transition is reduced; in other words, it is thermodynamically easier to freeze a solution with a higher H value. Note that the least powerful deicer (deionized water) has a high H value of 345 J/g (Akin and Shi, 2012).

Reducing the Corrosiveness to Metals

PNS dipping test and electrochemical corrosion test

Table 17 shows the PNS dipping test and electrochemical corrosion test results for CCM and agro-based deicers. The gravimetric test revealed that the CCM deicers feature slightly lower corrosivity to carbon steel than solid NaCl, whereas most agro-based deicers in both category B (except product B1) and category C feature much lower corrosivity to carbon steel than both solid NaCl and 23.3% NaCl brine.

Figure 29 presents some representative steel washers after the cyclic immersion exposure to various deicer solutions, with the rustier steel surface generally corresponding to the more corrosive deicer solution. The PNS dipping test provides the average corrosion rate of ASTM F436, Type 1 TSI® steel washers over the 72 hours of cyclic immersion, whereas the electrochemical test provides the instantaneous corrosion rate of ASTM A36 mild steel coupons at 24 hours of continuous immersion.

Table 17: Gravimetric and electrochemical test results for CCM and agro-based deicers

Deicer	Original state	PNS Dipping Test		Electrochemical Test		
		Average Corrosion Rate (MPY)	Percentage Corrosion Rate (%)	E_{corr} (mV, SCE)	I_{corr} ($\mu A/cm^2$)	Average Corrosion Rate (MPY)
3% Product A1	Solid	50.5	82.0	-683.0	7.2	32.8
3% Product A2	Solid	46.2	74.1	-709.0	8.3	37.8
3% Product B1	Liquid	42.8	80.2	-508.0	5.4	24.6
3% Product B2	Liquid	15.1	30.8	-656.0	8.5	38.8
3% Product B3	Liquid	20.3	34.0	-704.0	7.6	34.7
3% Product B4	Liquid	29.5	52.9	-638.0	11.3	51.5
3% Product C1	Liquid	16.8	31.2	-556.0	6.3	28.7
3% Product C2	Liquid	18.1	38.7	-521.0	4.5	20.5
3% Product C3	Liquid	21.2	45.4	-685.0	8.9	40.6
3% Product C4	Liquid	14.3	30.6	-524.0	5.5	26.2
3% NaCl	Solid	56.3	100	-751.0	12.8	58.4
DI Water	Liquid	5.0	0	-	-	-



Figure 29: Steel coupons after the gravimetric corrosion test showing percent corrosion rate (PCR).

The corrosion rates measured via the electrochemical method exhibit significantly different trends than those via the gravimetric method (Table 17). It can be seen that some products attain the maximum corrosivity after 24 hours immersion when compared to PNS dipping test. Figure 30, Figure 31 and Figure 32 illustrates the potentiodynamic polarization curves of three steel coupons exposed to 3% NaCl solution (control) and those exposed to 3% CCM and agro-based products.

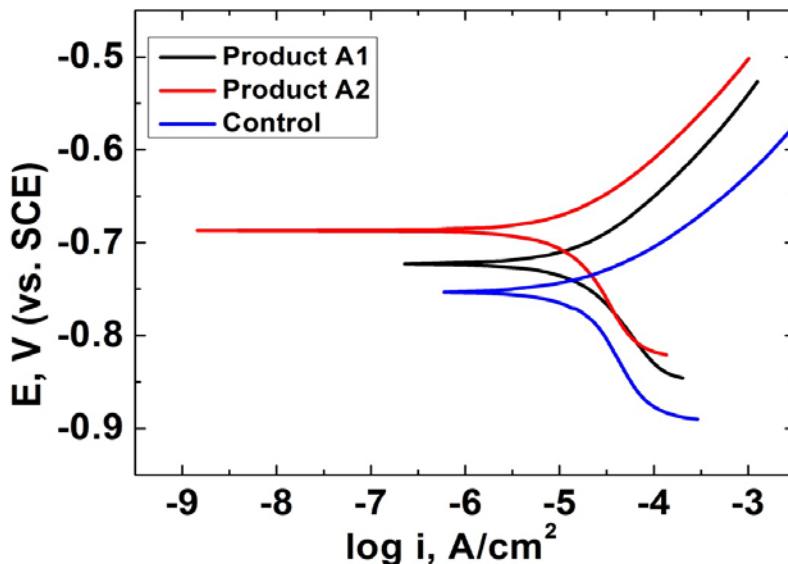


Figure 30: Potentiodynamic polarization curves of carbon steel coupons for CCM based product – Category A at 24 hr of continuous immersion.

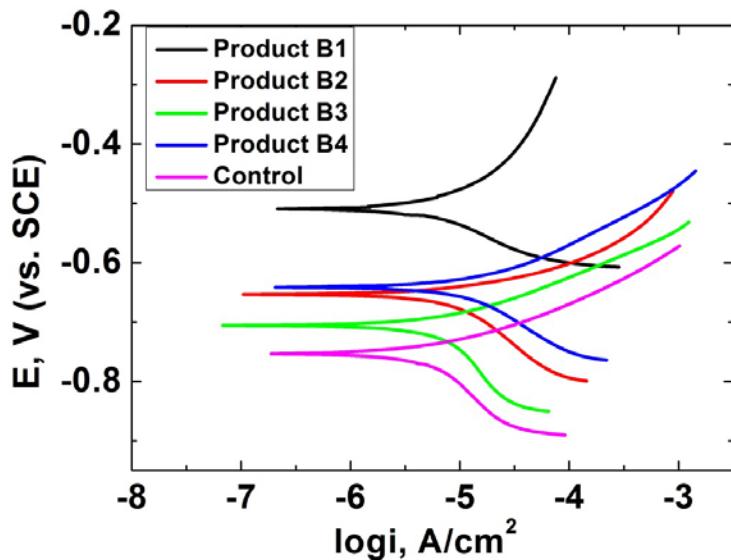


Figure 31: Potentiodynamic polarization curves of carbon steel coupons for agro-based product - Category B at 24 hr of continuous immersion

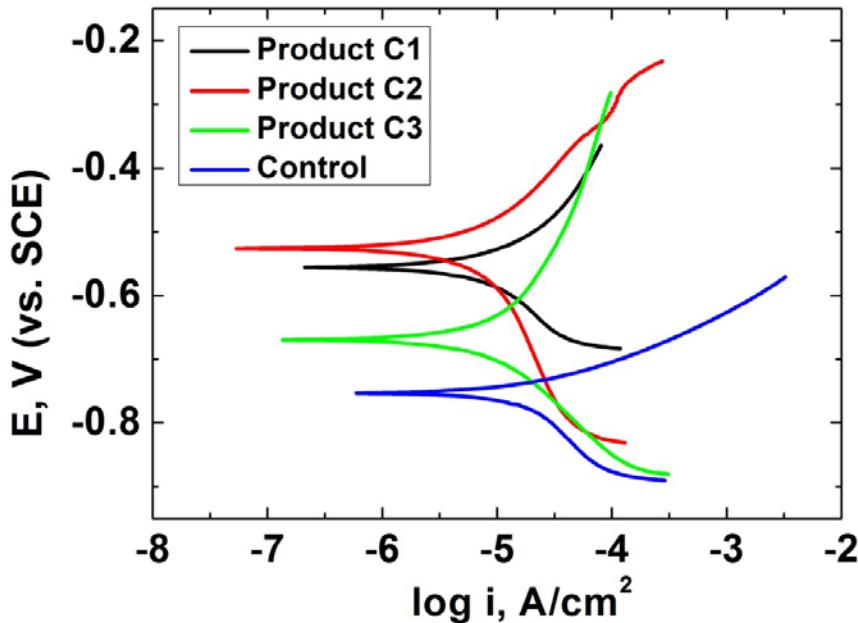


Figure 32: Potentiodynamic polarization curves of carbon steel coupons for agro-based product - Category C at 24 hr of continuous immersion

Weakening of Ice Bond to Pavement

Figure 33 (A, B, C) shows the results of bond strength between the snow and pavement for CCM and agro-based products at 25°F. It can be noted that all three category products (A, B, C)

showed reduced bond strength when compared to no-product on the pavement. This is consistent with a recent study which demonstrated that anti-icers not only depress the freezing point of the solution on pavement but also physically weaken the ice on pavement (Klein-Paste & Wåhlin, 2013). The whisker bars in Figure 33 and Figure 34 show the error rates, or difference in the results between replicated samples.

For CCM based products (category A products), it can be noted that product A1 showed a reduce bond strength compared to rock salt, but this was not statistically significant. Product A2 showed a slightly reduced bond strength compared to rock salt with statistical significance. For agro-based products in both categories B and C, the bond strength between the snow and pavement was significantly reduced compared to salt brine with statistical significance.

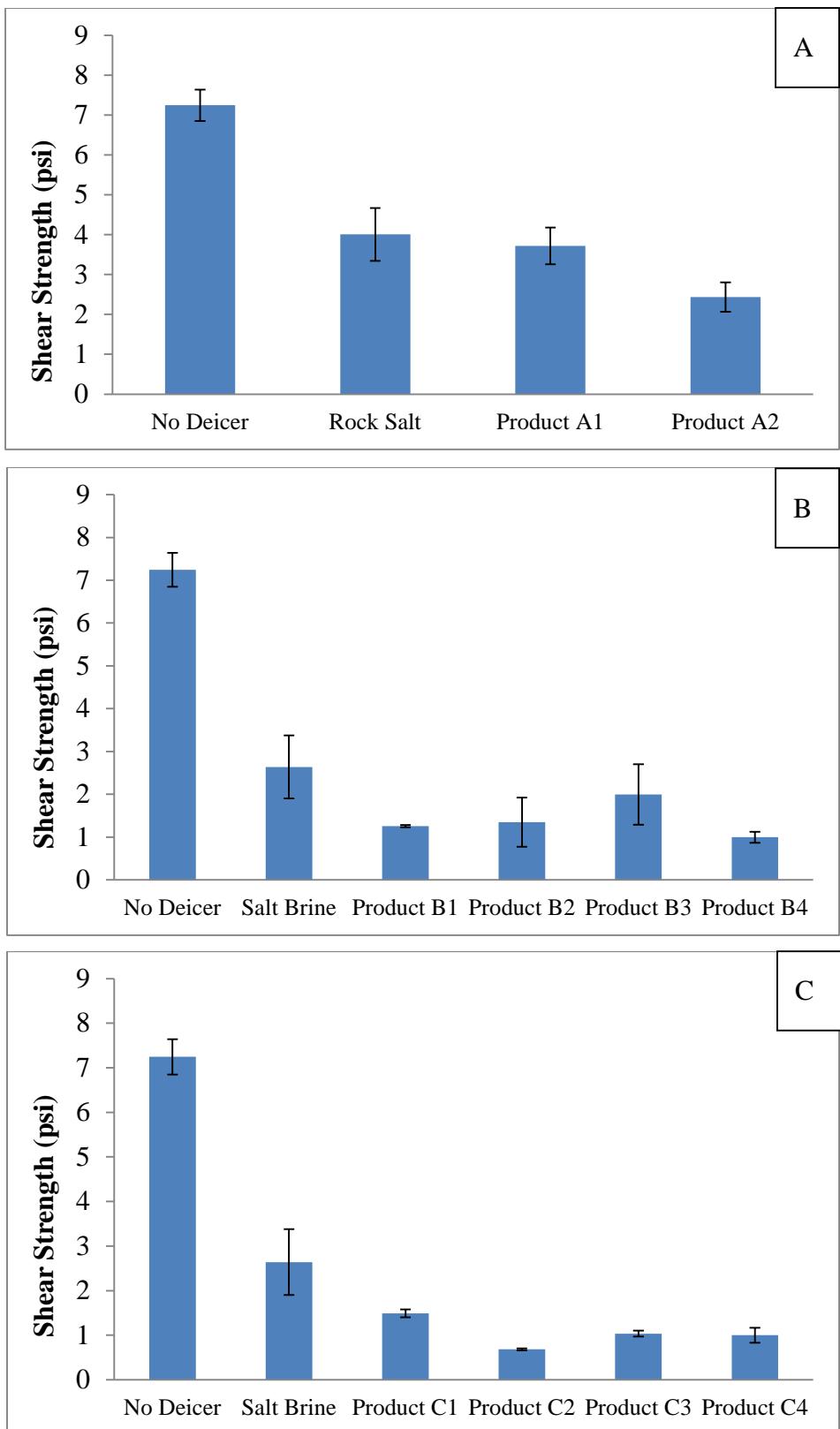


Figure 33: Bond Strength between snow and pavement at 25°F for A) CCM based products (Category A), B) Agro-based products (Category B), C) Agro-based products (Category C)

To further investigate bond strength at lower temperatures, three liquid agro-based products (products B4, C1, and C4) were tested for bond strength at 15°F and 5°F. Figure 34 (A, B) shows that liquid agro-based products help to reduce the bond strength between snow and ice and the pavement at the lower temperatures of 15°F and 5°F compared to salt brine. It should be noted that bond strength between the pavement and snow increases with the decrease in temperatures, irrespective of the product type (Figure 34).

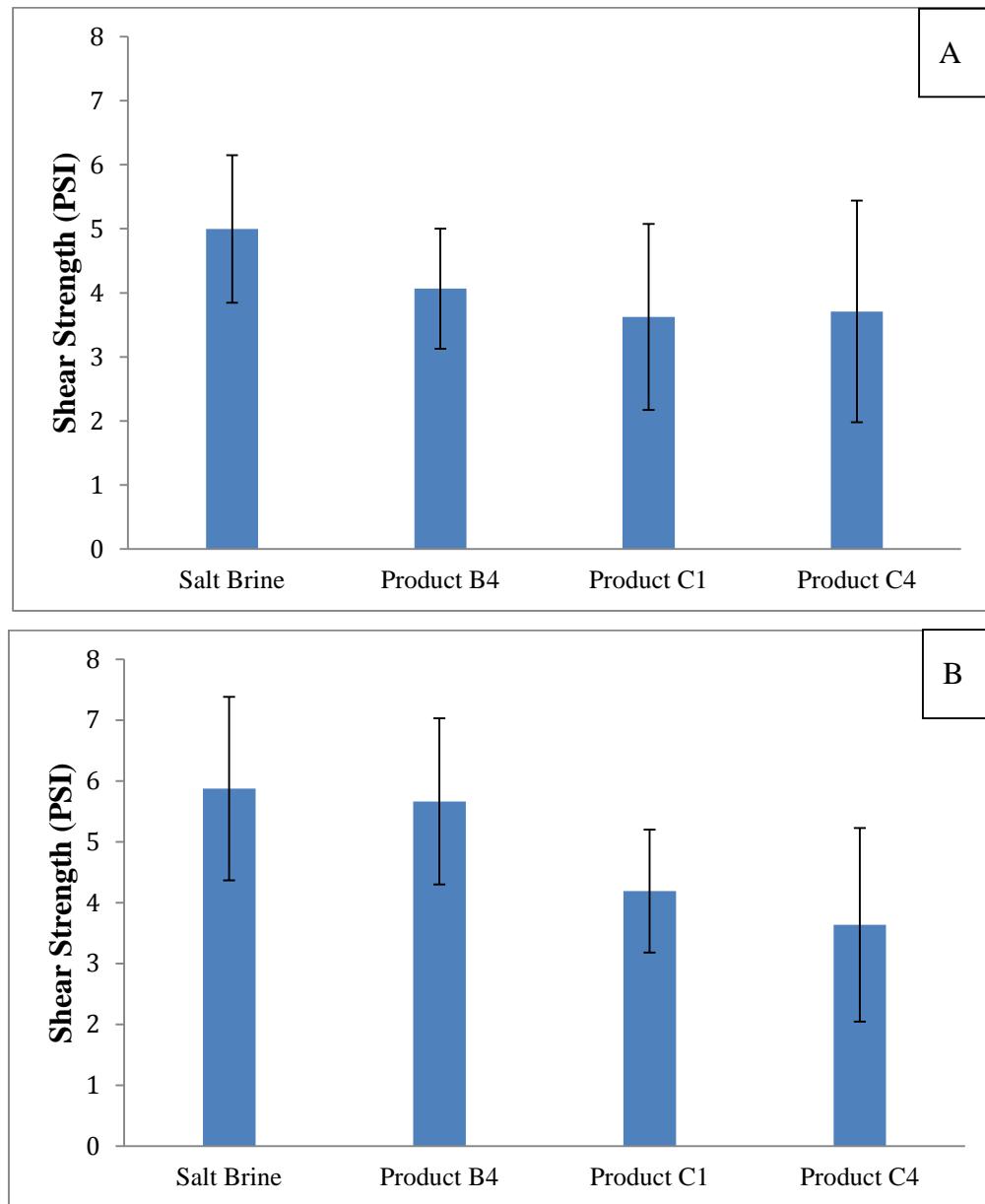


Figure 34: Bond Strength between snow and pavement for selected agro-based products at A) 15°F and B) 5°F

It can be noted that Product C1 and Product C4 did significantly reduce the bond strength compared to salt brine at 15°F and 5°F. However, Product B4 was not effective at reducing the bond strength at 5°F, when compared to its effectiveness at 15°F.

In order to understand the mechanism behind the weakening of the bonded ice to the pavement, viscosity and specific gravity of the selected three liquid agro-based products (products B4, C1, and C4) was measured using viscometer and hydrometer (Table 18). The viscosity of the agro-based products (B4, C1, and C4) was generally higher than that of the salt brine control at room temperature (68°F). Viscosity increased with the decrease in temperature irrespective of the product type. For salt brine, the addition of agro-based product resulted in the increase of viscosity. For instance, the viscosity of product B4 (70% salt brine and 30% agro-based additive) almost doubled for each incremental temperature decrease when compared to salt brine, irrespective of temperatures. However, there is no increase in specific gravity with the decrease in temperatures, irrespective of the product type.

Table 18: Viscosity and specific gravity measurements for the agro-based products

Product	Concentration	Temperature	Viscosity (mm ² /s)	Specific Gravity
Product B4	70% salt brine and 30% agro-based concentrate	68°F	2.4	1.20
		25°F	5.5	1.21
		15°F	7.3	1.21
		5°F	9.2	1.21
Product C1	As-received	68°F	23.0	1.22
		25°F	102.9	1.23
		15°F	169.4	1.24
		5°F	283.1	1.24
Product C4	As-received	68°F	9.2	1.33
		25°F	16.4	1.33
		15°F	21.8	1.34
		5°F	25.5	1.34
Salt Brine	23%.wt of Rock salt	68°F	1.5	1.17
		25°F	2.8	1.18
		15°F	4.1	1.19
		5°F	4.6	1.19

A recent study found that products with higher viscosity do not mix as well with snow and ice (Wahlin & Klein-Paste, 2015). Instead, the more viscous products remain on the pavement surface instead of being wicked up into the snow pack via capillary forces. In another study, it was found that doubling the viscosity of a product can slow down the speed of grain boundary penetration by as much as 30% (German, 2009). To apply this concept to the products tested, the agro-based products with higher viscosity would have much slower grain boundary penetration than the salt brine with lower viscosity. This may result in more product spread on the pavement surface resulting in reduction in bond strength between ice and pavement surface. However, data does not show a linear relationship between viscosity and reduction in bond strength, i.e., products with higher viscosity do not necessarily have the lowest bond strength.

Improving the Product Longevity on the Road Surface

In order to measure the product longevity on the road surface, the pavement was treated with selected liquid agro-based product B4, C1 and C4, compacted and trafficked as illustrated in the previous section (Friction performance and weakening of ice bond to pavement). The methods were modified, such that after measuring the bond strength, snow was again applied on the pavement surface without adding more products, followed by additional compaction and trafficking. This process was repeated for 250 passes, 500 passes, and 750 passes of simulated traffic and compaction. The bond strength and friction coefficient were measured after each cycle.

Figure 35 (A, B) shows that bond strength increased after each cycle of plowing, compaction, and trafficking. The increased bond strength suggests a reduction in the amount of residual product left on the pavement after each cycle, irrespective of temperature. As anticipated, bond strength increased with the decrease in temperature, irrespective of the product type for the same application rate. As shown in Figure 35A, liquid agro-based products performed better than salt brine after 250, 500 and 750 passes at 15°F. For product C1 and product B4 bond strength did not increase significantly after repeated snow and trafficking. Conversely, bond strength of product C4 increased significantly after repeated snow application. In Figure 35B, except for product C1, bond strength of all other products increased after repeated snow application and trafficking at 5°F.

It is known that the presence of anti-icing chemicals on a pavement surface helps to reduce the formation of a bond between pavement and ice and snow. For products tested which show only a slight increase in bond strength between pavement and ice and snow after repeated snow application, trafficking, and plowing, may be caused by more residual product on pavement, such as would occur with more viscous products.

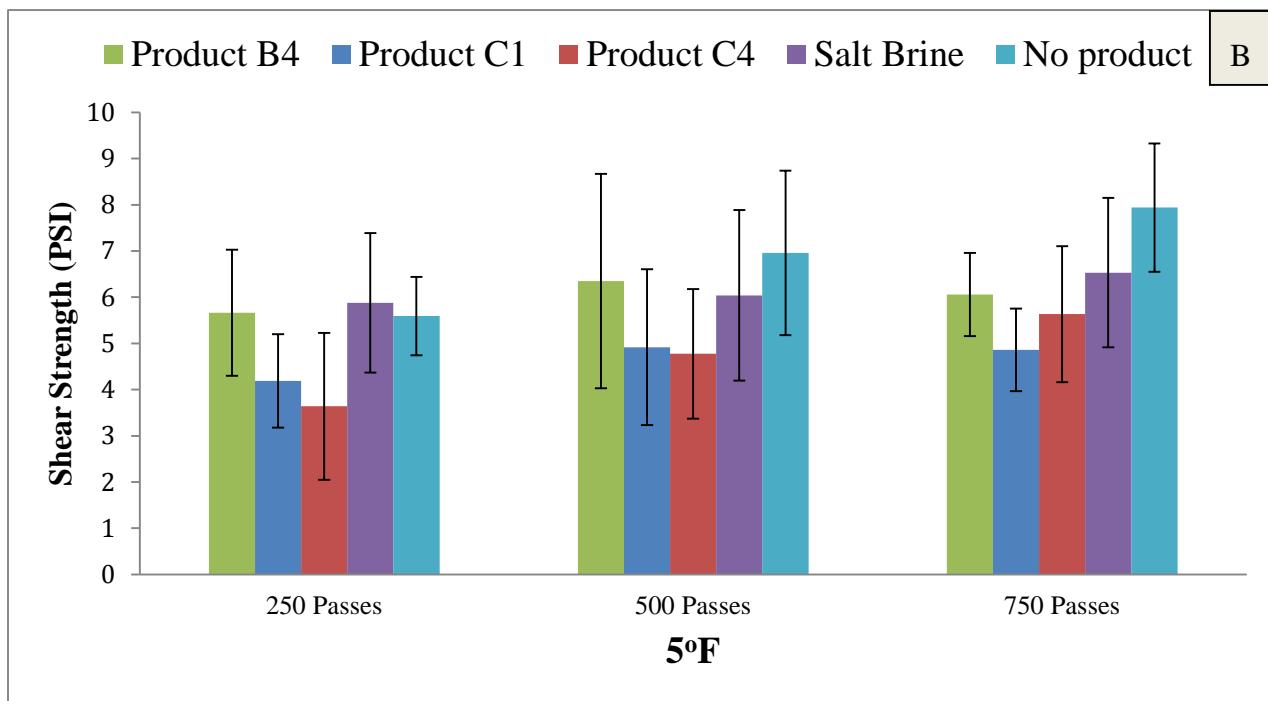
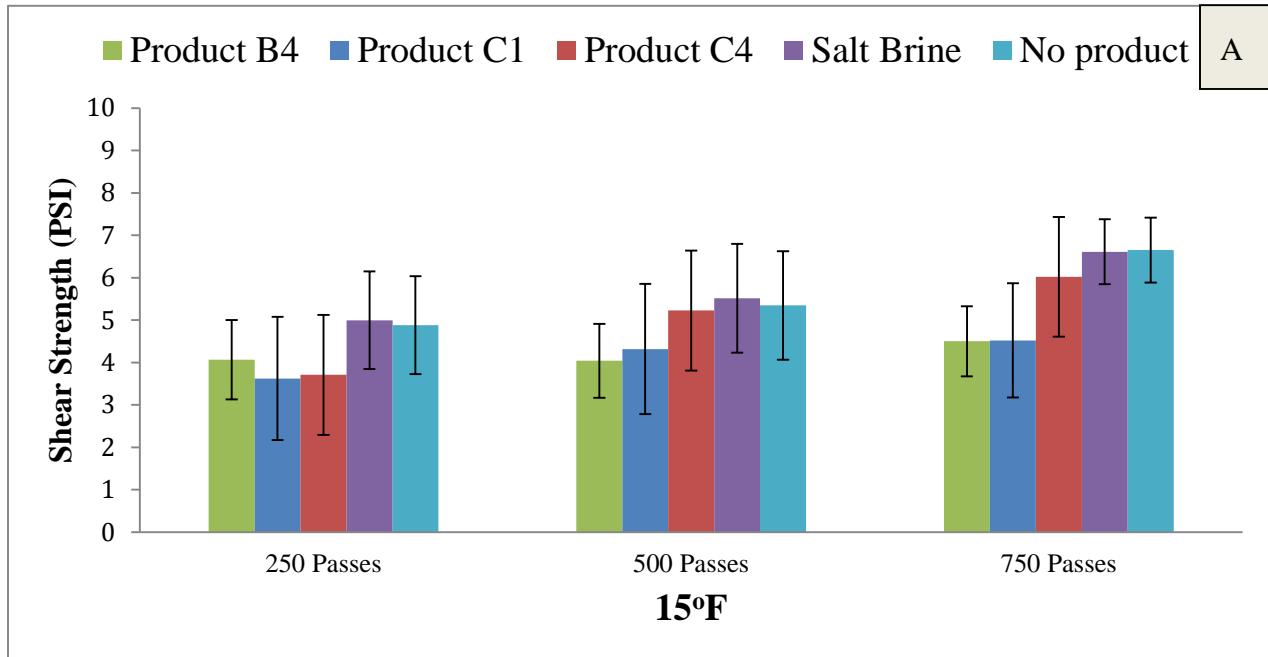


Figure 35: Bond strength between snow and pavement for selected agro-based products after repeated snow application, compaction and trafficking at A) 15°F and B) 5°F

To further understand the mechanism behind the improved longevity on the road surface (which may in turn lead to reduced bond strength), the residual product in the snow was measured using chloride concentration and UV-vis method. Chloride concentration was measured for product B4

and salt brine. For product C1 and product C4, UV-vis was used to measure the amount of residual product in the snow using absorbance values. It should be noted that 800 grams of snow was added prior to each additional trafficking and plowing, and the remaining snow left on the pavement after trafficking was collected and melted to determine chloride concentration or UV-vis analysis to determine agro-based product concentration.

Figures 36A and B show the percentage of chloride recovered for product B4 and salt brine from the snow pack removed after trafficking and plowing at 15°F and 5°F. For salt brine, after the first cycle of snow application, trafficking and plowing 76% of the chloride was recovered along with snow at 15°F. For product B4, only 45% of the chloride was recovered with the snow. This implies that for product B4 more product remained on the pavement surface after 250 passes, instead of being wicked up by the snow pack, when compared to salt brine. These results are consistent with the findings of bond strength in Figure 35A, where product B4 showed reduced bond strength between the snow and pavement surface, and therefore performed better after repeated snow and trafficking than salt brine at 15°F. On the other hand, 78% and 92% of the applied chloride from product B4 and salt brine was found in the snow after first cycle of compaction, trafficking, and plowing respectively at 5°F (Figure 36B). This implies that at lower temperatures, most of product B4 was removed with the plowed snow similar to salt brine. Once again, this is consistent with the findings in Figure 35B, where product B4 and salt brine had similar and higher bond strength after repeated snow and trafficking at 5°F.

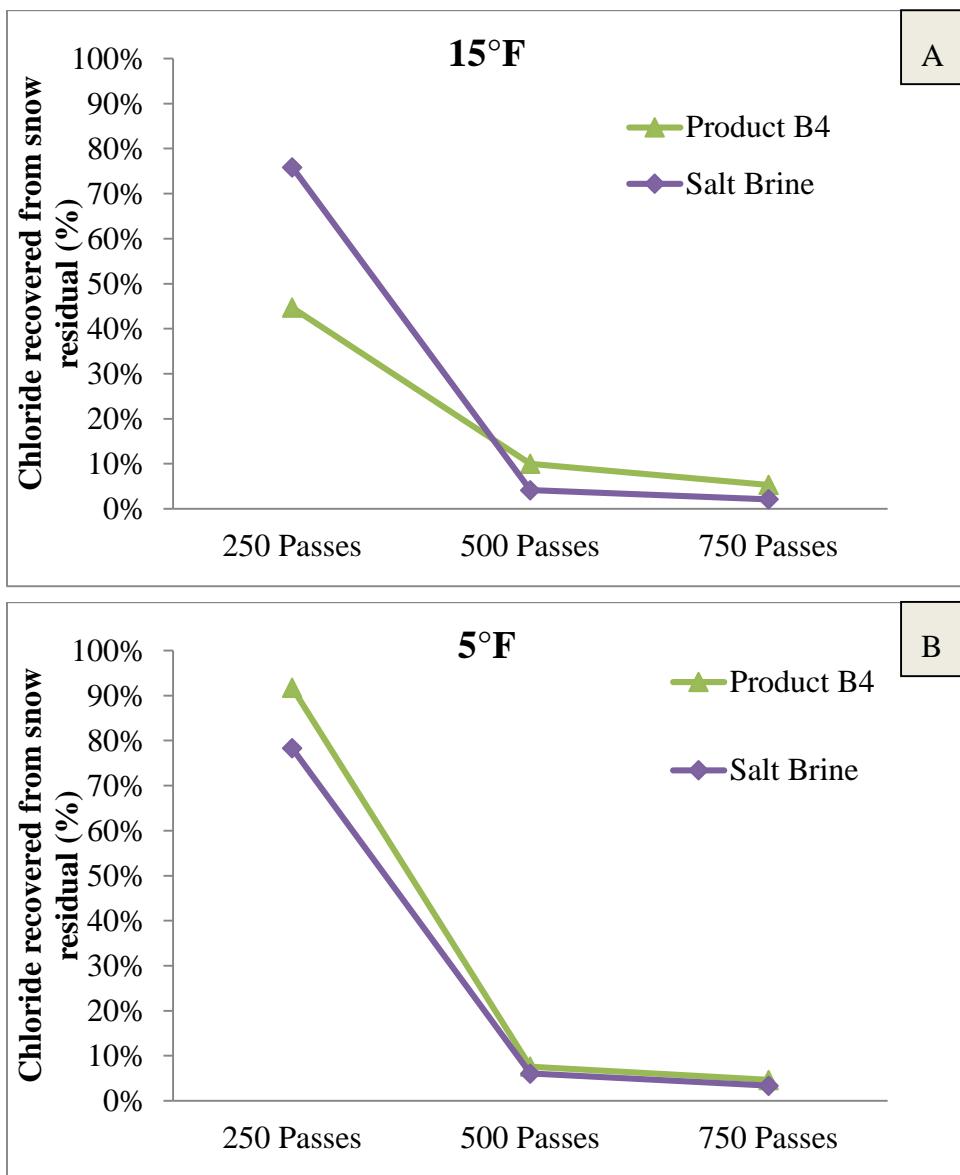


Figure 36: Chloride measured in residual snow after repeated snow application, compaction and trafficking for product B4 at A) 15°F and B) 5°F

Figure 37 shows the absorbance, measured using UVvis, for products C1 and C4 at 15°F and 5°F. It should be noted that the control sample used was prepared by mixing 800 grams of snow and the amount of product (B4, C1 and C4) applied on the pavement surface during testing. This would mimic the scenario of all the deicing product being dissolved into the snow.

Figure 37A and B shows that absorbance peaks for product C1 at 5° and 15°F, respectively. The higher the absorbance peak value, the greater the concentration of product in the residual snow. Absorbance peak values decreased after repeated cycles of snow application and trafficking, similar to decreased chloride concentrations with repeated cycles of snow application and

trafficking. However, for product C4 absorbance peak values after the first cycle of snow application and trafficking were very low, implying that little to no product was present in the snow, as shown in Figure 37C and D.

This indicates for product C4, that most of the product was removed after the first cycle of snow application and trafficking. Whereas for product C1, the absorbance peaks measured after the second and third cycles of snow application and trafficking indicates the presence of product on the pavement which was being recovered after each plowing process. This is consistent with findings of bond strength (Figure 35), where the bond strength for product C4 increased more significantly compared to product C1 for each repeated application of snow, trafficking, and plowing.

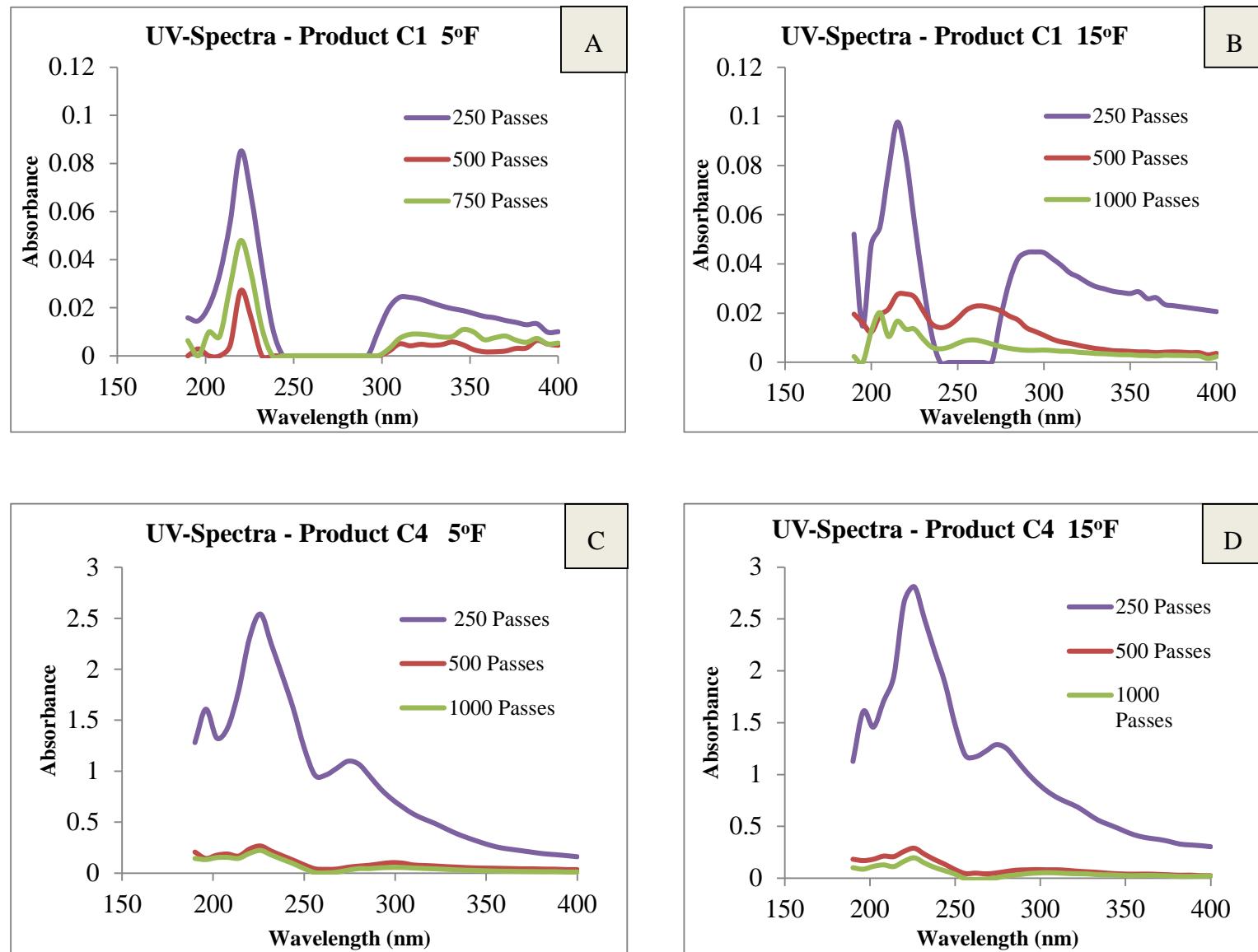


Figure 37: UV-spectra for product C1 and C4 after repeated snow application, compaction and trafficking at 5°F and 15°F

Overall, it can be noted that the presence of more product on the pavement surface (or less product removed in the snow) after the first cycle of snow application and trafficking resulted in better performance after the second and third cycles of snow application and trafficking. Also, product C1 has the highest viscosity (Table 18) and it performed either equally or better than product C4, product B4, and salt brine (in terms of reduced bond strength) at 5°F and 15°F after the second and third cycles of snow application and trafficking (Figure 35 A, B). As illustrated in the previous section (Weakening of Ice Bond to Pavement), high viscosity of a deicing solution could potentially help in spreading more product on the pavement surface instead of penetrating into the snow. In addition, spread of product on pavement may result in more products left on the pavement after the first cycle of plowing. However, the percentage of product left on the pavement varies by temperatures. At 5°F, it was found that more product was removed with the snow (Figure 36B) when compared to 15°F (Figure 36A). This could be due to the need for more product to melt ice at the colder temperature. Once the product is spread on the pavement, the amount of product that dissolves into the snow could be dependent on its ice melting capacity. The product which has lower ice melting capacity could completely dissolve into the snow and be removed along with the snow during plowing. In this case, product C1 has the highest viscosity (which may mean that more product spread out on the pavement surface) and ice melting capacity (less product dissolves in to snow) compared to product C4 and product B4.

Prevention of Ice Formation or Refreeze prevention

For testing the mechanism behind the effectiveness of the selected products in the prevention of ice formation or refreeze prevention, friction measurements were made after each plowing cycle as explained in the previous section. It should be noted that deicing products were applied only once before the first cycle of snow application, compaction, and trafficking. Figures 38A and B shows the measured friction coefficient for agro-based products after 250, 500, and 750 trafficking passes, and at 15°F and 5°F. It can be noted that friction coefficient decreases after each cycle of plowing, compaction, and trafficking at 15°F and 5°F which again validates that deicing product is being removed after each snow removal cycle as shown in Figure 36 and Figure 37.

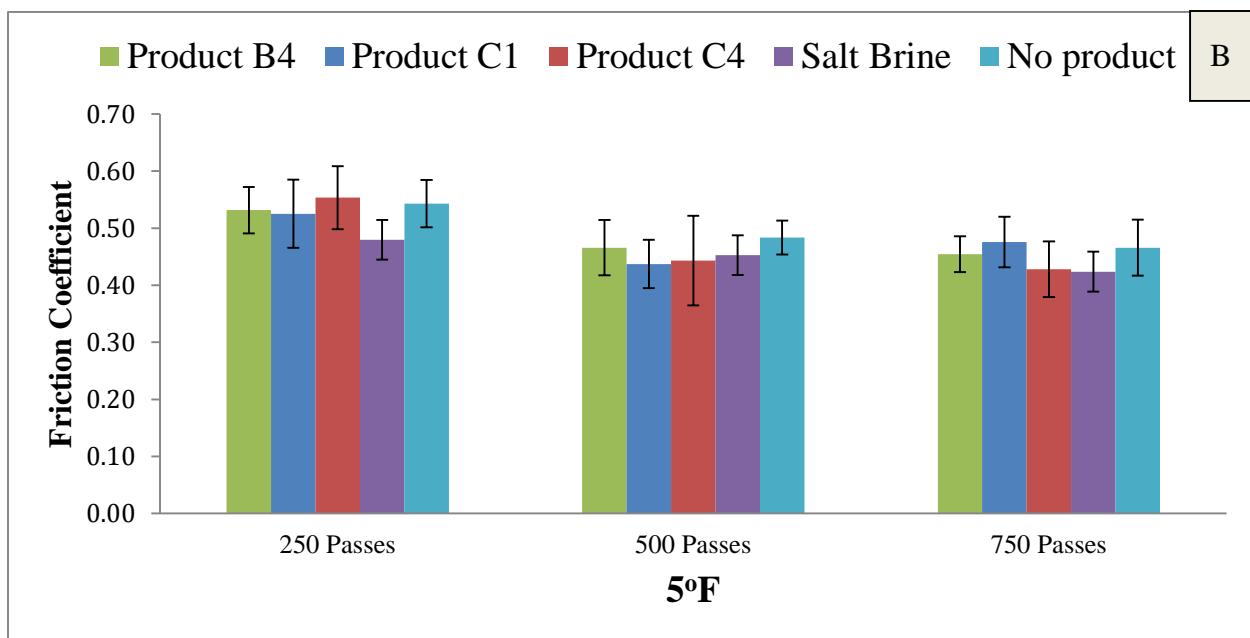
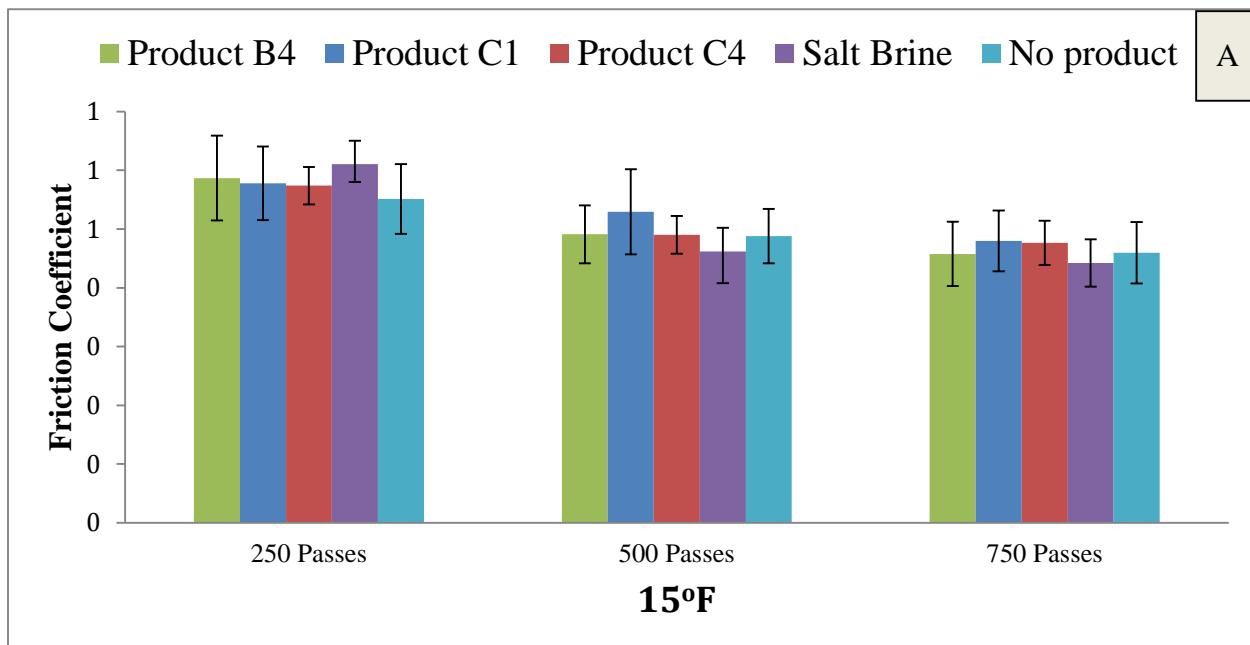


Figure 38: Friction coefficient for selected agro-based products after repeated snow application, compaction, and trafficking at A) 15°F and B) 5°F

Interestingly at 15°F, after the first cycle of snow removal, the friction values of agro-based products are almost identical with salt brine. However, by 500 passes, the friction values for agro-based products are higher compared to salt brine. In particular, product C1 has higher friction coefficient values than the other agro-based products. For 5°F, friction values were

higher for agro-based products when compared to salt brine at 250 passes. In fact, the control which had no product applied on the pavement performed better than salt brine at 250 passes. This is consistent with previous findings, such that at extreme low temperatures application of salt brine could lead to icy conditions. However, repeated snow application, compaction, and trafficking (e.g., 500 and 750 passes) resulted in equally low friction values for agro-based products and salt brine.

The main reason for the reduction in friction coefficient on the pavement is due to the formation of ice on the pavement surface. During ice formation, a single ice crystal is formed by ice nucleation (nucleation point) and triggers the ice growth. Cryoprotectants are substances that prevent ice nucleation, inhibitors which prevent the association of water with ice nucleators. As illustrated in the previous section from eutectic curves (Lowering the Freezing Point of Water/Improving the Ice Melting Capacity), agro-based products significantly reduced the freezing point of water. Previous studies have shown that alcohol sugars, sugars, and agricultural by-products can depress the freezing point of water. The products C1, C4, and B4 are glycerin, lignin, and beet based, respectively. It is possible that the agro-based products could act as cryoprotectants and delay the freezing point of water.

Absorbance of Sunlight

Figure 39 A, B, C, D shows the observed ice melt for the agro-based (category B and C) and CCM (category A) product at 15°F and 5°F. It can be noted that there is a significant increase in the ice melting capacity irrespective of the product type in the presence of sunlight. The agro-based product C4 and product B4 (darker color products) produced more ice melt compared to the salt brine. The higher standard deviations observed in Figure 39A and C are due to higher intensities, such as 700 - 750 W/m², observed in specific locations indicating less difference in ice melting capacity between products at higher intensities. The exposure of the CCM based product to sunlight did not significantly increase the ice melting capacity compared to rock salt.

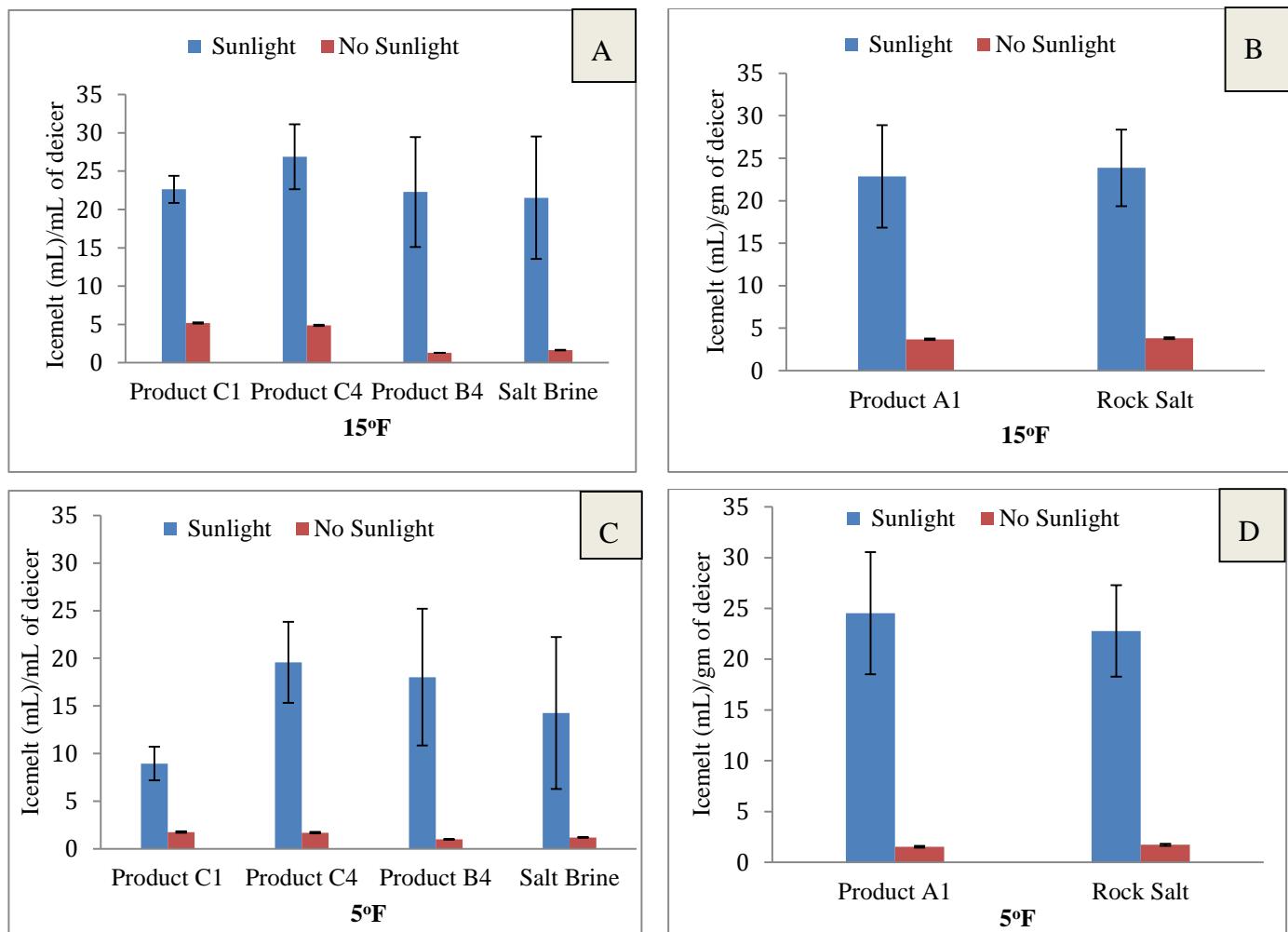


Figure 39: Ice melt with and without sunlight for A) agro-based product at based product at 15°F B) CCM based product at 15°F C) agro-based product at based product at 5°F D) CCM based product at 5°F

Chapter 5: Best Practices Manual

In this chapter a manual of best practice for the effective use of *agricultural and mineral by-products* in winter highway operations is presented using information gained from literature review, survey, and laboratory testing.

Product Types and Key Attributes

The most common de-icer is rock salt (sodium chloride, NaCl) obtained from several underground mines in the U.S. and Canada, and above ground solar ponds. Rock salt, also called “road salt,” has been used for nearly a century for roadway snow and ice control. It is effective, cheap, readily available in large bulk quantities, and easily stored, handled and applied. Though still widely used, concern mounted in recent decades over the environmental damage to soil, surface, and underground water, air, plants and wildlife, and chemical damage to vehicles, bridge structures, pavements, and metal roadside hardware. Furthermore, because salt does not melt snow or ice below 15°F, the addition of magnesium chloride ($MgCl_2$) and calcium chloride ($CaCl_2$) can lower the effective melting range to -10°F or more. All chlorides are highly corrosive and can be caustic, warranting consideration of other options. Transportation agencies, academia, and industry have searched for products that would be effective, affordable, and continually available with minimal or reduced environmental impacts. Such materials are of two types: mineral and organic.

Mineral types are limited to a few products in the United States, such as mined rock salt. For example, Ice Slicer is a homogenous non-blended (complex chloride) road salt containing 90% sodium chloride and many trace minerals—including calcium, iron, magnesium, manganese, phosphorous, potassium, zinc, and many more. Organic materials are agricultural by-products, mainly beet juice, corn syrup, molasses, and glycerin-containing natural sugars. The agricultural by-products are typically used as additives to chlorides at either 70:30 or 80:20 volume ratio.

Table 19 provides a summary of information on ten snow and ice control products made with complex chlorides and snow and ice control products with an agriculturally derived component. These products were identified through the literature review and survey and were used in the laboratory testing.

Table 19: Summary of ten products, categorized by manufacturer, with information regarding components, percent salt brine, general description, and measured chloride concentration.

Product Name	Manufacturer	Major Components	% Added to salt brine*	Description	Reference	Chloride Concentration from Mohr's chemical titration method	
Ice Slicer®	Redmond Minerals, Inc	NaCl: 90-98%; Trace amounts of MgCl ₂ , KCl, CaCl ₂	As-Received	Blend of complex chlorides	MSDS	58.90%	Reagent grade NaCl, features a theoretical Cl content of 60.7%.
Thawrox®	North American Salt Company	NaCl: 60-100%; Thawrox Treated Salt Liquid Additive: 1-5%		Thawrox treated rock salt	MSDS	59.60%	
Beet 55	Smith Fertilizer and Grain	NaCl: 17.2%	30 (70% salt brine)	Beet based product	PNS Qualified product list: Category A3	0.25 M	Note: For 23.3% NaCl reagent grade would feature Cl content of 3.99 M
Boost™ SB	America West	NaCl: 18.8%; CaCl ₂ : 2.3%	20 (80% salt brine)	Molasses based product with salt brine	PNS Qualified product list: Category A2	0.62 M	
Snow Melt®	Smith Fertilizer and Grain	Glycerin: 15 - 20%; Polyether Polymer: 10 - 20%; Sodium Lactate: 4 - 10%; Sorbitol: 2-4%; Sodium Formate: 1 - 4%; 1, 2 - Butanedoil: 1 - 4%	30 (70% salt brine)	Corn based product	MSDS	0.05 M	
Geomelt® 55	SNI Solutions	NaCl: 18.1%	30 (70% salt brine)	Beet based product	PNS Qualified product list: Category A3	0.55 M	
Apogee™	Envirotech Services, Inc.	Glycerin: % unknown (Proprietary)	As-Received	Glycerin based product	MSDS	1.05 M	
Boost™ CCB	America West	Molasses: % unknown CaCl ₂ : % unknown (Proprietary)		Molasses based product with CaCl ₂	MSDS	0.62 M	
Ice Ban® 305	GMCO	Ice Ban Concentrate: 10 - 20%; MgCl ₂ (30% Solution): 80 - 90%		Corn based product	MSDS	1.11 M	
ThermaPoint IB 7/93	Millennium Roads, Inc	CaCl ₂ : 93% ; OBFE (Organic based performance enhancer (Proprietary))": 7%		Other (Lignin based)	MSDS	0.73 M	

The chlorides concentrations presented in Table 19 were measured (Mohr's method using 0.01 M silver nitrate solution) from the as-received samples. For Beet 55, Boost SB, Snow Melt, and Geomelt 55 (or Category B products) chloride concentration was measured before they were blended with any type of chlorides. Note that Mohr's method is prone to interferences from compounds like sulfides, phosphates, etc.

The products listed in Table 19 have been categorized as follows for testing purposes:

Category A: solid complex chlorides/minerals (CCM) based products were used as-received for testing purposes.

Product A1 - *Ice Slicer*®;

Product A2 - *Thawrox*®

Category B: Liquid agro-based deicers were prepared by mixing the vendor-provided concentrates with a 23.3 wt. % NaCl aqueous solution, at either 70:30 or 80:20 volume ratio, depending on the vendor specification.

Product B1 - *Beet 55*®;

Product B2 - *BoostTM SB*;

Product B3 - *Snow Melt*®;

Product B4 - *Geomelt*® 55

Category C: Liquid agro-based deicers were used as-received from the manufacturer for testing purposes.

Product C1 - *ApogeeTM*;

Product C2 - *BoostTM CCB*;

Product C3 - *Ice Ban*® 305;

Product C4 - *ThermaPoint IB 7/93*

Best Practices Based on Laboratory Results

This section provides an overview of the findings from the laboratory testing of solid complex chloride and mineral products (CCM), liquid agro-based products blended with 23.3% salt brine, and non-chloride liquid agro-based products (as received from the manufacturer); and the associated best practices based on the findings.

The findings are categorized by the following product capabilities that were evaluated through the laboratory testing:

- Lowering the freezing point of water and improving the ice melting capacity
- Weakening the ice bond to pavement
- Improving product longevity on the road surface
- Prevention of ice formation
- Absorbance of sunlight
- Corrosion to carbon steel

Table 20: Research findings and associated best practices from the laboratory assessment of how CCM and agro-based products lower the freezing point of water and improve ice melting capacity.

Goal	Research Findings	Associated Best Practices
Lowering the freezing point of water & Improving the Ice melting capacity	<p><u>Solid Complex chloride and mineral products (CCM)</u></p> <ul style="list-style-type: none"> Did not significantly reduce the freezing point of water compared to NaCl* Did not produce more ice melt than the NaCl[†] at 25°F Produced more ice melt than the NaCl[†] at 15°F Did not produce more ice melt than the NaCl[†] at 5°F Needs sufficient time (more than 60 minutes) for the product to achieve full ice melting potential Survey respondents observed improved performance at lower temperatures <p><u>Liquid agro-based products blended with 23.3% salt brine</u></p> <ul style="list-style-type: none"> Significantly lowered the freezing point of water compared to NaCl* Did not produce more ice melt than salt brine (NaCl, liquid) alone at 25°F, 15°F and 5°F Within 20 minutes the product achieved full ice melting potential Survey respondents indicated they preferred using these products at lower temperatures (below 20°F) 	<ul style="list-style-type: none"> At temperatures warmer than 25°F and at temperatures colder than 10°F, CCM based products may not be a better replacement for NaCl[†] for improving ice melting capacity. While at colder temperatures between 25°F to 10°F, CCM based products may be a better replacement for NaCl[†] for improved ice melting performance. Plowing operations should not occur for at least 90 minutes after application of CCM based products to allow time for the CCM product to react with the snow or ice. When temperatures are dropping and/or with continued snow fall, the delay in plowing operations could cause refreeze of the snow or ice melted by CCM based products (similar to NaCl[†]). <ul style="list-style-type: none"> Irrespective of pavement temperature, agro-based products blended with salt brine may not melt more ice or snow than salt brine. When used as an anti-icer, agro-based products blended with salt brine may be effective for temperatures around 15°F. Agro-based products blended with salt brine may delay the refreezing of melted snow or ice during reducing temperatures and/or continuous snowfall more than salt brine alone. Before plowing operations begin, at least 20 minutes should be allowed after application of agro-based products blended with salt brine to react with the snow or ice. Application rates of agro-based products blended with salt brine cannot be less than those used for salt brine (NaCl, liquid) to achieve the same level of service.

Goal	Research Findings	Associated Best Practices
Lowering the freezing point of water & Improving the Ice melting capacity	<u>Non-chloride liquid agro-based products (as received from the manufacturer)</u> <ul style="list-style-type: none"> • The freezing point for these products was determined to be below -45°F • Produced more ice melt than NaCl* at 25°F, 15°F and 5°F • Within 20 minutes the products achieved full ice melt potential • Survey respondents indicated they preferred using these products at lower temperatures (below 20°F) 	<ul style="list-style-type: none"> • Agro-based products (as received) may be effective in cold weather conditions (below 5°F). • Irrespective of pavement temperature, agro-based products (as received) will melt more ice or snow than salt brine (NaCl, liquid). • Before plowing operations begin, at least 20 minutes should be allowed after application of agro-based products (as received) to react with the snow or ice. • Agro-based products (as-received) will delay the refreezing of melted snow or ice when temperatures are falling and/or during continuous snowfall. • Application rates can be lower than salt brine (NaCl, liquid) for temperatures up to 15°F to achieve the same level of service.

* Reagent grade NaCl powder

† Rock salt (white pellets from North American Salt Company, Overland Park, Kansas)

Table 21: Research findings and associated best practices from the laboratory assessment of how CCM and agro-based products weaken the ice bond with the pavement.

Goal	Research Findings	Associated Best Practices
Weakening of the ice bond to pavement	<u>Solid Complex chloride and mineral products (CCM)</u> <ul style="list-style-type: none"> • Slightly reduces the bond strength between ice and pavement compared to NaCl[†] at 25°F and 15°F 	<ul style="list-style-type: none"> • When used as a deicer on compacted snow or ice, CCM based products may facilitate easier plowing, and less snow or ice residual might be left on pavement compared to NaCl.
	<u>Liquid agro-based products blended with 23.3% salt brine</u> <ul style="list-style-type: none"> • Significantly reduces the bond strength between ice and pavement compared to salt brine (NaCl, liquid) at 25°F, 15°F and 5°F. • The addition of agro-based products to salt brine increased the overall viscosity of the products, resulting in better coverage of product on the pavement surface. • Less penetration of product into the snow or ice occurred compared to salt brine. • Viscosity of the products increased as temperatures decreased. 	<ul style="list-style-type: none"> • Irrespective of pavement temperature, agro-based products blended with salt brine reduce bond strength between snow and ice and pavement better than salt brine. • When used as an anti-icer, agro-based products blended with salt brine spread more evenly and remain longer on the pavement surface compared to salt brine (NaCl, liquid), resulting in more even/consistent reduced bond strength between snow and ice and the pavement. • Higher viscosity products may require additional pumping capacity. Check to the pump capacity, and consider field testing prior to use.
	<u>Non-chloride liquid agro-based products (as received from the manufacturer)</u> <ul style="list-style-type: none"> • Significantly reduces the bond strength between ice and pavement compared to salt brine at 25°F, 15°F and 5°F. • As received agro-based products typically have very high viscosity resulting in more even spread of product on the pavement surface. • Less penetration of product into the snow or ice occurred compared to salt brine. • Viscosity of the products significantly increased as temperatures decreased. 	<ul style="list-style-type: none"> • Irrespective of pavement temperature, as received agro-based products reduce bond strength between snow and ice and pavement better than salt brine. • When used as an anti-icer, as-received agro-based products spread more evenly and remain longer on the pavement surface compared to salt brine (NaCl, liquid), resulting in more even/consistent reduced bond strength between snow and ice and the pavement.

Table 22: Research findings and associated best practices from the laboratory assessment of how CCM and agro-based products improve product longevity on the road surface.

Goal	Research Findings	Associated Best Practices
Improving product longevity on the road surface	<p><u>Liquid agro-based products blended with 23.3% salt brine</u></p> <ul style="list-style-type: none"> Repeated cycles of snow application, trafficking, and plowing increased the bond strength between snow and ice and the pavement over time. After the first cycle of snow application, trafficking, and plowing, more product remained on the pavement surface compared to salt brine (NaCl, liquid) at 15°F. After first cycle of snow application, trafficking, and plowing, almost an equal amount of product was left on the pavement surface for agro-based products blended with salt brine and for salt brine (NaCl, liquid) alone at 5°F. Survey respondents noted a residual effect (increased longevity on the road surface) as one of the observed benefits of using agro-based products blended with salt brine. 	<ul style="list-style-type: none"> At temperatures of 15°F and warmer, application rates for agro-based products blended with salt brine can be reduced when re-treating a pavement surface. At temperatures below 15°F, application rates for agro-based products blended with salt brine should not be reduced when re-treating a pavement surface.
	<p><u>Non-chloride liquid agro-based products (as received from the manufacturer)</u></p> <ul style="list-style-type: none"> Repeated cycles of snow application, trafficking, and plowing increased the bond strength between snow and ice and the pavement over time. After the first cycle of snow application, trafficking, and plowing, more product residual was left on the pavement surface at 15°F and 5°F, than was for salt brine (NaCl, liquid). Survey respondents noted a residual effect (increased longevity on the road surface) as one of the observed benefits of using agro-based products blended with salt brine. 	<ul style="list-style-type: none"> At temperatures of 5°F and warmer, application rates for agro-based products blended with salt brine can be reduced when re-treating a pavement surface.

Table 23: Research findings and associated best practices from the laboratory assessment of how CCM and agro-based products prevent ice formation.

Goal	Research Findings	Associated Best Practices
Prevention of ice formation	<p><u>Liquid agro-based products blended with 23.3% salt brine & Non-chloride liquid agro-based products (as received from the manufacturer)</u></p> <ul style="list-style-type: none"> Friction values on the pavement surface were almost identical between agro-based products and salt brine at 25°F and 15°F. Friction values on the pavement surface improved significantly with the application of agro-based product compared to salt brine at 5°F. At 5°F, friction values associated with the application of salt brine were worse (lower) than when no product was applied. Commonly, friction on the pavement surface decreased with increasing temperature. Repeated cycles of snow application, trafficking, and plowing reduced the friction on the pavement surface for all product types. Agro-based products act as ice crystal nucleation point inhibitors¹, delaying the formation of ice compared to salt brine (NaCl, liquid). 	<ul style="list-style-type: none"> Around 25°F and 15°F, it is expected that agro-based products and salt brine will perform similarly in preventing ice formation. When temperatures are dropping and during continuous snowfall, agro-based products will outperform salt brine (NaCl, liquid) in preventing ice formation. At cold temperatures (below 15°F), application of salt brine on pavement surface may lead to reduced friction and dangerous icy conditions. At cold temperatures (below 15°F), application of agro-based products could help to prevent the formation of ice on the pavement surface.

¹ During ice formation, a single ice crystal is formed by ice nucleation (nucleation point) and triggers the ice growth. Cryoprotectants are substances that prevent ice nucleation, which are inhibitors that prevent the association of water with ice nucleators.

Table 24: Research findings and associated best practices from the laboratory assessment of how CCM and agro-based products absorbance of sunlight influences ice melting capacity.

Goal	Research Findings	Associated Best Practices
Absorbance of sunlight	<u>Solid Complex chloride and mineral products (CCM)</u> <ul style="list-style-type: none"> Ice melting capacity of the product improved in the presence of sunlight compared to no sunlight for all product types and NaCl. At higher intensity sunlight, ice melting capacity was similar irrespective of the product type at 15°F and 5°F. At medium intensities of sunlight, ice melting capacity of CCM based product is slightly higher than NaCl[†] at 15°F and 5°F. 	<ul style="list-style-type: none"> During clear sky conditions and at locations with high altitudes, ice melting performance may not benefit from CCM products compared to NaCl. It is possible that during clear sky conditions with occasional cloud cover, CCM products could improve the ice melting performance compared to NaCl.
	<u>Liquid agro-based products blended with 23.3% salt brine & Non-chloride liquid agro-based products (as received from the manufacturer)</u> <ul style="list-style-type: none"> Ice melting capacity of the product improved in the presence of sunlight compared to no sunlight for all product types and NaCl. At higher intensity sunlight, ice melting capacity was similar irrespective of the product type at 15°F and 5°F. At lower temperatures, darker colored agro-based products had higher ice melting capacity than lighter color agro-based products and salt brine. 	<ul style="list-style-type: none"> During daylight, use of darker colored products could improve the ice melting. During clear sky conditions and at locations with high altitudes, ice melting performance may not benefit from agro-based products compared to salt brine (NaCl, liquid). It is possible that during clear sky conditions and occasional cloud cover, agro-based products could improve the ice melting performance compared to salt brine (NaCl, liquid).

Table 25: Research findings and associated best practices from the laboratory assessment of how CCM and agro-based products corrode carbon steel.

Goal	Research Findings	Associated Best Practices
Corrosion to Carbon Steel	<p><u>Solid Complex chloride and mineral products (CCM)</u></p> <ul style="list-style-type: none"> CCM based products have a slightly reduced corrosion rate to carbon steel when compared to salt brine. <p><u>Liquid agro-based products blended with 23.3% salt brine & Non-chloride liquid agro-based products (as received from the manufacturer)</u></p> <ul style="list-style-type: none"> Agro-based products have a significantly reduced corrosion rate to carbon steel when compared to salt brine. 	<ul style="list-style-type: none"> Use of CCM based products will produce slightly reduced corrosion for automobiles and highway infrastructures compared to NaCl. <ul style="list-style-type: none"> Using of agro-based products will reduce corrosion for automobiles and highway infrastructures compared to CCM and NaCl. Due to the higher viscosity of agro-based products, they may be sticky and difficult to clean from automobiles and highway infrastructures. This could potentially increase the corrosivity of agro-based products over a longer time period.

Table 26: Summary of information on organically derived and or ag-based products commonly used in snow and ice control operation.

	Product Type	Liquid/solid	Application rate	Conditions and pavement temperature ranges	Cost	Performance	Storage and Handling Needs
Organically derived/ag-based	Corn syrup, corn steepens, and other corn derivatives; Beet juice; lignin/lignosulfonate; molasses; brewers/distillers by-product	Solid/Liquid	Application rates vary depending on blended ratio	Used as additives; mixed with solids, liquids and abrasives to improve performance. There is evidence to suggest these products reduce the freezing point.	Corn syrup: \$12-35/ton; corn steepens: \$156-192/ton; Cane Molasses: \$345/ton Distillers grain: \$95-140/ton	Reduces deicer corrosiveness and enhances longevity of deicer treatments on the road when used as an additive.	Solid material - Should be stored inside on a non-permeable surface. Loading should occur inside the building or on a non-permeable pad. Any spilled material should be cleaned up as soon as is possible. The storage building and loading pad should drain to a water collection pond, or have secondary containment to prevent the loss of material off site. Liquids - Should be stored in tanks, ideally double walled, inside or outside on a non-permeable pad. Isolation values are recommended when multiple liquid tanks are plumbed together. Pads should drain to a water collection pond. All storage tanks should have secondary containment at least large enough to retain 110% volume of the largest tank. Spilled material should be cleaned as soon as is possible.

Table 27: Summary of information on common issues, impacts, and benefits of organically derived and/or ag-based products used in snow and ice control operations

	Common Issues	Impacts					Quantified benefits	
		Air	Surface and Ground Water	Soil	Vegetation	Fauna		
Organically derived/ag-based	Clogging of equipment has occurred if not filtered or left for long periods of time.	Overall low impact including deicer aerosols.	Can cause temporary oxygen depletion in surface waters. Can contaminate water by nitrates. Localized DO depletion could occur from high phosphate, nitrate, or total organic contents. Phosphorus from deicers is usually introduced into the environment in concentrations of 14 to 26ppm, and it spurs the growth of algae, thus reducing DO for other aquatic biota. Algae growth may be spurred by critical levels of dissolved phosphorus as low as 20ppb.	May acidify the soil or cause leaching of metals into surrounding waters. Can cause temporary anaerobic soil conditions. The breakdown of organic matter may lead to temporary anaerobic soil conditions.	N/A	N/A	N/A	Reduces corrosion rates for chloride based products.

Table 26 and Table 27 summarize key points regarding application, storage, handling and performance of organically derived and agro-based products (Fay et al., 2015). Cost data shown in Table 21 may vary regionally and represents data collected from survey respondents.

Storage Guidelines

Solid Product Storage

De-icers are shipped and stored as dry-bulk, dry-bagged, or liquids. Bulk de-icers should be stored similar to regular rock salt on impervious paved surfaces under cover. Ideally this would be in a permanent structure such as an open-facing bin or barn with a door (Figure 40). Or, for a short duration, the material can be kept under a secured waterproof tarp on a paved surface with provision for capturing and retaining any runoff water.



Figure 40: Salt dome style salt storage structure with a barn door and paved loading pad.
Photo courtesy of Kansas DOT

Any spillage must be promptly cleaned up. Stockpiles should be checked regularly for integrity of the storage structure (cracks, bulges, roof leaks, etc.). Open run-off retention structures should be checked after heavy rains.

The following information is summarized from the Clear Roads Environmental Best Management Practices for Snow and Ice Control (Fay et al., 2015).

Material storage options include bins, pads, domes, rectangular sheds or barns, high arch structures, and silos, which can be made of wood, steel, aluminum, fiberglass, concrete, or fabric. The Salt Institute (2013) developed a reference guide for building size and type and snow and ice control product pile size, loading and storage styles, and techniques. Table 28 provides a list of pros and cons for common salt storage facilities used in Ohio (Ohio Water Resources Council, 2012).

Table 28: Salt storage facilities pros and cons (the more + the better) (OWRC, 2012)

	Affordable	Accessible	Strong	Durable	Effective in preventing runoff
Any structure without an impervious base and/or sidewall. 	+++	++	+	+	++
Any roof type on 3-sided impervious concrete base. 	++	+++	++	++	+++
Any 4-sided or dome structure on an impervious concrete base. 	+	+	+++	++	++++

Identified best practices for the storage of solid products include:

- Storage facilities should be designed for typical runoff.
- Storage facilities should have impermeable surfaces and be covered.
- Loading of storage structures can be accomplished most efficiently with a conveyer. This minimizes the number of times you need to touch and move the product, and clean up spills. Loaders are also frequently used.
- Consider using the 10ft rule, where salt is stored at least 10 feet back from the door or in front of the storage structure.
- Do not over load the storage structure; piling too high or up walls can accelerate damage from corrosion, lead to loss of material, and cause damage from loading equipment.
- Wall should be free of cracks or gaps and sealed.
- Products with any percentage of salt, for example a salt-sand blend with 5% salt, should be stored to prevent the loss of the salt; they should be stored under cover on an impervious surface.

- When constructing the storage structure, consider the prevailing wind direction and position the building and doors to shelter loading operations, to minimize snow drifts around doorways, and to keep precipitation out of storage areas.
- Loading of vehicles should be indoors where possible, or on an impermeable loading pad with proper runoff capture in place.
- Conduct routine storage facility maintenance including checking for roof leaks, tears, or damage; and repair in a timely manner.
- Use good housekeeping practices – keeping storage facilities clean, orderly, and well maintained.

Bagged dry de-icers are best stored inside; because of the uniform size and weight of the bags, they can be stored on pallets for easier handling. Bags can range from 20lbs., up to 2000lbs. Otherwise they can be free-stacked up to a safe height determined by the user. In addition to common granular forms, some dry de-icers are also available in different shapes, each with particular benefits (Figure 41).



Figure 41: Varying shapes of solid snow and ice control product types; A) pellets, B) pastille pellets, C) flakes, D) crystals (Photo credit: MeltSnow.com)

Liquid Product Storage

Organic liquids de-icers may be obtained in small containers of 5-10 gallons, in drums or barrels up to 55 gallons, tanks of up to 250 gallons or in large bulk (tanker) quantities (Figure 42). They are stored the same as non-organic liquids such as calcium chloride. Fiberglass or polycarbonate (poly) tanks may be in-ground, permanent—mount above ground or trailer—mounted as delivered by the vendor. Tanks should be checked regularly and frequently for leaks, missing covers, electrical power, pipe, valve and hose problems. Examples of a poly tank inventory sheet and inspection form can be found in Appendix C (Oregon DOT, 2012). Inspections of poly tanks should include looking for damage, inspecting valves, gaskets and fittings, which may be misaligned for deteriorated; and looking for seepage, brittleness, or cracking (Oregon DOT, 2012; Purdue Extension, undated). Safety equipment such as emergency eye wash stations, chemical-resistant gloves, face shields, dust masks, and warning signs should be readily present and in good condition. Any spills or leaks need to be addressed immediately.



Figure 42: Liquid snow and ice control product storage options: a) drums, b) totes, c) poly tanks

The following information is summarized from the Clear Roads Environmental Best Management Practices for Snow and Ice Control (Fay et al., 2015).

Identified best practices for the storage of liquid products include:

- A spill can occur during production, delivery, transfer of liquid to storage tanks or to the spreader, and in storage if hoses or fittings break. Secondary containment should be used to capture any lost material and should be able to capture at least 110% of the largest storage tank.² Double walled tanks will not protect against broken fittings or hoses, and therefore should be within the secondary containment. If tanks are stored inside, a berm should be used to prevent the loss of liquids to floor drains or outdoors.
- Liquid storage tanks should be protected from vehicle impacts.

² Note that this recommendation comes from specifications developed by other industries. It is highly recommended that secondary containment be designed to capture all spilled material.

- Consult with local environmental regulatory authorities regarding siting and containment requirements for liquid storage facilities.
- Liquids should be stored in well-maintained and labeled storage tanks.
- Scheduled maintenance should be performed for all tanks, fittings, valves, and pumps; any leaks should be addressed immediately. Including periodically checking to ensure the valves are closed.

Material loading, Storage, and Mixing

- Loaders used to fill spreader vehicles are often fitted with buckets that are too large for the spreader hopper bodies, resulting in spillage. Though they have a slower production rate, smaller buckets are available for most loaders. Side dumping bucket attachments can also be used to provide quick precise loading.
- Whatever equipment is used for moving salt, it should provide a way of tracking the flow so the quantities can be reconciled. Pre-loaded drop-hopper loaders meter salt into spreader trucks. Overhead silos can be pre-filled with salt to similarly meter salt into spreader trucks.
- Traditionally, blending took place on the apron to the storage shed, with several buckets of sand spread level, followed by one bucket of salt trickled on the surface; the resulting blend was loaded in the dome, and the process was repeated. This method is highly inefficient and inaccurate, and produced inconsistent results on the pavement surface. Equipment to support high-production stacking and uniform, light blends now involves a dual-auger pugmill or a twin conveyor feed. In either case, two supply lines are metered to an accurate ratio and the final conveyor stacks the completed mixture.
- For this research project the manufacturer recommendation for blending ratios were used. If you deviate from the recommended blending ratios, we recommend tracking the blending ratios used, what worked and what did not work, and the reasoning for modifying the blending ratio.
- Proper design of storage facilities can aid in proper material handling.
- Liquid products may require agitation or mixing if stored for prolonged periods of time.

Brine Production Equipment

- Brine concentration should be checked with a hygrometer to measure the specific gravity of the solution. The percentage of saturation is determined by reference to specific gravity charts for the specific solution temperature.
- Water supply flow rates are a critical factor. Production sites may require cisterns to ensure adequate water supply where well production rates are poor.
- Manufactured salt brine can be pumped directly into tanks mounted on the spreaders or transferred to holding tanks at the maintenance yards.
- Stored brine will normally stay in solution as long as there is no evaporation or a drop in temperature below the eutectic point of the product.

- Corrosion or rust inhibitors, and organic or agriculturally derived products may require special handling or mixing, in which case agitation or recirculation should be considered. Sampling containers and a refractometer or hygrometer should be available for sampling and testing product concentration.

Application Methods and Guidelines

Organics, whether used for anti-icing or de-icing, are generally applied in the same manner as non-organic materials. Most of these products are liquids and the principal application methods are direct application as anti-icers which has shown the great success, or as a pre-wetting agent. An example of vendor provided guidelines for application of agro-based products can be found in Appendix B.

Pre-wetting solids (road salts, other solid chemicals, sands and gravels) improves the adhesion to pavement surface, reducing the amount of materials wasted when applied to roadways (Michigan DOT, 2012). Some evidence suggests that pre-wetting accelerates the process of melting ice and snow, as well as lowering the effective temperature of the salt (Shi et al. 2013; Luker, Rokash, and Leggert 2004).

Pre-wetting Methods

Pre-wet product can be purchased directly from a vendor. The pre-wet material is then delivered to the storage site, eliminating the need for agencies to store liquid materials and mix at the appropriate ratios. Purchasing pre-wet material can save time, space, and reduce personnel and machinery needed, but often costs more.



Figure 43: Pre-wetting, A) at the stockpile in storage and B) pre-wetting road salt prior to storage on impervious surface (Photo credits: Wilkinson Corp. and www.organicdeicing.com)

Agencies can pre-wet material at the stockpile if time, space, and machinery are available to apply liquids to dry salt or sand (Figure 43). Agencies should be careful to not store products too long, and to avoid overspray and loss of material. Pre-wetting can be done for each load prior to the truck leaving the yard (Figure 44). This method is only recommended when a short

turnaround time is needed, and agencies should be careful of overspray. Pre-wetting can also be accomplished at the truck spreader using liquid storage tanks on trucks (Figure 45). This method requires on board liquid storage tanks and an application method, which can significantly increase the cost of vehicles. This equipment requires frequent and regular calibration and maintenance; but is highly effective and economical in the long run.



Figure 44: Pre-wetting a load on an out-bound truck. (Photo credit: Wilkinson Corp.)



Figure 45: On board pre-wetting apparatus A) side mounted and B) tailgate mounted tanks
(Photo credit: www.MeltSnow.com and Wilkinson Corp.)

Typical application rates for pre-wetting are 8 to 20 gallons per ton of solid material, but rates as low as 3 to 6 gallons per ton have been specified by some vendors.

Slurry Pre-wetting

Slurry technology is essentially pre-wetting at a high ratio, typically 70/30 percent (solid/liquid) or approximately 200 lbs/l-m (pound per lane mile) of solid with 9 gallons of liquid added (Fay et al., 2013). The pre-wet slurry has an oatmeal or clumpy consistency. The solid salt grains are

extremely saturated with this technique because the liquid is introduced at multiple locations on the truck bed using an auger and adding liquid at the spinner for commercially available equipment. Slurry apparatus on trucks essentially grinds road salt and at the same time mixes it with brine before application to the road surface (Figure 46). Maine DOT utilized existing equipment and retrofitted their trucks with a similar system they made in-house. The in-house system developed slurry function to the full extent of the commercially available products. Maine DOT published an evaluation of six retrofit designs and determined the approximate cost of each.

Slurry is like the “slush” on pavement; it seems messy, but it indicates that the chemicals are actively melting. Applying “ready-made slush” or slurry accelerates the de-icing process. The slurry has been observed to go into action quicker on the road, acting immediately, and lasting longer on the road (up to 5 days under the right conditions) when compared to typical pre-wetting, while also minimizing bounce and scatter of product (Fay et al., 2013). Field crews reported that using a “heavier application” on the pass followed by smaller applications, worked best and allowed for product savings. Crews also stated the importance of getting out early in the storm.



Figure 46: Rear-mounted slurry equipment

Photo credit: Monroe Equipment and (Taylor et al., 2010)

Anti-icing and Direct Liquid Application

Anti-icing is the application of liquid material via spray or stream nozzles from the truck to the road surface, generally prior to a storm (Figure 47). Direct liquid application (DLA) is the application of liquids directly to the roadway. Advantages of using liquid snow and ice control products include (Amsler, 2006):

- Liquids tend to stay on the roadway better than solids,
- Liquids reduce bounce and scatter of pre-wet solids,

- Liquids start melting instantly upon contact.

However, liquid chemicals cannot be used to effectively treat thick ice or snow pack. Liquid deicers will become diluted (and may refreeze) more quickly than solids during heavy snow and ice storms. Though liquid agriculturally derived or organics are commonly blended with chlorides or other liquid snow and ice control products, they can be used straight. Either way, it is important to be aware of the vendor specific guidelines and instructions for handling and application.



Figure 47: Anti-icing application to a road using stream nozzles

Photo credit: www.MeltSnow.com and <http://www.gchloride.com/de-icing-ice-control.htm>.

Identified Issues with Agro By-Products

There have been some anecdotal reports of road slickness due to application of agro de-icers; research has indicated that there is potential for this to occur, but an investigation of actual field conditions that may lead to the reported conditions is needed for a conclusive finding. Over-application could be one contributing factor, and should be avoided.

Other observed problems include clogging of spray equipment due to placing beet juice-derived product into systems that had been used for CaCl_2 . In the past, this was resolved by ensuring that the liquid application systems were flushed and cleaned before changing from one material to another. Additionally, if agro-based products are going to be stored for long periods of time, such as over the summer, it is recommended to stir, circulate, or agitate the stored materials on a regular basis and ensure that all product has been flushed from the hoses.

Growth of bacteria has occurred in organic products stored for long periods of time. Vendors recognized this unforeseen circumstance and have added inhibitors. They may also recommend a

date that product is no longer effective (shelf life), and if the vendor has any suggestions for long term storage (e.g., out the sunlight, cool temperature controlled room, periodic mixing, etc.).

There have been concerns about wildlife being attracted to the sweet taste and smell of the agro by-products. These reports are anecdotal and no clear evidence or correlation of this to wildlife vehicle collisions or roadside deaths has been quantified.

Conclusions

Chlorides are currently the most commonly used products in snow and ice control operations due to cost, availability, and ease of use. Solid complex chlorides (also commonly used) and mineral products, agro-based products, and agro-based products blended with salt brine have been identified as snow and ice control products that may function as well or better than traditional chlorides in specific conditions with reduced impacts to the environment and infrastructure. This document summarizes best practices for the use of solid complex chlorides and minerals and agro-based liquid products in snow and ice control operations identified in the literature review, survey, and laboratory testing.

Key Finds from the Laboratory Testing

Solid Complex chloride and mineral products

CCM based products may be a good replacement for NaCl for improved ice melting performance at temperatures between 25°F to 10°F, but at temperatures warmer than 25°F CCM based products may not be worth the extra cost. At temperature colder than 25°F, snow and ice melted by both CCM and NaCl could refreeze if the plowing operations are delayed. CCM based products were slightly better than NaCl at breaking the bond between snow and ice and the pavement, which will result in less snow and ice left on the pavement after plowing operations. CCM based products may perform better than NaCl during clear sky and occasional cloud cover conditions. CCM based products are slightly less corrosive to automobiles and highway infrastructures than NaCl.

Liquid agro-based products blended with 23.3% salt brine

Agro-based products blended with salt brine do not necessarily melt more ice than salt brine. However, adding agricultural by-products to salt brine delays the freezing of water when used as anti-icer. In particular, agro-based products blended with salt brine are more effective than salt brine at temperatures around 15°F.

Due to higher viscosity, agro-based products blended with salt brine spread more evenly on the pavement surface, and remain on the pavement surface longer, instead of penetrating into snow and ice pack. This helps to weaken the bond between snow and ice and the pavement for a longer period of time, resulting in less snow and ice residual on the pavement surface following plowing operations. At lower temperatures, agro-based products blended with salt brine remain on

pavement longer and reduce the freezing point better than salt brine, making it a more effective product at colder temperatures.

Increased presence of agro-based products blended with salt brine after snow application, trafficking, and plowing indicates the presence of residual product on the pavement surface specifically at 15°F. Based on this finding, a lower application rate can be used when re-treating the same pavement surface with agro-based products blended with salt brine. However, at lower temperatures (below 10°F), the application rate should not be reduced when retreating the pavement surface.

In conditions where temperatures are dropping and snowfall continues, agro-based products outperform salt brine in preventing ice formation on the pavement surface. Additionally, darker colored agro-based products have higher ice melting performance during daylight conditions. Finally, agro-based products have a lower corrosion rate to automobiles and highway infrastructures than salt brine. However, it is anticipated that due to their high viscosity agro-based products may become sticky and difficult to clean from automobiles and highway infrastructures, which could increase the corrosivity over a longer time period.

Non-chloride liquid agro-based products (as-received from the manufacturer)

Agro-based products (as-received) melts significantly more ice and reduces the freezing point of water as compared to salt brine. In particular, agro-based product (as-received) could be very effective in colder conditions (below 10°F). Due to its higher viscosity than salt brine, the products spread more evenly on the pavement surface, and have limited penetrating into the snow and ice pack. Agro-based products (as-received) persistence on the pavement surface, weakens the bond between snow and ice and the pavement, which will result in less snow and ice left on the pavement after plowing operations. At lower temperatures, agro-based products blended with salt brine remain on pavement longer and reduce the freezing point better than salt brine, makes it a more effective product at colder temperatures.

Increased presence of agro-based products (as-received) after snow application, trafficking, and plowing indicates the presence of residual product on the pavement surface down to 5°F. Based on this finding, a lower application rate can be used when re-treating the same pavement surface with agro-based products (as-received) at all temperatures.

Similar to agro-based products blended with salt brine, in conditions where temperatures are dropping and snowfall continues, agro-based products outperform salt brine in preventing ice formation on the pavement surface. Additionally, darker colored agro-based products have higher ice melting performance during daylight conditions. Finally, agro-based products have a lower corrosion rate to automobiles and highway infrastructures than salt brine. However, it is anticipated that due to their high viscosity agro-based products may become sticky and difficult to clean from automobiles and highway infrastructures which could increase the corrosivity over a longer time period.

Storage Guidelines

Solid complex chlorides and mineral products and liquid agro-based products should be stored and handled similarly to typically used solid and liquid snow and ice control products. All solid products should be stored on an impervious surface and covered. All liquid products should be stored in secured tanks or drums, with secondary containment. Solid and liquid storage areas should be routinely inspected, kept clean and orderly, well labeled, and any maintenance should be performed as soon as possible. Spills should be captured, cleaned up quickly, and disposed of appropriately.

Application Methods and Guidelines

Application methods discussed include pre-wetting, slurry pre-wetting, anti-icing, and direct liquid application. Application methods of solid pre-wet complex chloride and mineral products and liquid blended agro-based products are similar to those typically used for pre-wet solids and liquid snow and ice control products. Identified best practices for pre-wetting include: pre-wetting at the stockpile or with slurry equipment, and the use of pre-wetting to reduce bounce and scatter of solid material, which reduces the loss of applied product, keeps the product on the road longer, requires less material, and activates the product quicker. Identified benefits of using anti-icing and direct liquid application include: liquids tend to stay on the roadway once applied, with reduced loss of material compared to pre-wet solids, starts melting instantly upon contact, and uses less product. Liquids can dilute quicker than solids, reducing the amount of time they are present in sufficient quantity on the roadway to prevent ice from forming.

Identified Issues with Agro-based Products

Anecdotal evidence suggests that agro-based products may lead to reduced friction on the roadway, but there is no laboratory or field data to support this claim. However, over application of product should be avoided. Clogging issues have been reported when agro-based products are used with CaCl_2 . To avoid this issue, flush all equipment prior to changing to a different product type. If storing agro-based products for a long period of time, such as over the summer, flush all hoses prior to storage, and agitate the product to eliminate settling of solids. Also, long-term storage can lead to biological growth in agro-based products; check with the vendor regarding the shelf life and storage requirements for the product.

Chapter 6: Conclusions

Agro-based products and CCM based products are increasingly employed in snow and ice control operations, either used alone or more commonly as additives for chloride-based products. Past studies and manufacturers claim that agro-based or CCM based products provide benefits such as freeze depressant qualities, ability to prolong performance of deicers on the road surface, the ability to attract and utilize UV light as an aid to ice prevention, and various environmental benefits. However, the effectiveness of such products has been limited to qualitative field observations and their specific role in snow and ice control is poorly understood. This study consist of systematic laboratory investigation of agro-based and CCM based products to understand the chemical or physical processes behind the effectiveness, with a focus on 1) Lowering the freezing point of water and improving the ice melting capacity, 2) Weakening the ice bond to pavement, 3) Improving product longevity on the road surface, 4) Prevention of ice formation, 5) Absorbance of sunlight, and 6) Corrosion to carbon steel. Components of the study included a literature review, a national survey, a laboratory investigation, and a development of best practices manual.

For the purpose of this study, two complex chlorides/minerals (CCM) based products and eight agro-based deicers were identified by the project panel for laboratory testing. Four agro-based deicers were prepared by mixing the vendor-provided “concentrates” with a 23.3 wt. % NaCl aqueous solution, at either 70:30 or 80:20 volume ratio, depending on the vendor specification. Additionally, four agro-based products were used as received for laboratory testing purposes. Further, the CCM based products were also used as received.

Literature review

The main composition of agro-based products include desugared beet molasses, corn by-products, cheese brewing by-products, beer brewing by-products, succinate salts, Urea, and starch. These products are either used alone or as additives with other winter maintenance chemicals to improve performance and/or to reduce corrosion and environmental impacts. The use of complex chlorides and naturally available mineral products (Ice Slicer®, QwikSalt®, DriRox Coarse Salt®, Natural Alternative Ice Melt®, etc.) are becoming increasingly employed for snow and ice control operations.

Overall, recent studies have shown improved performance of agro-based products and naturally occurring chloride and non-chloride products in snow and ice control operations and less risk to highway infrastructure and environment. To the best of our knowledge, few studies have been performed to examine the modes of action by which these newly developed products help in improving performance and reducing negative impacts on highway infrastructure and environment.

Concluding Remarks

The main aim of literature review was to identify the existing anti-icers/deicers that contain agricultural products and solid complex chloride/mineral products. In addition, existing evaluation methods to assess the effectiveness of deicing/anti-icing products are discussed. Further, modes of action by which the deicing/anti-icing products work in performing various winter maintenance activities are discussed. Finally, a brief discussion was conducted on the impacts of deicing/products on highway infrastructure and environment. The main findings of the literature search are provided as follows.

- The main composition of agro-based products include desugared beet molasses, corn by-products, cheese brewing by-products, beer brewing by-products, succinate salts, Urea, and starch. These products are either used alone or as additives with other winter maintenance chemicals to improve performance and/or to reduce corrosion and environmental impacts.
- Another emerging class of liquid deicers features the unique synergy of complex chlorides and naturally available mineral products.
- Existing evaluation methods mainly focus on testing the ice melting capacity, ice penetration, ice bonding, and thermal properties of agro-based and solid chloride/mineral products.
- Modes of action by which anti-icers/deicers help winter maintenance activates depend on its ability to lower the freezing of water, stay on road for long time, absorb/retain more sunlight, weaken the bond between ice and pavement and reduce corrosion. Limited studies have been performed to study the underlying mechanism(s) behind each mode of action.
- Further, deicers/anti-icers used for snow and ice control may cause significant damage to highway infrastructure and environment which highlight the need of agro-based products and naturally occurring mineral products.

Overall, recent studies have shown improved performance of agro-based products and naturally occurring chloride and non-chloride products in snow and ice control operations and less risk to highway infrastructure and environment. Most of the studies have analyzed the product either in comparison with non-agro based product or individually accessing its ice melting capacity, corrosivity, damage to the environment, etc. To best of our knowledge, few studies have been performed to examine the modes of action by which these newly developed products help in improving performance and reducing negative impacts on highway infrastructure and environment.

The knowledge gained from this literature review was helpful in devising experiments to investigate the chemical or physical processes by which the identified unconventional products work in terms of snow and ice control on pavements.

National Survey

Thirty one respondents representing 16 states participated in an online survey to document the current state of knowledge of non-chloride liquid agricultural by-products and solid complex chloride/mineral products primarily used for winter maintenance activities.

- Some respondents prefer using non-chloride agro-based products at low temperatures (below 20°F).
- Longevity on the road surface (residual effects) was one of the stated observed benefits for agro-based products.
- Improved performance at low temperatures and reduced material usage are common benefits observed from using CCM based products.
- Very little research has been done by responding agencies about agro-based and CCM based products.

Laboratory Results

Lowering the freezing point of water & Improving the Ice melting capacity

CCM based products did not significantly reduce the freezing point of water compared to NaCl and did not produce more ice melt than the NaCl at 25°F and 5°F. However, CCM based product produced more ice melt than the NaCl at 15°F

Liquid agro-based products blended with 23.3% salt brine significantly lowered the freezing point of water compared to NaCl and did not produce more ice melt than salt brine (NaCl, liquid) alone at 25°F, 15°F and 5°F. Agro-based products (as-received) significantly lowered the freezing point of water compared to NaCl and produced more ice melt than salt brine.

The addition of agro-based by-products acted as freezing point depressants (potentially serving as a cryoprotectants, preventing ice nucleation from occurring). In addition, agro-based products exhibit significantly lower characteristic temperature and lower enthalpy values. This suggests that the amount of thermal energy corresponding to the aqueous brine solution's liquid/solid phase transition is reduced by the addition of agro-based by-products; making the agro-based by-products mixed with brine more difficult to freeze than salt brine alone.

Weakening of ice bond to pavement

For CCM based products, the bond strength between ice and pavement is slightly reduced compared to NaCl[†] at 25°F and 15°F

For agro-based products, the bond strength between ice and pavement compared to salt brine (NaCl, liquid) was significantly reduced at 25°F, 15°F and 5°F when used as anti-icer. The addition of agro-based products to salt brine increased the overall viscosity of the products. The agro-based products with higher viscosity compared to salt brine would have much slower grain boundary penetration than the salt brine with lower viscosity. This may result in more product

spread on the pavement surface resulting in reduction in bond strength between ice and pavement surface.

Improving the product longevity on the road surface

Agro-based products tend to stay on the road surface longer than salt brine. Longevity of the product on the road surface depends on the amount of product dissolved in to the snow before each cycle of plowing. Agro-based products tend to dissolve less in to snow when compared to salt brine when used as anti-icer.

Prevention of Ice Formation/Refreeze prevention

Agro-based products tend to have better friction values during extreme cold snow events (around 5°F) and during repeated warm snow events (25°F and 15°F). Agro-based products act as ice crystal nucleation point inhibitors, delaying the formation of ice compared to salt brine.

Absorbance of sunlight

For CCM based products, at higher intensity sunlight, ice melting capacity was similar, irrespective of the product type at 15°F and 5°F. At medium intensities of sunlight, ice melting capacity of CCM based product is slightly higher than NaCl at 15°F and 5°F.

For agro-based products, at higher intensity sunlight, ice melting capacity was similar irrespective of the product type at 15°F and 5°F. At lower temperatures, darker colored agro-based products had higher ice melting capacity than lighter color agro-based products and salt brine.

Best Practices Manual

Finally, a best practices manual was developed based on the results from laboratory investigation. Other components of the best practices manual include storage guidelines, material loading, storage and mixing, brine production equipment, application methods and guidelines, anti-icing and direct liquid application, and identified issues with agro-based products.

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Appendix A
National Survey

Survey Results

Q1. Please indicate the group that you belong to and provide contact information.

Survey responses were from DOT (32%), County (29%), and City (19%) winter maintenance professionals and a university (3.2%). Others include a program manager and a technical assistant. Specific response count and response percent for each group were presented in Table 1

Table 1: Number of responses for each group

Answer Options	Response Percent	Response Count
DOT winter maintenance manager	32.3%	10
DOT winter maintenance supervisor	3.2%	1
County winter maintenance manager	29.0%	9
City winter maintenance manager	19.4%	6
Contractor	0.0%	0
Research	3.2%	1
Others*	12.9%	4
<i>answered question</i>		31

*Others include State DOT winter maintenance engineer, program manager, technical assistant, and Maintenance Bureau Chief, of which the State DOT winter maintenance engineer and the Maintenance Bureau Chief were included 42% of responses that represented the DOT.

Q2: Please provide your name, phone number, email address, and agency name.

A total of 31 responses from 16 States within the U.S. were received from Alaska (n=1), Colorado (n=2), Iowa (n=2), Kansas (n=3), Massachusetts (n=2), Michigan (n=1), Missouri (n=1), Nebraska (n=1), New Hampshire (n=1), New York (n=1), North Dakota (n=2), Ohio (n=1), Oregon (n=1), Utah (n=1), Washington (n=1), and Wisconsin (n=10) (Figure 1).

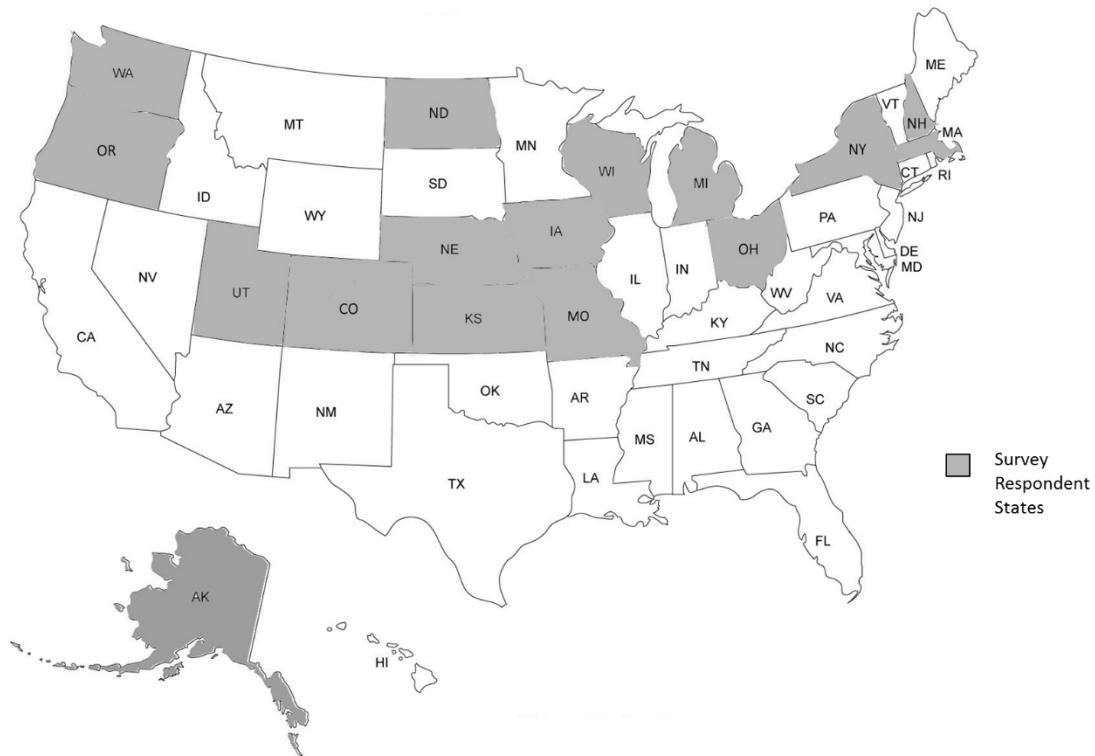


Figure 1: States that responded to the survey.

Q3. Have you used any of the following liquid agricultural by-products for anti-icing/deicing operations? If so, please rate their effectiveness. "Liquid agriculture by-products include, but not limited to, liquid sugar beet and corn by-products (Ice Bite®, [REDACTED], GeoMelt, Ice Ban®, Ice B'Gone®, etc.)."

There were 18 responses collected for this question, of which 4 respondents only had descriptive comments, which implies that of the agencies that responded to this survey, many lack experience using these liquid agricultural by-products for anti-icing/deicing operations, and it further validates the need for this research.

The most commonly used liquid agriculture by-products currently adopted by survey respondents was GeoMelt 55 (about 40%) and Beet 55 (about 20%) as shown in Figure 2. For the liquid agriculture by-products that have been used, GeoMelt 55 was also reported with the major share (23.5%), and the following products with less responses included Beet 55 (11.8%), Boost CCB (11.8%), and SnowMelt (11.8%). Similar feedback was also found in the effectiveness evaluation. Among the 17 responses for this part of the question, almost half of them rated GeoMelt 55 to be “Very Effective” (11.8%), “Effective” (29.4%), and “Somewhat Effective” (5.9%); followed by 3 responses for Beet 55 as an “Effective” product (17.6%).

³ Reference to this product name has been redacted at the request of the manufacturer.

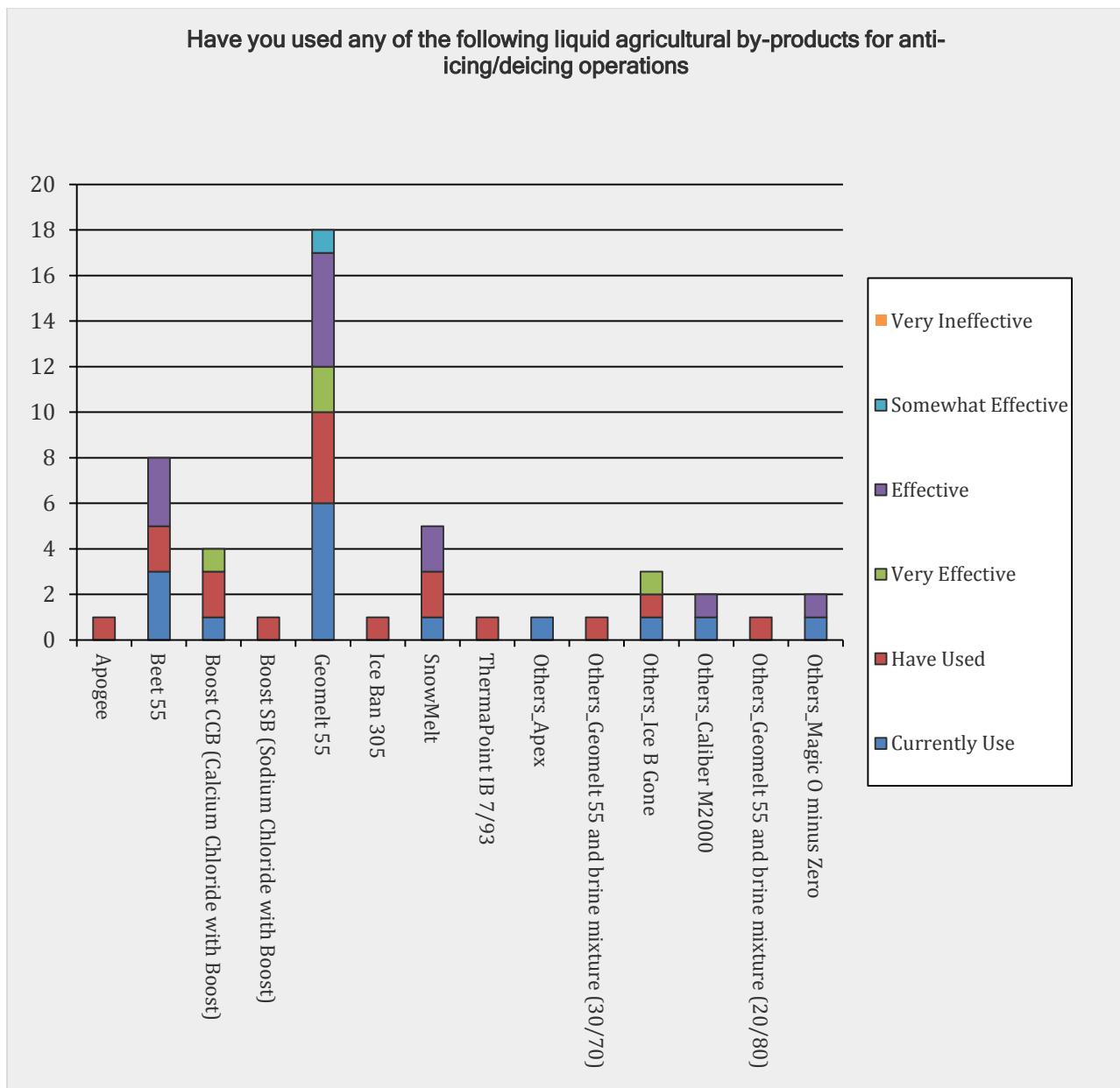


Figure 2: Service conditions of liquid agriculture byproducts and the number of response that fall into each category.

The respondents also specified some other products they used currently and have been used in the categories of “Others”. According to responses, these products included Apex, Ice B Gone, Caliber M2000, Magic O minus Zero, GeoMelt55 - salt brine mixture (30/70), and GeoMelt55 - salt brine mixture (20/80). Survey respondents provided additional comments on the effectiveness and drawbacks of these products which were provided in Table 2.

Table 2: Additional comments from survey respondents on the effectiveness and drawbacks of liquid agriculture by-products

Agency	Comments
Michigan, City of Farmington Hills	GeoMelt helps not only lower the working temperature; it gives us a significant amount of residual (on the road). Also it helps us anti-ice 3-5 days in front of an event as opposed to 1-3 days with straight brine.
Colorado, Denver	Use Apex by Envirotech, good product for downtown streets, begins to lose effectiveness at temperatures lower than 15°F.
Kansas, City of Olathe	Had clogging issues with GeoMelt and discontinued use.
Iowa DOT	We currently do not use any type of non-chloride products. In the past we have conducted tests and calculated the cost of using products such as GeoMelt 55 and Beet 55. We concluded that these products were not cost effective as compare to straight salt or salt brine.
Wisconsin, Juneau County	We premix all salt with GeoMelt 55 and salt brine at 30% GeoMelt 55 and 70% salt brine on all roads other then I 90/94 there we use the same and top dress it with 80% brine and 20% GeoMelt 55.
Utah DOT	We have never used liquid agricultural byproducts in any snow fighting application.
Washington State DOT	Calcium chloride & Boost (CC&B) is a superior product due to its ability to work at colder temperatures than other chloride blends, and its longevity on the road.
Wisconsin, Oneida County	Tried pretreating salt with GeoMelt 55 seemed to activate salt quicker at a lower temp (3-6 degrees lower), but it seemed that at the right humidity it did the opposite by not activating the salt.
Missouri DOT	We see similar performance in the GeoMelt 55 and Beet 55 products. The main drawback is that the product changes from year to year due to changes in sugar production. They both help reduce bounce and scatter and are at colder temperatures.
Wisconsin, Monroe County	GeoMelt 55 does work at lower temperatures for pre-wetting, we use it for frost prevention and it has been very valuable in that respect. A couple drawbacks include the need for agitation and it does plug some of our screens on the trucks.
New York State DOT	We use Caliber M2000 (Innovative Municipal Products) Magic O (Innovative Municipal Products).
Wisconsin, Waukesha County	Works longer at colder temperatures reducing material use, less bounce and scatter, lasts longer on pavement than liquid calcium. We see no drawbacks to the use of GeoMelt 55.

Agency	Comments
Wisconsin, Ashland County	GeoMelt can cause screens to plug- need to filter when receiving product.

Q4. Have you used any of the following complex chloride/mineral products for anti-icing/deicing operations? If so, please rate their effectiveness. "Complex chloride/mineral products include, but not limited to, mined and evaporated solid salt products with naturally occurring chloride and non-chloride constituents (Ice Slicer®, QwikSalt®, DriRox Coarse Salt®, Natural Alternative Ice Melt®, etc.) ".

There were 14 responses to this question with 2 of them only having descriptive comments and providing general service conditions of solid complex chloride/mineral products. According to the collected data, currently Ice Slicer (25%), Thawrox (16.7%) and Rapid Thaw (16.7%) were used more in practice, with Ice Slicer had more adoption in the past with a larger share (44.4%) compared to all the other products (Figure 3). In the performance evaluation part, generally products were rated to be "Effective" (64.3%) among total 14 responses, of which Ice Slicer got a bigger share of 3 responses as an "Effective" product. The other products evaluated by the respondents were also listed in Figure 3, including, M-80 Fire Rock, Solar Qwicksalt, and Dri-Rox. Additional comments on the effectiveness and drawbacks of these specified products were reported in Table 3

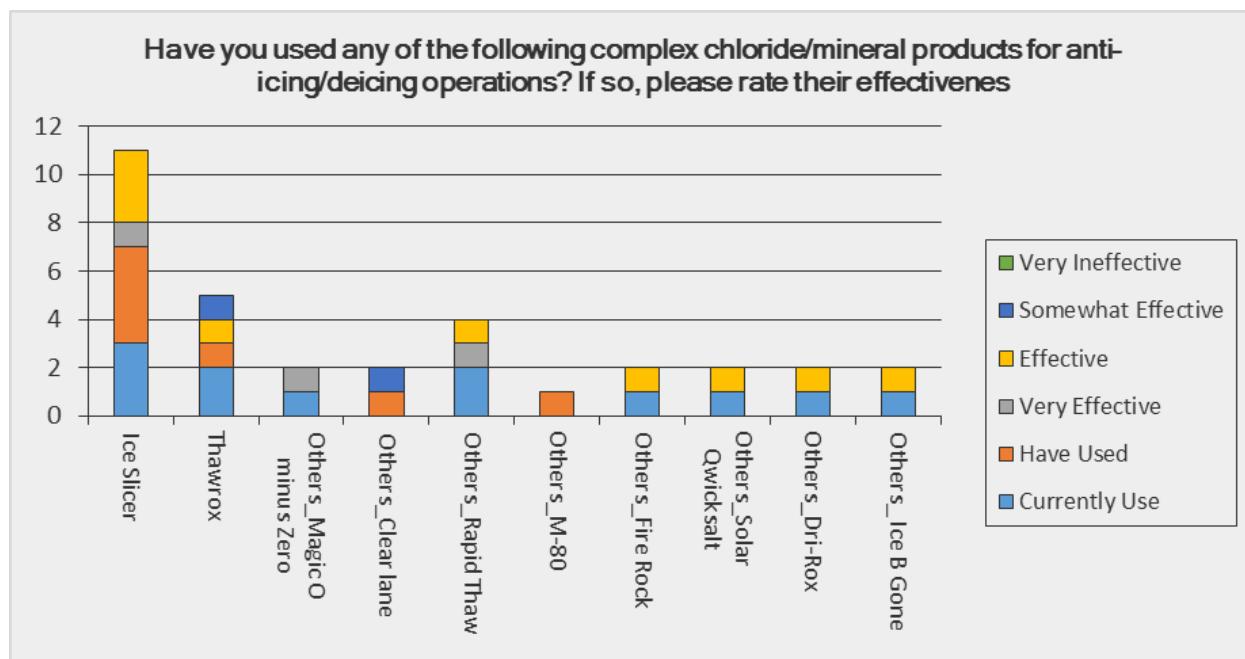


Figure 3: Service conditions of listed complex chloride/mineral products and the number of responses that fall into each category.

Table 3: Survey results showing additional comments on effectiveness and drawbacks of solid complex chloride/mineral products

Agency	Comments
Colorado, Denver	Adds traction as well as bond breaking. Good at very low temperatures. Not used in downtown because of PM10 concerns.
Massachusetts, Town of Lexington	Magic O minus zero from innovative surface solutions. MgCl ₂ with molasses. Use with brine in 70/30 mix, great residual and less salt usage.
Kansas, City of Olathe	We used Clear lane, but for the price it wasn't as effective as at spinner pre-wet and did not react as fast as pre-wetting at the spinner.
Utah DOT	Ice Slicer works very well at low temperatures, reduces volume applied. Rapid-Thaw penetrates fast to undercut packed snow and ice. Dri-Rox melts fast, but tends to refreeze if not watched closely.
Washington State DOT	Ice Slicer was the contract solid product for many years at WSDOT. We switched to regular (white) road salt under a new contract. Did not have a noticeable reduction in performance and saved a lot of money.
Kansas DOT	Ice Slicer is used to reduce corrosion on a new bridge.
Wisconsin, Oneida County	Have tried pretreating salt in storage with M-80 (80% magnesium chloride and 20% beat juice), this is a similar product to Thawrox). Definitely lowers the temperature of use of salt (by up to 10 degrees), but added the cost per ton by \$8.00.
Kansas DOT	Requires less material than sodium chloride.
Wisconsin, Monroe County	It does seem to work at the lower temperatures when untreated salt does nothing.
New York State DOT	We use Fire Rock (American Rock Salt Company) and Ice B' Gone (International Salt)
Colorado DOT	Others 1 - Rapid Thaw, Others 2 - Solar Qwiksalt. Use of these two is minimal compared to our use of liquid MgCl ₂ and Ice Slicer. From FY 9 through FY 13 (ending June 30, 2013) we used 195,843.035 tons (85% of total solids) of Ice Slicer compared to 9,448.010 tons (4% of total solids) of Rapid Thaw and 24,322.52 tons (11% of total solids) of Solar Qwiksalt.

Q5. What does your agency use such products for?

Figure 4 shows the number of agency responses indicating the main purpose of using non-chloride liquid agricultural byproducts and complex chloride/mineral products. Solid complex chloride/mineral products were reported as most commonly used for de-icing (45.8%), followed by anti-icing (29.2%). Non-chloride liquid agricultural byproducts were most commonly used for anti-icing (38.5%) and pre-wetting (38.5%).

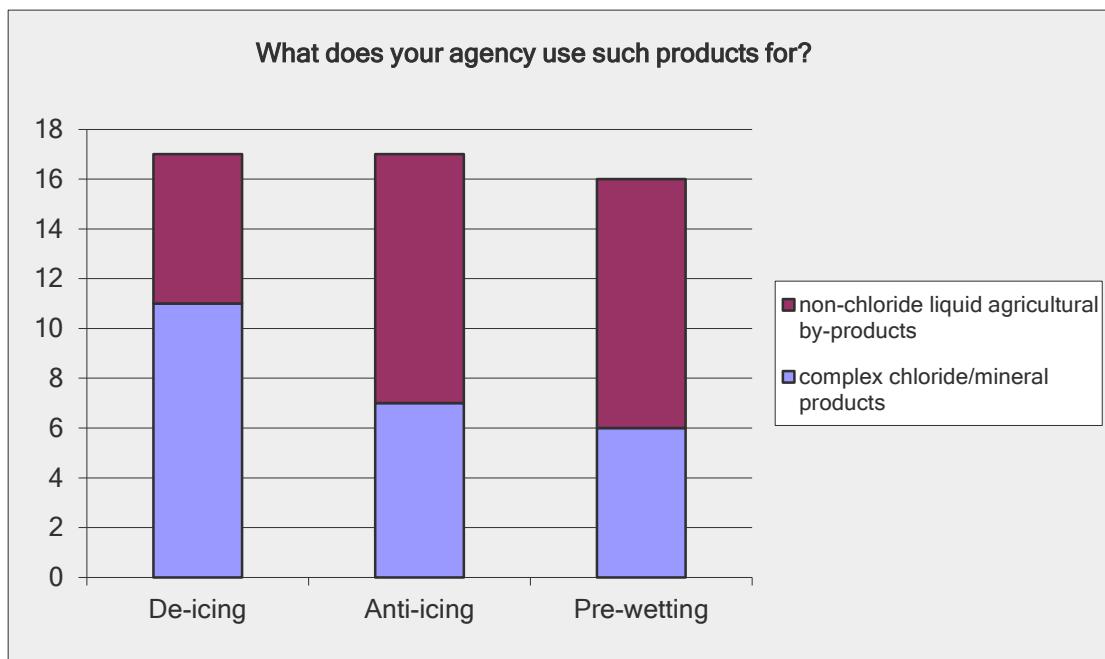


Figure 4: The main purpose of agencies using non-chloride liquid agricultural byproducts and complex chloride/mineral products.

Q6 & Q7. For each of the chosen products (from Q3 & Q4) how do you use them? Question is repeated again (Q7) if you have chosen more than one product.

There were 25 complete responses to questions 6 & 7. Table 5 summarized the respondents experience of the products from Q3 and Q4, including the product name, estimated annual usage, blending ratios, and typical temperature range used, and additional comments. Several agencies used a wide range of products such as GeoMelt 55, Beet 55, Ice Slicer, and Ice B Gone with estimated annual usage ranging from 2,600 to 35,000 gallons for cities and counties and 200 to 800,000 gallons for state DOTs. The non-chloride liquid agricultural byproduct were listed as being used as additives to brine, the blending ratios mostly were 80/20 for brine/products, and typical temperature ranges reported were within 0-34°F.

Table 5: Survey respondents experience using various non-chloride liquid agricultural by-products and complex chloride/mineral products

Agency	Product name	Estimated annual usage (in gallons or tons)	As additives with brine - Blending ratio	As additives with other salt - Other Salt Name & Blending ratio	Typical temperature range used	Comments
Michigan, City of Farmington Hills	GeoMelt 55	10,000 gal	80/20	N/A	0-34°F	
	Snow Melt	3,000 gal	90/10			
Denver, Colorado	Apex	600,000 gal annually			15-32°F	Application rate 35 gal/ln-mi
	Ice Slicer	16,000 tons annually			Lower than 30°F	Good for all purpose deicer, must sweep within 4 days for PM10
Kansas, City of Olathe	GeoMelt	No longer used		Formerly used to pre-wet salt at the spinner	Below 26°F	Had system plugging issues.
	Clear Lane pretreated salt				Formerly used on all temps during snow and ice control	
North Dakota, City of Fargo	Beet 55	45,000 gal	80/20, 80/10	Bulk Highway Coarse De-Icing Salt, 14 gal per ton	8-32°F	
	GeoMelt 55					
Wisconsin, Juneau County	GeoMelt 55	4500 gal	70/30 (brine/GeoMelt)		All	
Utah DOT	Ice Slicer	85,000 tons	Do not use for brine	We use it straight	5-25°F	
	Rapid-Thaw	10,000 tons	N/A	N/A	10-32°F	
	DriRox	10,000 tons	Brew brine at 23% by weight	N/A	15-32°F	
North Dakota DOT	Beet 55	325,000 gal	80/20		0-32	
New Hampshire DOT	Ice B Gone	5,000 gal	80/20 (brine/IBG)	N/A	20≥ °F	

Table 5: Survey respondents experience using various non-chloride liquid agricultural by-products and complex chloride/mineral products (continued)

Agency	Product name	Estimated annual usage (in gallons or tons)	As additives with brine - Blending ratio	As additives with other salt - Other Salt Name & Blending ratio	Typical temperature range used	Comments
Washington State DOT	CC&B	3,500-4,000 tons annually		Use to pre-wet salt	15-30°F	Used alone or as pre-wet agent for salt
Kansas DOT	Ice Slicer	400 tons			All temps below 32°F	
Wisconsin, Oneida County	M- 80			7 gal/ton	All	
Missouri DOT	GeoMelt 55	All beet juice - 600,000-800,000 gallons	80/20 to 70/30 (brine/beet juice)	Treat NaCl stockpile with 4-6 gal/ton	Pavement temps above 10-15°F	
	Beet 55					
Kansas DOT	Ice Slicer	300 tons			Below freezing	Just used on a new bridge to reduce corrosiveness of NaCl
Wisconsin, Monroe County	GeoMelt		20 to 30 %		From zero degrees and warmer	
	Thawrox				0-15°F	
New York State DOT	Caliber M2000 and Magic O	<200 gallons	N/A	Plain Salt (8 gal/ton)	15-23°F	
Wisconsin, Waukesha County	GeoMelt 55	35,000 gal	85/10/5 (Brine/GeoMelt/ CaCl ₂)		20°F and lower	Used mainly as pre-wet agent with straight salt brine
Colorado DOT	Ice Slicer	25745 tons				
	Rapid Thaw	163 tons				
Wisconsin, Ashland County	GeoMelt	2,600 gal	85/10/5 to 75/15/10 (Brine/MgCl ₂ / GeoMelt)		Use 5% mix for temps down to 5°F, 10% mix for temps under 5°F	

Q8. Please provide the following for the products you have chosen?

More than half agencies provided complete responses for this question (n=18). In this question, each agency could list four kinds of products with name and application rates. The most widely used products were a GeoMelt blend with an application range of 10-65 gallons per lane mile (gal/l-m) for different snow and ice control purposes, Beet 55 and brine blend with an application range of 20-100 gal/l-m, and Ice Slicer with an application rate of about 200 pounds per lane mile. Table 6 summarizes the responses for this question.

Table 6: Name and application rate of products used by various agencies.

Agency	Name and Application Rate of Four kinds of Products [Liquid (gallons/mile) & Solid (tons/mile)]			
	1	2	3	4
Michigan, City of Farmington Hills	GeoMelt Blend, 10-25 gal/ton for pre-wet	GeoMelt blend, 40-50 gal/l-m for anti-icing	GeoMelt blend for de-icing (DLA), 30-65 gal/l-m	Snow melt, testing at different ratios
Colorado, Denver	Apex, 35 gal/l-m	Ice Slicer, 150 lbs/l-m		
Massachusetts, Town of Lexington	Brine with Magic O minus zero, 8 gal/ton of salt			
Kansas, City of Olathe	Mag Chloride blended 15% with 85% brine added at 15 gal/ton of rock salt	Rock salt typically 200 lbs/l-m		
North Dakota, City of Fargo	Beet 55/Salt Brine Blend, 54 gal/l-m	Beet 55/De-Icing Salt, Solid range 200-1,000 tons/l-m, liquid at 14 gal/ton		
Wisconsin, Juneau County	GeoMelt/brine, 7 gal/ton			
Utah DOT	Ice Slicer, 250 lbs/l-m	Rapid Thaw, 250 lbs/l-m	DriRox, 250 lbs/l-m	

Agency	Name and Application Rate of Four kinds of Products [Liquid (gallons/mile) & Solid (tons/mile)]			
	1	2	3	4
North Dakota DOT	Beet 55, liquid 20-100gal/mile			
Washington State DOT	CC&B, 10-25 gal/l-m			
Kansas DOT	One third the normal rate			
Wisconsin, Oneida County	M-80 7gal/ton			
Missouri DOT	Used only with brine or to treat stockpile (4-6 gal/ton)			
Kansas DOT	Ice Slicer, 200 lbs./l-m			
Wisconsin, Monroe County	GeoMelt, approx. 35 gal mile for frost prevention	Thawrox, 200 lbs/mile and higher		
New York State DOT	Caliber M2000 and Magic O, 8 gal/ton	Fire Rock and Ice B' Gone 115, 180 lbs/l-m		
Wisconsin, Waukesha County	Geeomelt 55, 8 gal/ton of salt on pre-wet. Our trucks with larger pumps and tanks do 20 gal/ton			
Colorado DOT	Ice Slicer, 0.05 to 0.15 tons l-m	Rapid thaw, 0.05 to 0.15 tons/l-m	Solar Qwicksalt, 0.04 to 0.15 tons /l-m	
Wisconsin, Ashland County	GeoMelt-Salt- Brine-Mag Chloride, 8-10 gal/l-m along with 200-400 lbs. salt			

Q9. How long has your agency used the product(s)?

There were 19 responses to this question. Based on the responses, for currently used non-chloride liquid agricultural by-products, around 60% of agencies had over 5 years using experience, followed by 23% having 1 to 3 years of use. For the solid complex chloride/mineral products, the majority of agencies had used them for more than 5 years, and only a small part (around 27%) used new types of solid complex chloride/mineral products in the past 3 years.

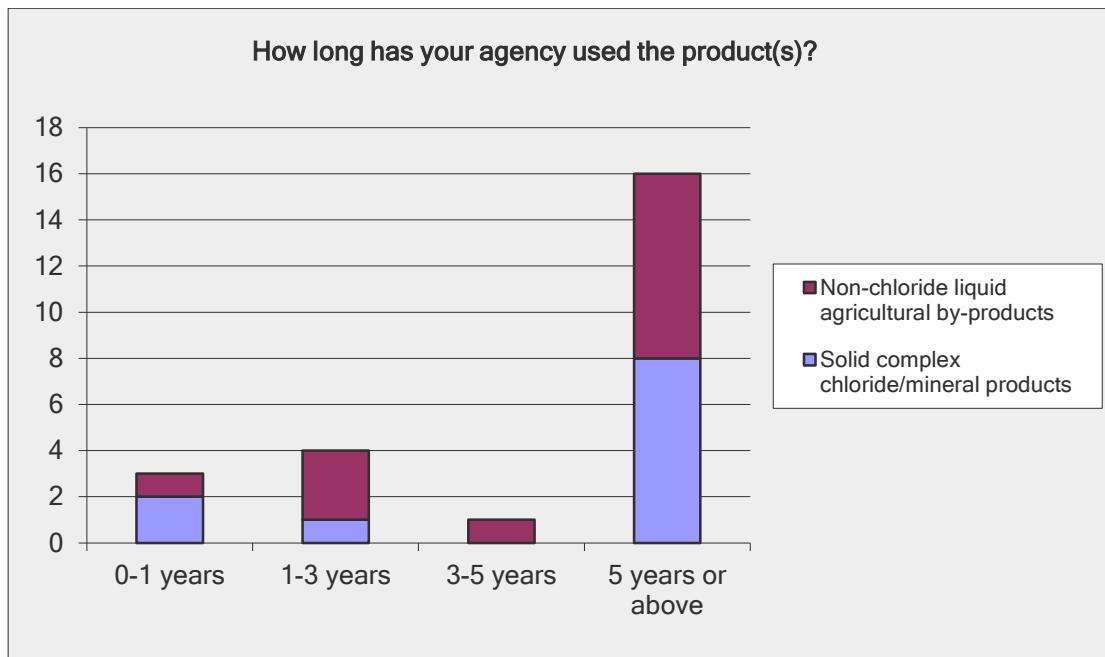


Figure 5: The numbers of years of experience respondents have had with using non-chloride liquid agricultural by-products and solid complex chloride/mineral products

Q10. How are the selected products used?

There were 19 responses to this question. For both non-chloride liquid agricultural by-products and solid complex chloride/mineral products, they were mainly used as a part of the agency's standard practices and polies (75% and 63.6% respectively), and only about 30% of them were reported to be used for trial basis (Figure 6).

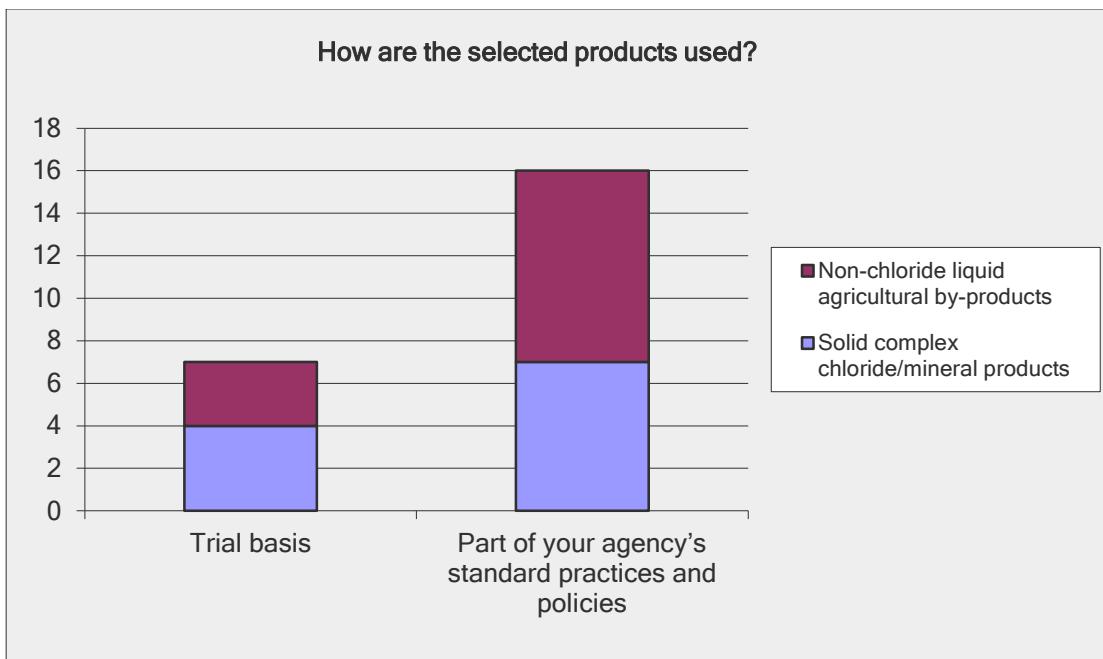


Figure 6: The reason the responding agency was using the non-chloride liquid agricultural by-product and solid complex chloride/mineral products

Q11. What is the Primary reason for choosing liquid agricultural by-products and complex chloride/mineral products for your winter maintenance operations?

A total of 19 responses were collected for this question. The top priority for selecting non-chloride liquid agricultural by-products was reported to be “Improved performance” (n=11) followed by “Reduced environmental damage” (n=6) and “Cost saving” (n=6). All four options for the primary reason for selecting solid complex chloride/mineral products in winter maintenance operations received equal weight by survey respondents. “Improved performance” was the primary reason for 36.4% of respondents, followed by “Reduced highway infrastructure damage” and “Reduced environmental damage” both noted by 22.7% of respondents. Generally speaking, product performance was regarded to be more important than cost saving when agencies selected snow and ice control products for winter maintenance operations.

Q12. Did you notice any of the following changes after using choosing liquid agricultural by-products and solid complex chloride/mineral products?

Compared to Q11, the answers to this question showed the effectiveness of non-chloride liquid agricultural by-products and solid complex chloride/mineral products in practice. There were 16 responses to this question. Observed changes from the use of non-chloride liquid agricultural by-products was showed to be “Improved performance” (n=11) and “Cost savings” (n=6). The observed changes from the use of solid complex chloride/mineral products were not as apparent as for the liquid agricultural by-products; this may be due to limited responses to this question. “Improved performance” was also the main changes observed after using solid complex chloride/mineral products (n=6), followed by “Cost savings” (n=3).

What is the PRIMARY REASON for choosing liquid agricultural by-products and complex chloride/mineral products for your winter maintenance operations?

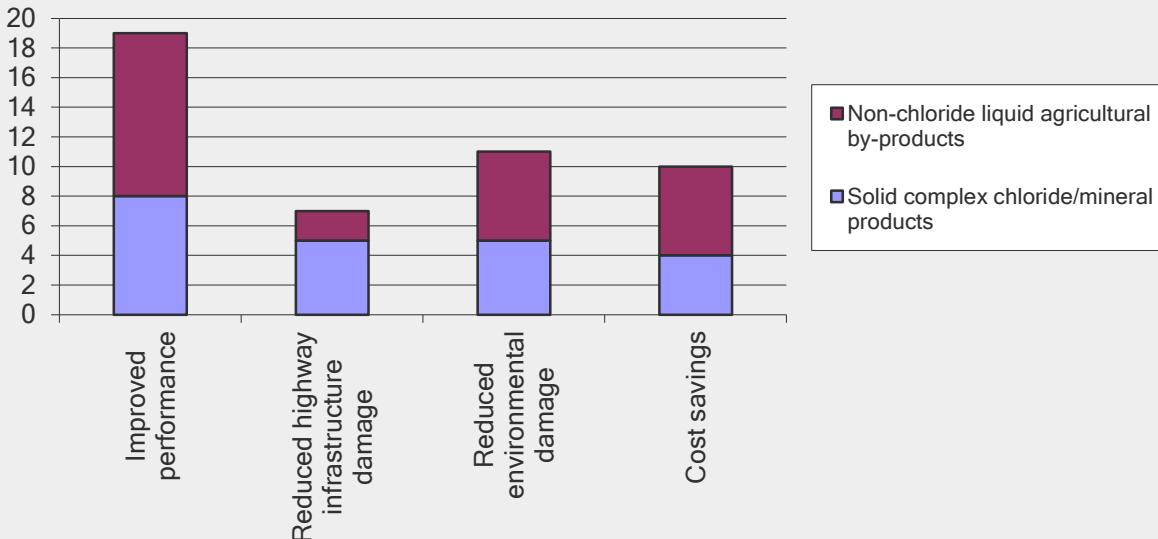


Figure 7: Survey results showing the primary reason products were chosen for use in winter maintenance operations

Did you notice any of the following changes after using choosing liquid agricultural by-products and solid complex chloride/mineral products?

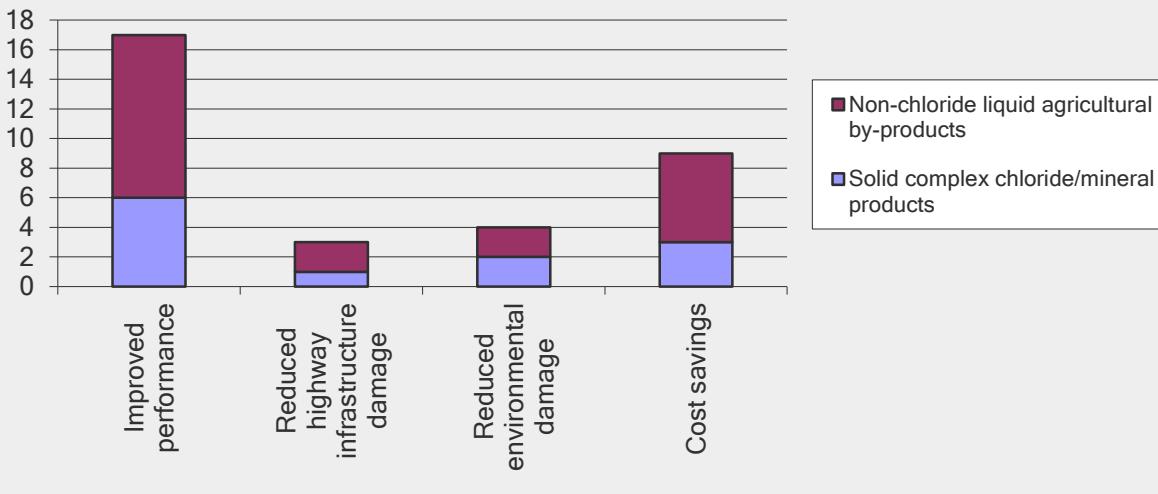


Figure 8: Number of responses to the observed changes seen after using non-chloride liquid agricultural by-products and solid complex chloride/mineral products

Q13. What quality control measures and tests are you using to verify the products you are using?

A total of 13 agencies reported the quality control measures and tests they were using to verify the products currently adopted and were provided Table 7.

Table 7: Survey results of quality control measures and test used by responding agencies

Agency	Quality control measures and tests
Michigan, City of Farmington Hills	Testing on different pavements, testing against straight salt and brine for comparison. Recording data within sensors for pavement temp.
Massachusetts, Town of Lexington	Residual effects were obvious.
Kansas, City of Olathe	Observation of side by side comparisons.
North Dakota, City of Fargo	Supervisor product log with rated control measure success.
Iowa DOT	Even though we do not currently utilize these products, we still have products such as these tested in our laboratory to validate the chemical makeup of the product. This is done to know what the chemical makeup is should we decide to test one of these products.
Wisconsin, Juneau County	We store it in small batches in the storage building. We have done test section with straight salt, top dressed pre-wet, and pile pre-wetted.
Utah DOT	We have vendors certify product performance and provide third-party certification. We also use our own contract labs to verify performance. We use the standard PNS tests.
Washington State DOT	N/A.
Kansas DOT	None.
New York State DOT	In-house material use compilations.
Wisconsin, Waukesha County	None.
Colorado DOT	We specify only products on the PNS QPL. We have a random testing program for our liquids and are developing one for our solid products.

Q14. What do you think is the “primary benefit” by which non-chloride liquid agricultural by-products work? You can select one or more.

There were 17 responses to this question. According to the responses, non-chloride liquid agricultural by-products were more effectiveness than solid complex chloride/mineral products at obtaining the identified benefits. The top five primary benefits of using non-chloride liquid

agricultural by-products include “Improving the product longevity on the road” (19%), “Improving the ice melting capacity” (15.5%), “Weakening of ice bond to pavement” (15.5%), “Lowering the freezing point of water” (13.8%), and “Prevention of ice formation” (13.8%) as shown in Figure 9. While for the solid complex chloride/mineral products, the top five primary benefits include “Lowering the freezing point of water” (20.7%), “Prevention of ice formation” (17.2%), “Improving the product longevity on the road” (13.8%), “Preventing refreeze” (13.8%), and “Weakening of ice bond to pavement” (13.8%).

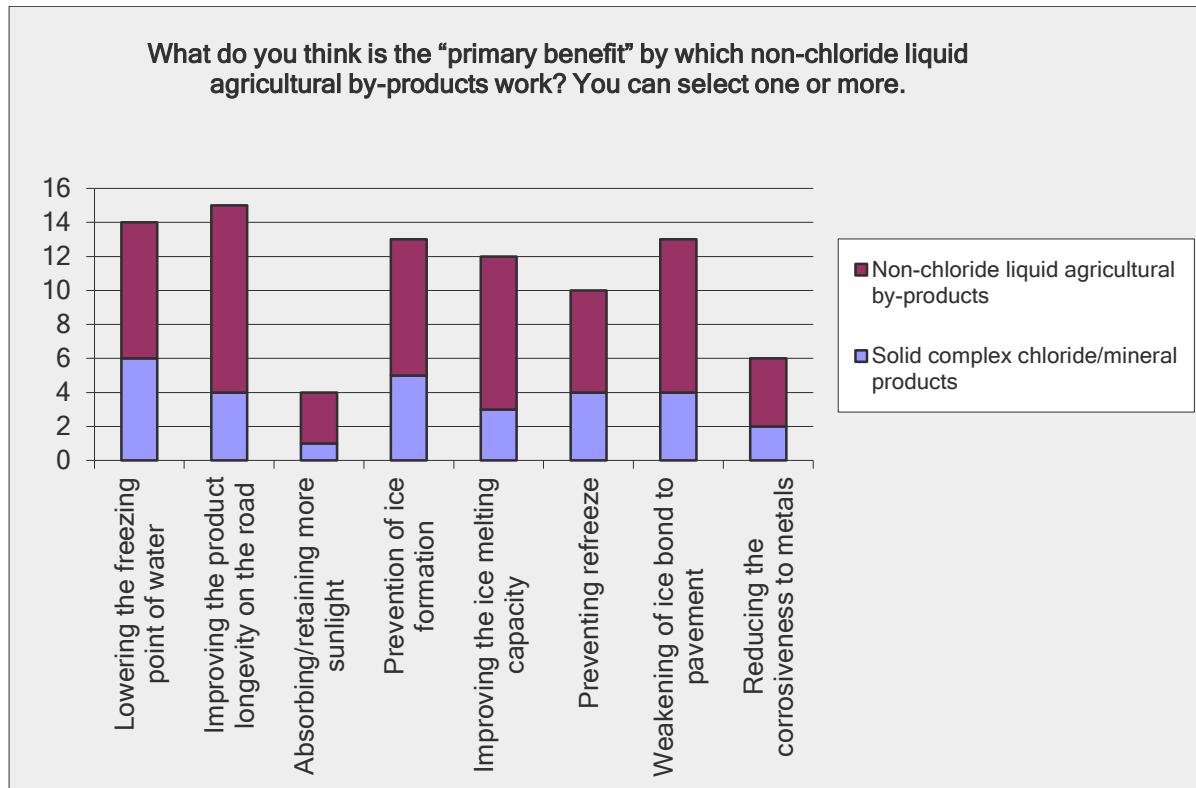


Figure 9: Number of responses to the primary benefit of using non-chloride liquid agricultural by-products and solid complex chloride/mineral products

Q15. Have you done any research to study the mode of action by which anti-icing/deicing chemical work? If yes, please email the document to me.

There were 16 responses to this question; 2 answered Yes and 14 answered No. Additional four comments indicating the reasons for their answers were shown in Table 8.

Table 8: Survey results showing response to the research into anti-icing/deicing chemical mode of action

Agency	Respon se	Comments
Michigan, City of Farmington Hills		Provided data tables for our DLA project.
Colorado, Denver	Yes	University of Colorado Denver did a study on the effects of Apex on early age concrete (less than 6 months old)
Massachusetts, Town of Lexington	No	
Kansas, City of Olathe	No	
University of Wisconsin - Madison	No	
North Dakota, City of Fargo	No	
Wisconsin, Juneau County	No	Went to some class
Utah DOT	No	
North Dakota DOT	No	
New Hampshire DOT	No	
Washington State DOT	Yes	You have the research.
Missouri DOT	No	
Wisconsin, Monroe County	No	
New York State DOT	No	
Wisconsin, Waukesha County	No	
Colorado DOT	No	
Wisconsin, Ashland County	No	

Q16. Are there any lessons learned for using such products in your snow and ice control operations? Are there any environmental benefits or risks? Any other problems experienced by your agency when using the products?

There were 17 responses to this question; 8 answered Yes and 9 answered No. There were 8 comments that offered information having potential value for evaluating any of the products, as shown in Table 9.

Table 9: Survey results showing additional comments regarding lessons learned for past product use

Agency	Response	Comments
Michigan, City of Farmington Hills	Yes	Start small; use smaller portions on different pavement types as well as different snow falls and moisture in the snow.
Colorado, Denver	Yes	Concrete placed on snow routes in the second half of summer should be sealed prior to winter to inhibit scaling of surface
Massachusetts, Town of Lexington	Yes	Residual effects are huge when it comes to the smaller 0-2" events that we have on a regular basis.
Kansas, City of Olathe	No	
University of Wisconsin - Madison	Yes	
Wisconsin, Juneau County	No	
Utah DOT	Yes	Application rates must match predicted storm intensity. Once roads are plowed, rates can drop back to 250 lbs/l-m. DriRox has to be stored indoors and some locations do not have covered storage. Most roadside soils in Utah are clay-rich and seem to trap chloride ions and prevent them from migrating into ground and surface waters. We have had no "problems" with any of the agents we use. We have had to teach maintenance crews how to use them and how to allow time for them to act before re-plowing.
North Dakota DOT	No	
New Hampshire DOT	No	

Washington State DOT	No	
Wisconsin, Oneida County	Yes	If applied as an anti-icing agent at a high rate on bridge decks it can become slimy
Missouri DOT	No	
Agency	Response	Comments
Wisconsin, Monroe County	No	Anti-icing has made a significant savings in our budget due to applying GeoMelt/brine mix on roads pre-storm or pre-frost by 3 trucks on regular time versus 13 employees salting their areas on time and a half.
New York State DOT	Yes	Sometimes can help reduce applications rates compared to plain salt; however when the price is too high compared to plain salt, we revert back to plain salt with slightly higher application rates.
Wisconsin, Waukesha County	Yes	We may start using the hot load mixture at all temperature ranges and not just below 20°F.
Colorado DOT	No	
Wisconsin, Ashland County	No	

Appendix B

Sample Application and Calibration Information from Vendors

BEET 55R Anti-icing Liquid Application

(http://www.sfgiowa.com/documents/SFG_Product_Book-V4.9.15.pdf)

- Residual will last 4-8 days
- Apply before storm event to prevent bonding
- Decreases needed man hours & increases equipment efficiency
- Beet 55R can be blended with salt brine (23.3% NaCl) up to a 50/50 ratio
- Beet 55R can be blended from 10% to 50% with salt brine and other chlorides
- Typically a salt brine blend is 75% salt brine and 25% Beet 55R
- Apply 40 to 60 gallons per lane mile
- Rates vary depending on environmental conditions

Anti-icing Liquid Application: Anti-icing Liquid Benefits:

- Beet 55R can be blended with magnesium (Mg) or calcium(Ca) chloride and have excellent results.
- Typical ratios are 80% to 90% chlorides mixed with 20% to 10% Beet 55R.

GEOMELT® 55 Anti-Icing/Deicing Fluid

Applications

GEOMELT® 55 anti-icing fluid is highly effective for anti-icing, prewetting, salt/sand stockpile treatment, and bulk material freezeproofing. The suggested usage levels should be considered as starting points and should be adjusted as needed based on operator experience and to meet local conditions such as current and expected road and air temperatures, precipitation, traffic volume, etc.

Anti-icing

- Apply to 20 to 30 gallons per lane mile (47 to 71 liters per kilometer).
- Stream apply. Do not fan spray or mist.
- Begin application when the pavement temperature is expected to drop to 32°F or below, ideally as precipitation is beginning.

Benefits:

- Prevents ice and snow from sticking to the pavement, making removal easier.
- Lowers maintenance costs, reducing applications/quantities needed.
- No dust-causing abrasives needed.

Prewetting

- Apply at 5 to 10 gallons per ton (21 to 42 liters per metric ton) at the spinner or directly to the salt/sand during loading.

Benefits:

- Enhances the deicing performance of dry salt/sand.
- Starts the deicing process immediately.
- Reduces bounce and scatter losses during application from 30% loss down to only 4% loss. Prewetted salt/sand stays on the road.
- Less salt/sand is needed for the same effectiveness.

GEOMELT® (anti-icing/deicing fluids are produced under U.S. Patent #6,080,330. Additional patents are pending).

Salt/Sand Stockpile Treatment

- Apply at 6 to 8 gallons per ton of salt (25 to 33 liters per metric ton) or 5 to 6 gallons per ton of sand (21 to 25 liters per metric ton). Mix well.

Benefits:

- Keeps the stockpile free flowing. Prevents freezing or chunking.
- Reduces the corrosive properties of treated materials.
- Enhances the deicing performance of dry salt/sand.
- Reduces bounce and scatter losses during application from 30% loss down to only 4% loss. Prewetted salt/sand stays on the road.
- Less salt/sand is needed for the same effectiveness.

Bulk Material Freeze proofing

- Apply 2 to 4 pints per ton (1 to 2 liters per metric ton) by overhead spray to aggregates, coal, glass, or bulk materials for shipment.

Benefits:

- Safe to use with many materials.
- Keeps materials free flowing.
- Prevents freezing or chunking during transfers and shipment.
- Reduces the corrosive properties of treated materials.

Deicing

Although developed primarily as an anti-icer, GEOMELT® 55 anti-icing fluid is also an effective deicer when mixed with salt brine. Since overall chloride concentration is lower, corrosion is reduced.

- Blend 1 to 1 with salt brine. Mix thoroughly.
- Stream apply. Do not fan spray or mist.
- Apply 20 to 30 gallons per lane mile (47 to 71 liters per kilometer) depending upon accumulation.
- Allow to penetrate accumulation then plow as usual.

Benefits:

- Eats through hardpack to spread along the pavement.
- Breaks the bond between the ice and snow and the roadway.
- Makes removal easier.
- No dust-causing abrasives needed.

Calibration

Calibration Chart for Ice Slicer

CALIBRATION CHART

Agency: _____

Location: _____

Truck No: _____ Spreader
No: _____
Date: _____ By: _____

Gate Opening (Hopper Type Spreaders)		DISCHARGE RATE (pounds discharged per mile)												
		A	B	C	TRAVEL SPEED AND COMPUTATION MULTIPLIER ()									
Control Setting	Shaft RPM (Loaded)	Discharge per Revolution (pounds)	Discharge per Minute (lb) (A x B)	5 mph (x 12.00)	10 mph (x 6.00)	15 mph (x 4.00)	20 mph (x 3.00)	25 mph (x 2.40)	30 mph (x 2.00)	35 mph (x 1.71)	40 mph (x 1.50)	45 mph (x 1.33)		
1			-	-	-	-	-	-	-	-	-	-	-	-
2	0.75	42	31.50	378	189	126	95	76	63	54	47	42		
3	4.75	42	199.50	2,394	1,197	798	599	479	399	341	299	265		
4	8	42	336.00	4,032	2,016	1,344	1,008	806	672	575	504	447		
5	10	42	420.00	5,040	2,520	1,680	1,260	1,008	840	718	630	559		
6	10.5	42	441.00	5,292	2,646	1,764	1,323	1,058	882	754	662	587		
7	10.5	42	441.00	5,292	2,646	1,764	1,323	1,058	882	754	662	587		
8	0	42	-	-	-	-	-	-	-	-	-	-		
9		42	-	-	-	-	-	-	-	-	-	-		
10	10.5	42	441.00	5,292	2,646	1,764	1,323	1,058	882	754	662	587		

THE ACTUAL APPLICATION RATE (POUNDS PER LANE MILE) ON THE HIGHWAY

IS THE DISCHARGE RATE DIVIDED BY THE NUMBER OF LANES BEING TREATED

Appendix C

Poly Tanks Inventory Sheet and Inspection Form (Oregon DOT, 2012)

Poly Tank Inventory Sheet



District: _____

Section

Tank	Product	Capacity	Date Installed	Purchase or Manufacture Date	Specific Gravity	Location	Tank Equipment Number	Asset Number
1								
2								
3								
4								
5								
6								
7								
8								
9								
10								
11								
12								
13								
14								
15								
16								



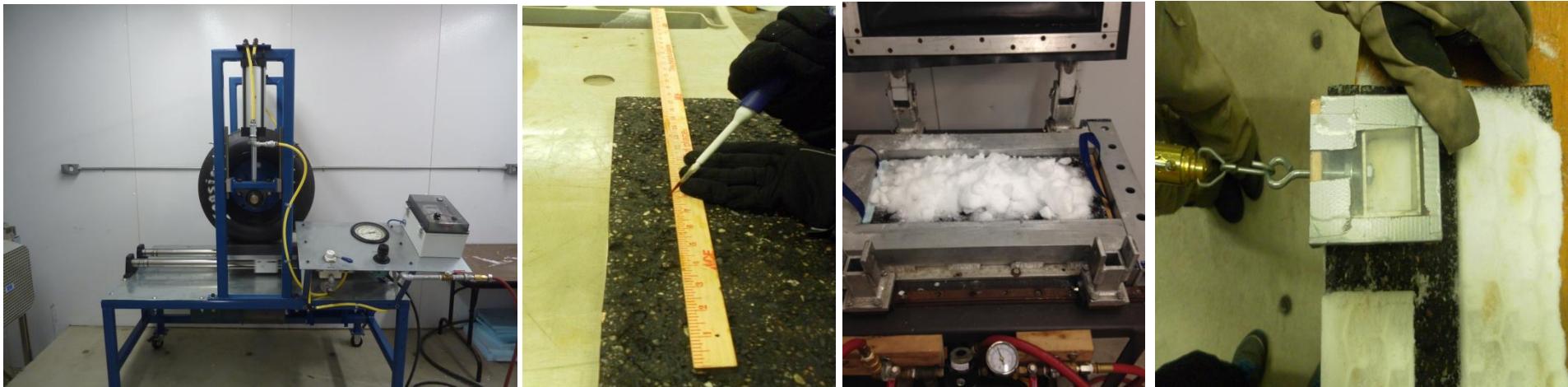
Stationary Poly Tank Inspection Form

DATE		LOCATION OF TANK				ASSET NUMBER	
OKAY	NEEDS ATTN.	ITEM	SEVERITY			ITEM	
			OKAY	MINOR	MODERATE	SIGNIFICANT	SEE COMMENTS
EQUIPMENT REVIEW		TANK REVIEW					
		Are pipes cracked or broken?					
		Is there damage to pipes from vibration, expansion, settlement, or impact?					
		Are there leaks or drips (unusual moisture) along the pipe runs?					
		Is the tank lid broken or missing?					
		Are fittings or flanges pulling away from the tank?					
		Are the tanks, pipes, and fittings adequately supported and secured?					
		Are valves or gaskets misaligned, loose, brittle, or deteriorated?					
		Are pumps and other equipment adequate for the workload?					
		Are plumbing fittings or hoses loose, broken, or worn?					
		Do pumps or other equipment need servicing or replacement?					
DETAILED INSPECTION of POLY TANK							
<i>Complete one or both tests if any response other than "okay" is checked on a tank review question</i>							
BLACK MARKER TEST – for a specific area							
Are stress cracks visible in the tested area?							
LIGHT TEST – for the whole tank							
Are stress cracks visible?							
<i>Complete test if stress cracks are observed. Recheck for stress cracks after baseball bat test.</i>							
BAT TEST – for affected areas							
Did the impact affect the tank?							
COMMENTS:							
INSPECTION FREQUENCY IS BASED ON THE SEVERITY OF VISIBLE DETERIORATION OKAY = ANNUAL; MINOR OR MODERATE = 6 MONTHS; SIGNIFICANT = OUT OF SERVICE				NEXT INSPECTION DUE BY:			
INSPECTED BY:				REVIEWED BY:			
CREW SUPERVISOR:							

Appendix D

Final Report Power Point Presentation

Understanding the Effectiveness of Non-Chloride Liquid Agricultural By-Products and Solid Complex Chloride/Mineral Products



Anburaj Muthumani, Laura Fay, Dave Bergner, Xianming Shi

Western Transportation Institute – Montana State University

*Monte Vista Associates, LLC
Washington State University*

Acknowledgements

- Clear Roads Pooled Fund and member states, and Minnesota Department of Transportation.
- Technical Advisory Committee - Ron Wright, Tom Peters, Michael Lashmet, Tim Peters, Larry J. Gangl, and Mike Mattison, and project coordinators Colleen Boss and Greg Waidley and CTC & Associates.
- WTI Support Staff

Introduction

- Complex chloride minerals (CCM) and agro-based products are increasingly employed in snow and ice control operations.
- Used alone or more commonly as additives.
- Past studies have shown that these products improve
 - Deicing and/or anti-icing performance
 - Reduce the corrosion
 - Reduce environmental impacts
- “Modes of action” by which agro-based by-products provide benefits is poorly understood

Objectives

- Literature review
- Survey
- Systematic laboratory investigation:
 - To assess the chemical or physical processes by which CCM and agro-based products are of value in winter road maintenance by:
 - Lowering the freezing point of water
 - Improving ice melting capacity
 - Weakening of ice bond to pavement
 - Reducing the corrosiveness to metals
 - Improving the product longevity on the road surface,
 - Preventing ice formation or refreeze prevention,
 - and Assessing the influence of the absorbance of sunlight.

Objectives

- Best Practices Manual based on findings
- Final Report and Presentation
- Video (Created the MLT Group)

Results – Literature Review

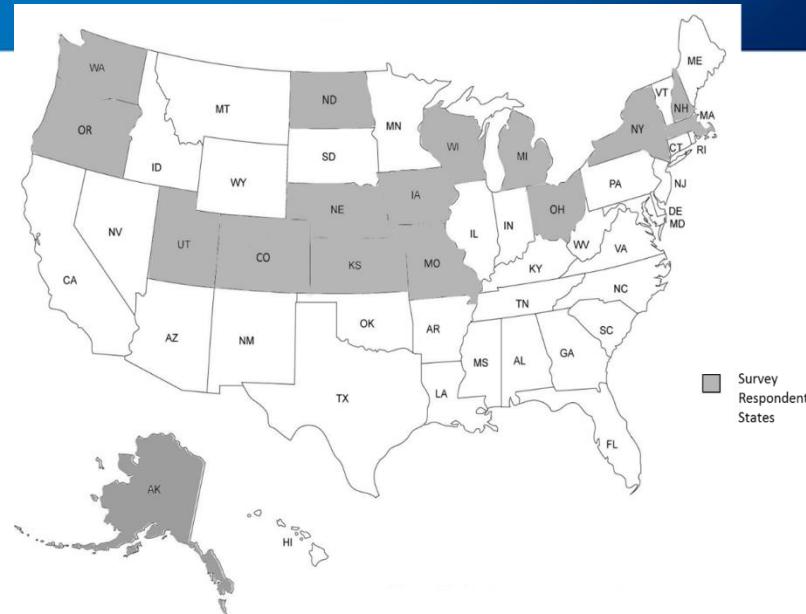
- The main composition of agro-based products:
 - desugared beet molasses,
 - corn by-products,
 - cheese brewing by-products,
 - beer brewing by-products,
 - succinate salts,
 - urea,
 - and starch.
- These products are either used alone or as additives with other winter maintenance chemicals to improve performance and/or to reduce corrosion and environmental impacts.
- An emerging class of liquid deicers features the blend of complex chlorides and naturally available mineral products.

Results – Literature Review

- Recent studies have shown improved performance from agro-based and naturally occurring chloride and non-chloride based products in snow and ice control operations.
- Additionally, studies have shown use of these products leads to reduced risk to highway infrastructure and the environment.
- At this time, limited research has been performed to examine the modes of action by which these products help in improving performance and reducing negative impacts on highway infrastructure and the environment.

Results – Survey

- 31 respondents from 16 states
- Summary of information from survey responses:
 - Some respondents prefer using non-chloride agro-based products at low temperatures (below 20°F).
 - Longevity on the road surface (or the residual effect) was one of the stated observed benefits of using agro-based products.
 - Improved performance at low temperatures and reduced material usage were common benefits observed by survey respondents when using CCM based products.
 - Limited research has been conducted by survey respondents on agro-based and CCM based products.



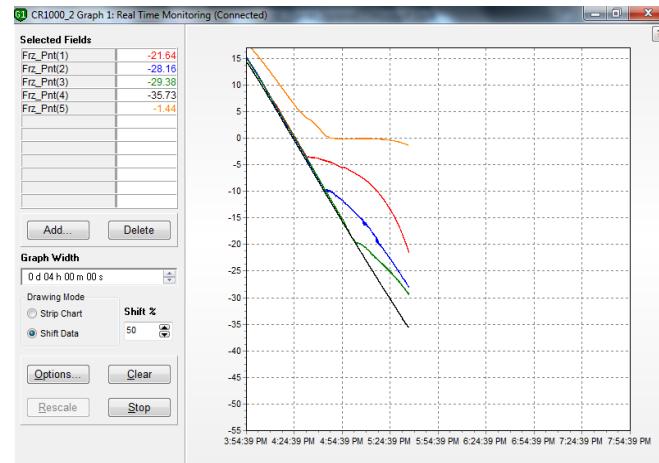
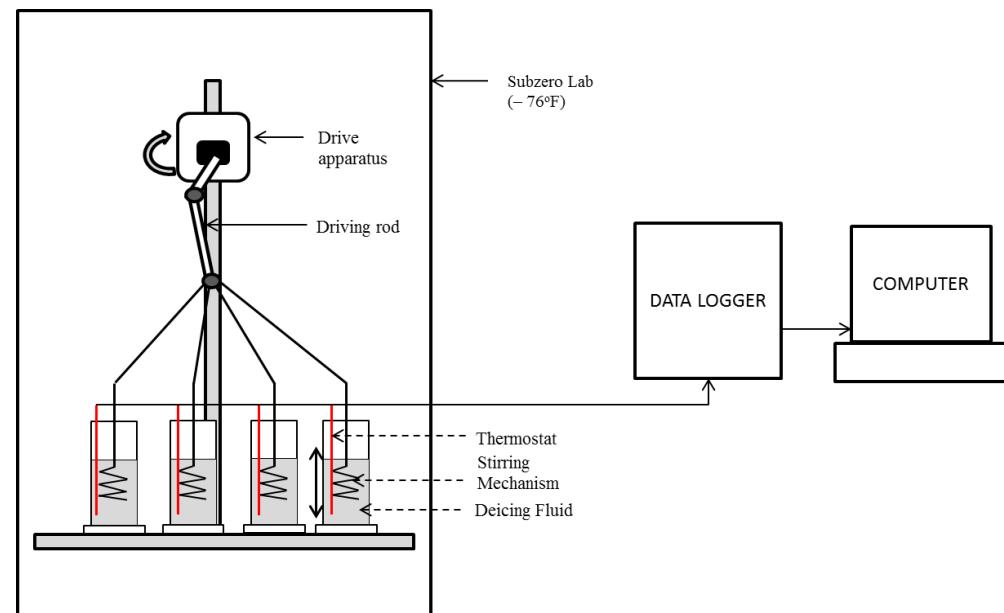
Products Selected for Testing

- **Category A:** solid complex chlorides/minerals (CCM) based products were used as-received for testing purposes.
 - Product A1 - *Ice Slicer*®;
 - Product A2 - *Thawrox*®
- **Category B:** Liquid agro-based deicers which were prepared by mixing the vendor-provided concentrates with a 23.3 wt. % NaCl aqueous solution, at either 70:30 or 80:20 volume ratio, depending on the vendor specification.
 - Product B1 - *Beet 55*®;
 - Product B2 - *Boost™ SB*;
 - Product B3 - *Snow Melt*®;
 - Product B4 - *Geomelt*® 55
- **Category C:** Liquid agro-based deicers which were used as-received from the manufacturer for testing purposes.
 - Product C1 - *Apogee™*;
 - Product C2 - *Boost™ CCB*;
 - Product C3 - *Ice Ban® 305*;
 - Product C4 - *ThermaPoint IB 7/93*

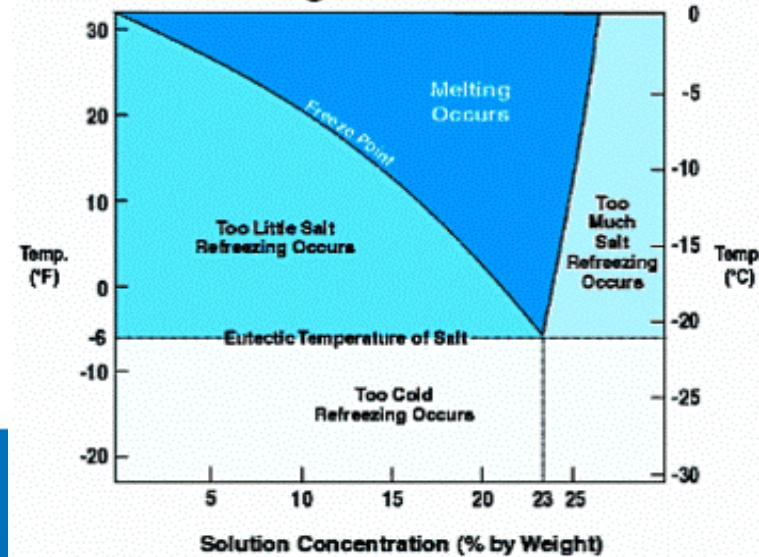
Product Name	Manufacturer	Major Components	% Added to salt brine*	Description	Reference	Chloride Concentration from Mohr's chemical titration method	
Ice Slicer®	Redmond Minerals, Inc	NaCl: 90-98%; Trace amounts of MgCl ₂ , KCl, CaCl ₂	As-Received	Blend of complex chlorides	MSDS	58.90%	Reagent grade NaCl, features a theoretical Cl content of 60.7%.
Thawrox®	North American Salt Company	NaCl: 60-100%; Thawrox Treated Salt Liquid Additive: 1-5%		Thawrox treated rock salt	MSDS	59.60%	
Beet 55	Smith Fertilizer and Grain	NaCl: 17.2%	30 (70% salt brine)	Beet based product	PNS Qualified product list: Category A3	0.25 M	Note: For 23.3% NaCl reagent grade would feature Cl content of 3.99 M
Boost™ SB	America West	NaCl: 18.8%; CaCl ₂ : 2.3%	20 (80% salt brine)	Molasses based product with salt brine	PNS Qualified product list: Category A2	0.62 M	
Snow Melt®	Smith Fertilizer and Grain	Glycerin: 15 - 20%; Polyether Polymer: 10 - 20%; Sodium Lactate: 4 - 10%; Sorbitol: 2-4%; Sodium Formate: 1 - 4%; 1, 2 - Butanediol: 1 - 4%	30 (70% salt brine)	Corn based product	MSDS	0.05 M	
Geomelt® 55	SNI Solutions	NaCl: 18.1%	30 (70% salt brine)	Beet based product	PNS Qualified product list: Category A3	0.55 M	
Apogee™	Envirotech Services, Inc.	Glycerin: % unknown (Proprietary)	As-Received	Glycerin based product	MSDS	1.05 M	
Boost™ CCB	America West	Molasses: % unknown CaCl ₂ : % unknown (Proprietary)		Molasses based product with CaCl ₂	MSDS	0.62 M	
Ice Ban® 305	GMCO	Ice Ban Concentrate: 10 - 20%; MgCl ₂ (30% Solution): 80 - 90%		Corn based product	MSDS	1.11 M	
ThermaPoint IB 7/93	Millennium Roads, Inc	CaCl ₂ : 93%; OBFE (Organic based performance enhancer (Proprietary)): 7%		Other (Lignin based)	MSDS	0.73 M	

Results – Laboratory Testing

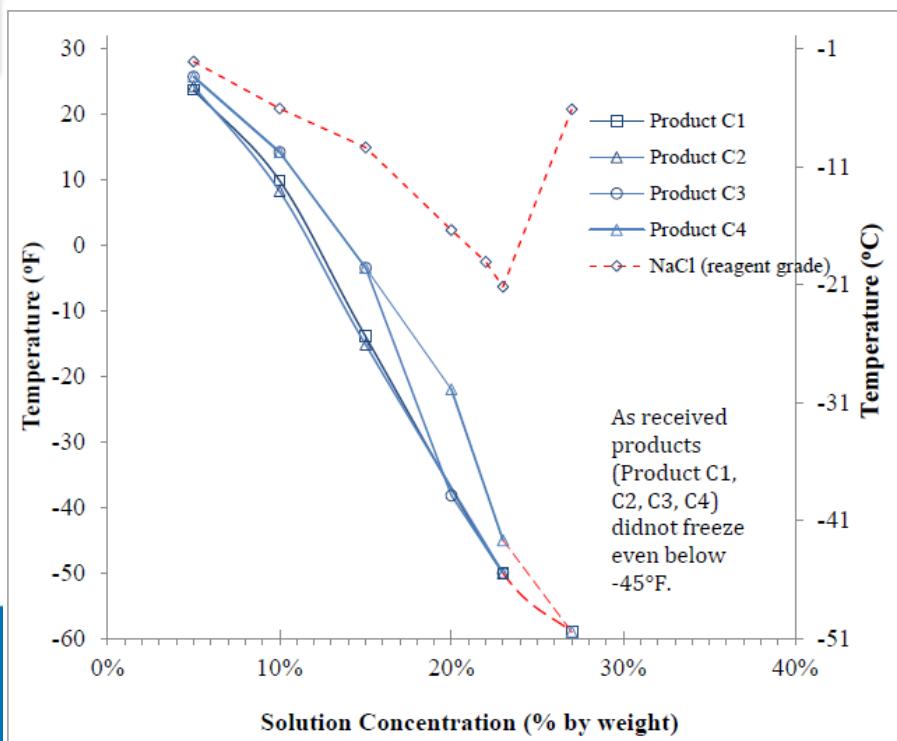
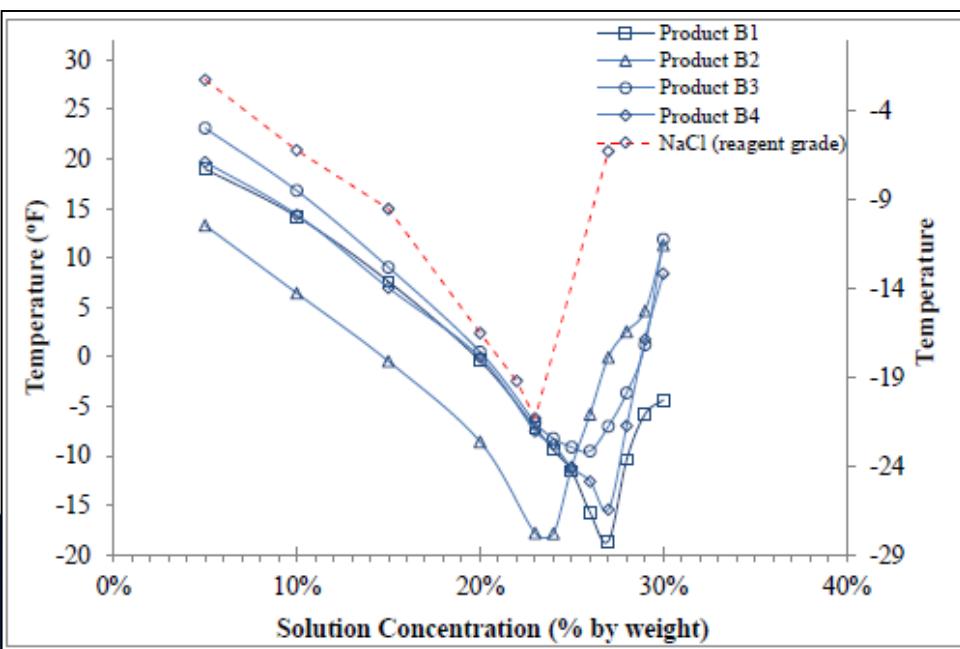
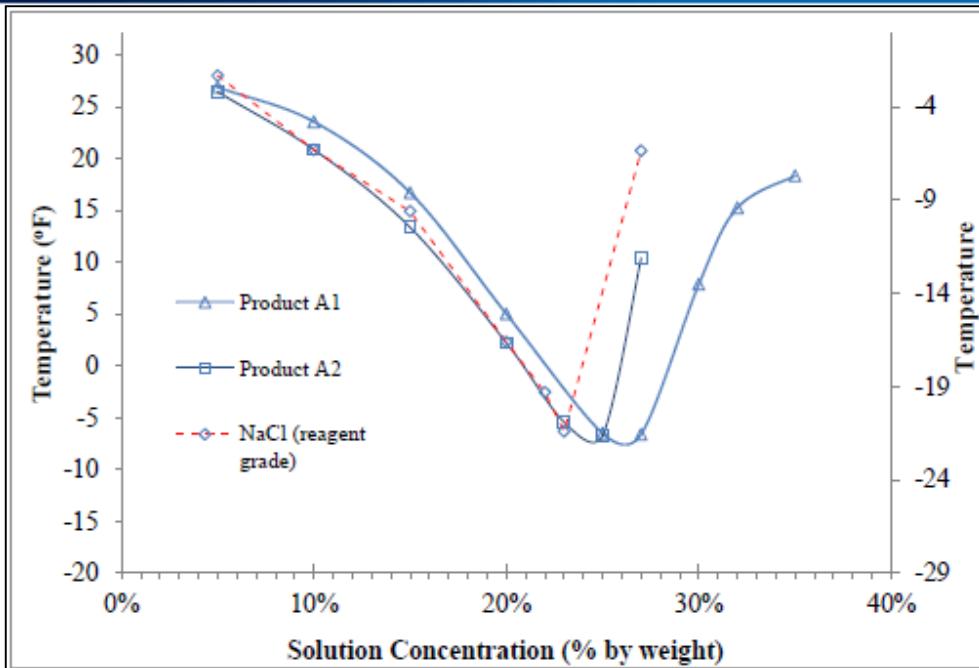
Lowering the freezing point of water



Phase Diagram for Salt



- Eutectic curves for all products tested.



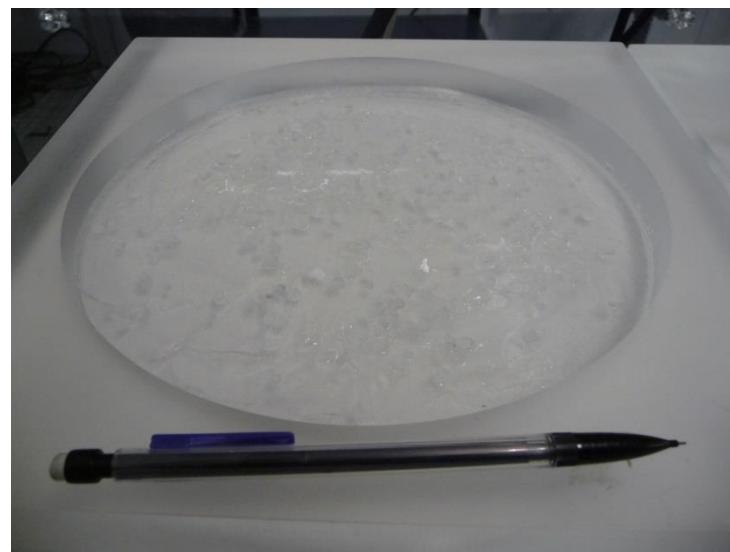
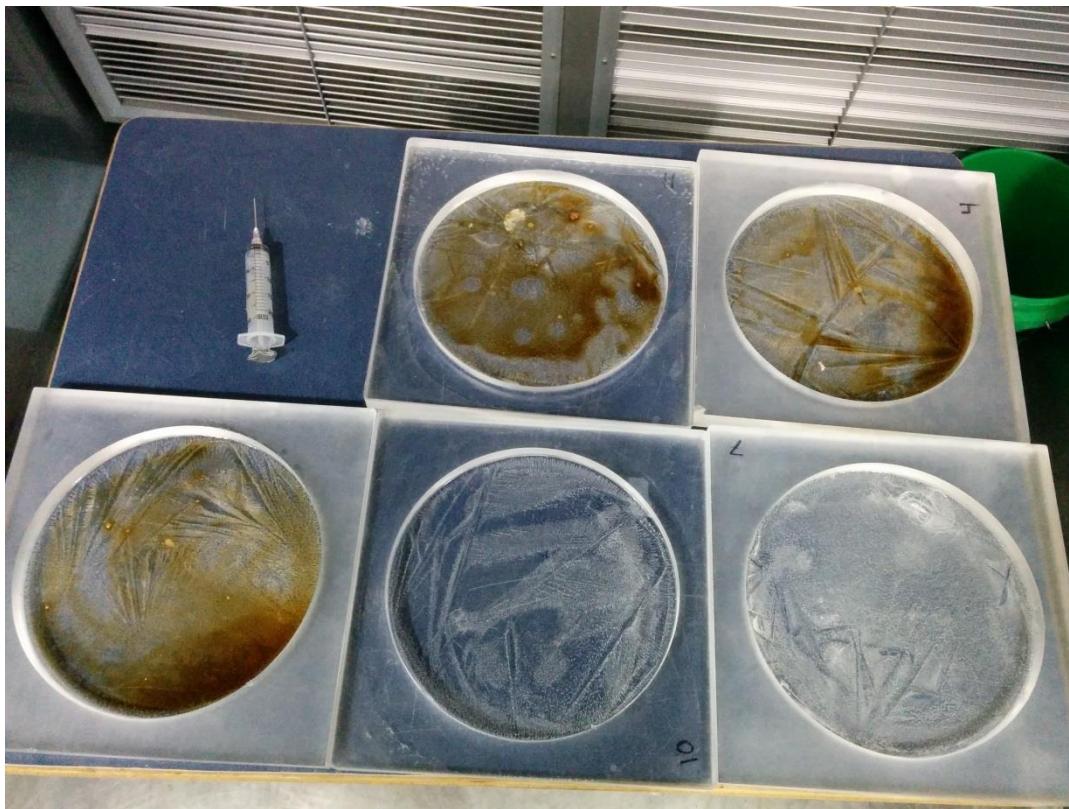
Results – Laboratory Testing

Lowering the freezing point of water

- CCM based products
 - Do not significantly reduce the freezing point of water compared to NaCl and did not produce more ice melt than the NaCl at 25°F and 5°F.
- Liquid agro-based products blended with 23.3% salt brine
 - significantly lowered the freezing point of water compared to NaCl
- Agro-based products (as-received)
 - significantly lowered the freezing point of water compared to NaCl and produced more ice melt than salt brine.
- Agro-based by-products acted as freezing point depressants (or cryoprotectants).

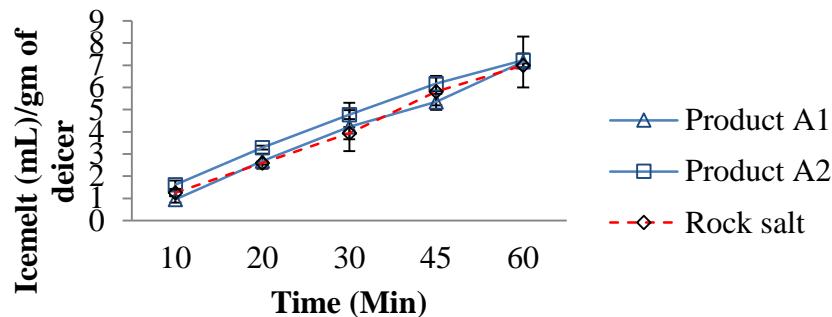
Results – Laboratory Testing

Improved ice melting capacity

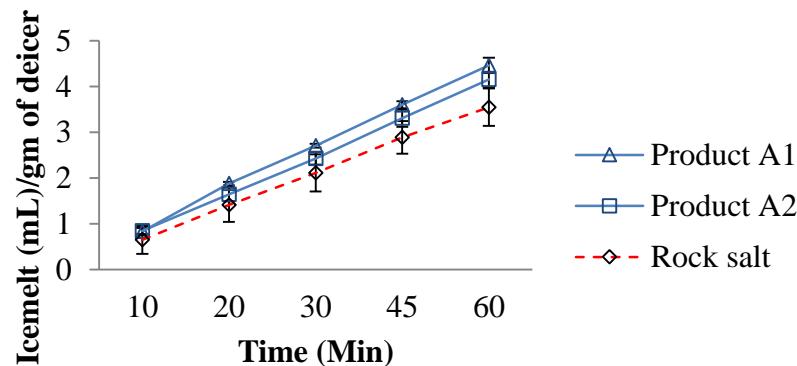


Ice Melting Test Results

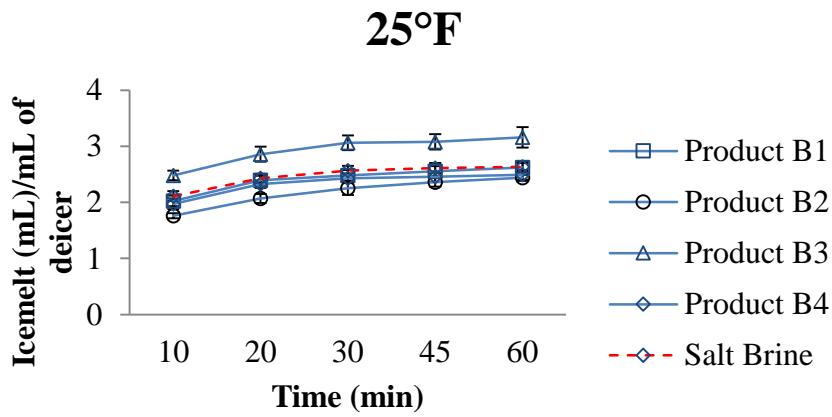
25°F



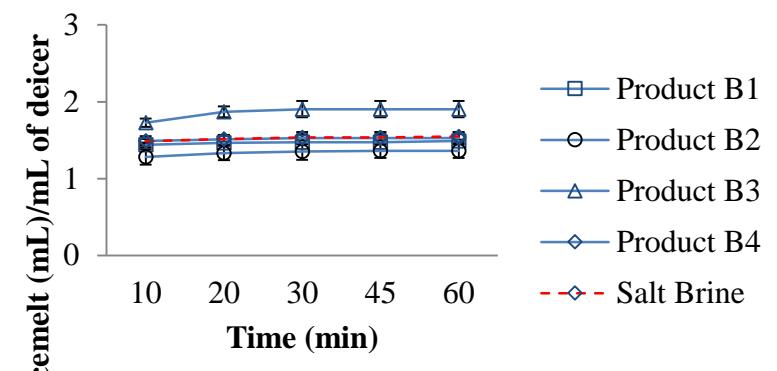
15°F



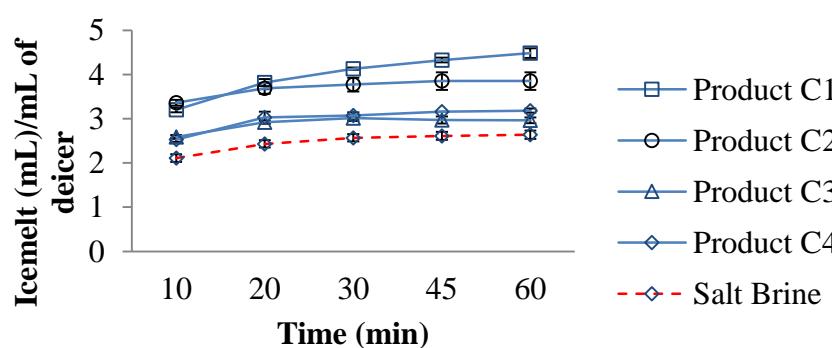
25°F



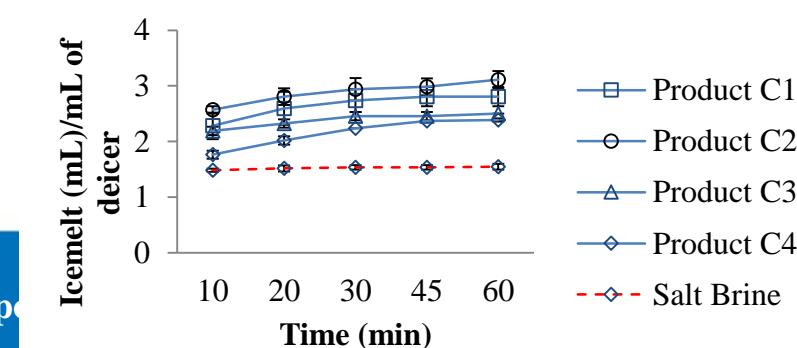
15°F



25°F



15°F



DSC Results

Product	Original State	Characteristic Temperature Peak		Enthalpy of fusion (J/g)		Eutectic Curve		Ice Melt		
		Average (°F)	COV	Average	COV	Eutectic Temperature °F	Eutectic Concentration (wt.%)	60 min @ 25°F	60 min @ 15°F	60 min @ 5°F
								(ml/g for solid, ml/ml for liquid)		
Product A1	Solid	28	20%	162.2	8%	-6.61	27%	7.15	4.46	1.53
Product A2	Solid	22.9	1%	89.4	4%	-6.70	25%	7.23	4.16	-
Product B1	Liquid	24.8	3%	138.7	3%	-18.64	27%	2.62	1.49	-
Product B2	Liquid	30.4	42%	156.1	7%	-17.86	24%	2.44	1.36	-
Product B3	Liquid	25.4	4%	136.1	6%	-9.52	26%	3.16	1.90	-
Product B4	Liquid	28.1	23%	176.1	4%	-15.43	27%	2.49	1.53	1.14
Product C1	Liquid	16.2	2%	120.9	6%	< 45	as-received	4.48	2.81	1.58
Product C2	Liquid	6.1	6%	124.6	4%	< 45	As Received	3.85	3.11	-
Product C3	Liquid	8.9	4%	161.1	10%	< 45	As Received	2.96	2.50	-
Product C4	Liquid	6.4	5%	131.5	6%	< 45	As Received	3.18	2.39	1.58
NaCl (reagent)	Solid	23.5	2%	197.7	3%	-6.34	23%	-	3.90	-
Rock salt	Solid	-	-	-	-	-	-	6.99	3.55	1.72
Salt Brine (Rock 23.3 wt%)	Liquid	-	-	-	-	-	-	2.64	1.55	1.10

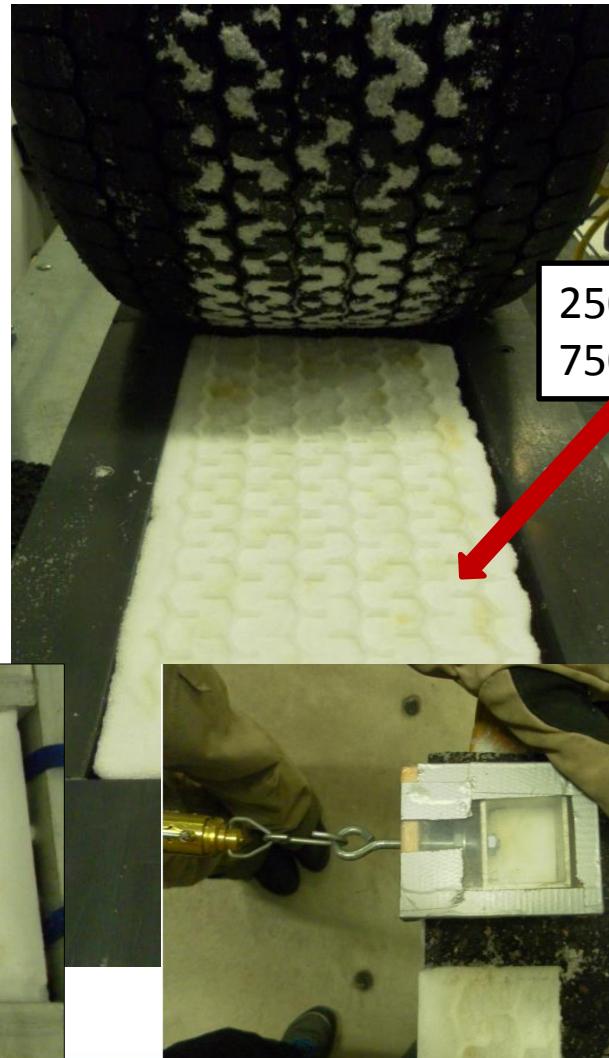
Results – Laboratory Testing

Improved the ice melting capacity

- CCM based products
 - produced more ice melt than the NaCl at 15°F
- Liquid agro-based products blended with 23.3% salt brine
 - did not produce more ice melt than salt brine (NaCl, liquid) alone at 25°F, 15°F and 5°F.
- Agro-based products (as-received)
 - Produced more ice melt than salt brine.
- Agro-based products exhibit significantly lower characteristic temperature.
 - This suggests that the amount of thermal energy corresponding to the aqueous brine solution's liquid/solid phase transition is reduced by the addition of agro-based by-products; making the agro-based by-products mixed with brine more difficult to freeze than salt brine alone.

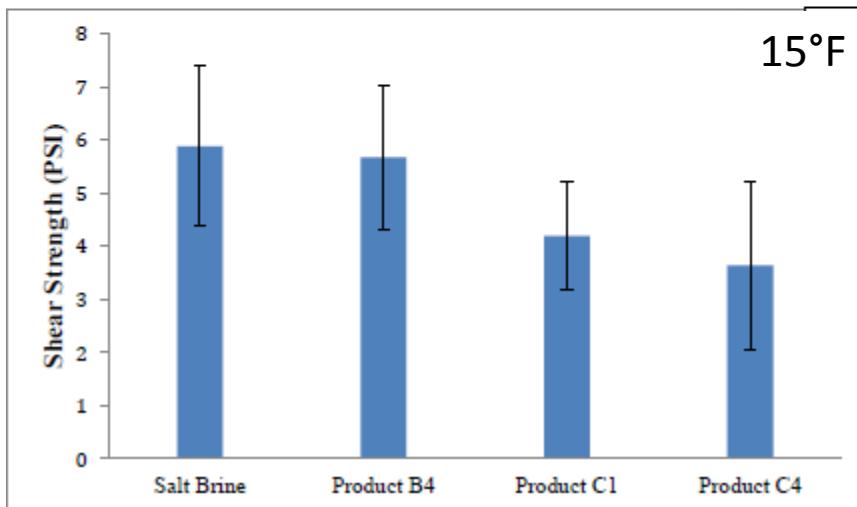
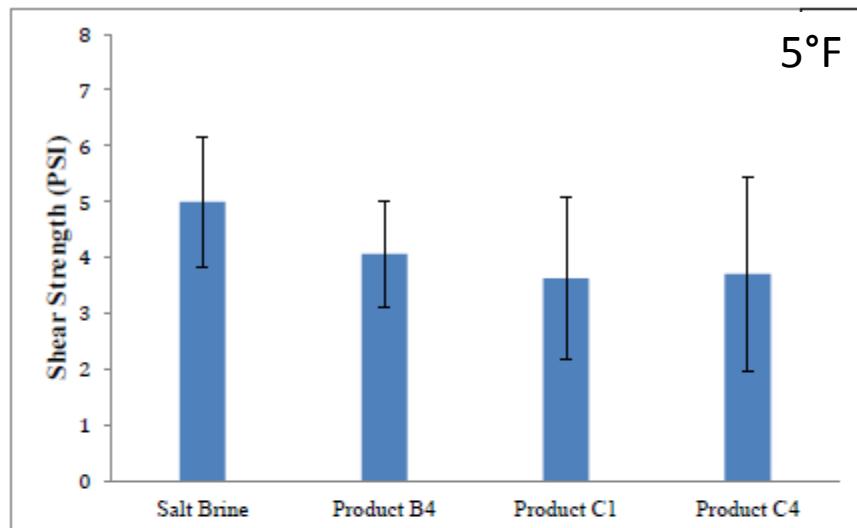
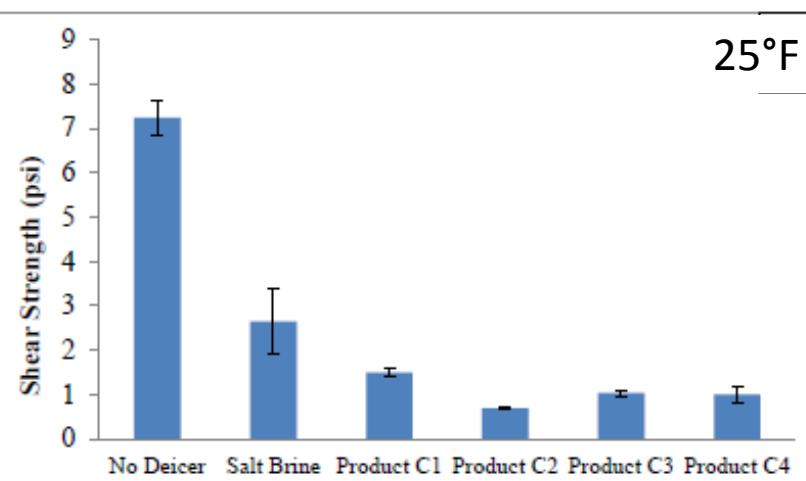
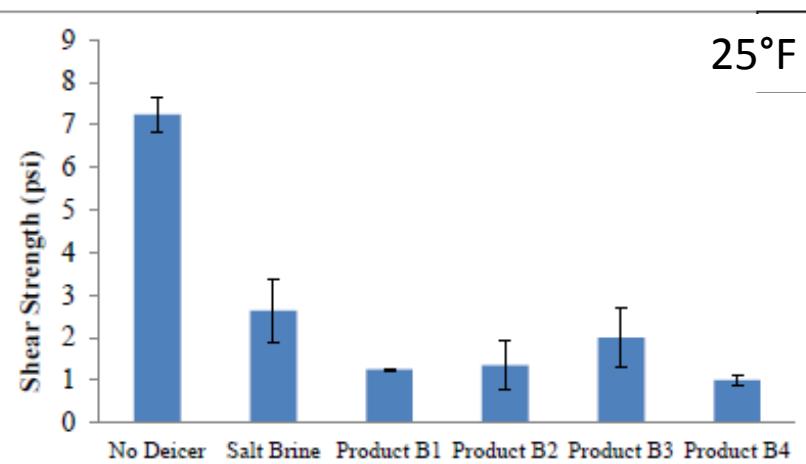
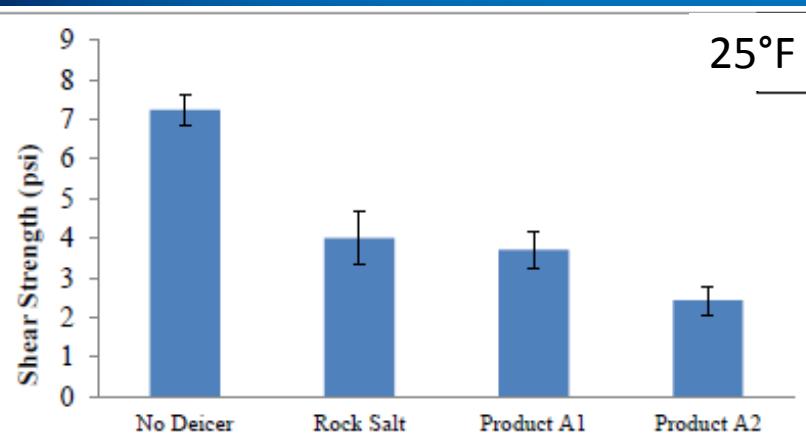
Results – Laboratory Testing

Weakening of ice bond to pavement



250, 500,
750 passes





Results – Laboratory Testing

Weakening of ice bond to pavement

Product	Concentration	Temperature	Viscosity (mm ² /s)	Specific Gravity
Product B4	70% salt brine and 30% agro-based concentrate	68°F	2.4	1.20
		25°F	5.5	1.21
		15°F	7.3	1.21
		5°F	9.2	1.21
Product C1	As-received	68°F	23.0	1.22
		25°F	102.9	1.23
		15°F	169.4	1.24
		5°F	283.1	1.24
Product C4	As-received	68°F	9.2	1.33
		25°F	16.4	1.33
		15°F	21.8	1.34
		5°F	25.5	1.34
Salt Brine	23%.wt of Rock salt	68°F	1.5	1.17
		25°F	2.8	1.18
		15°F	4.1	1.19
		5°F	4.6	1.19

- Product C1 was the most viscous, followed by product C4.

Results – Laboratory Testing

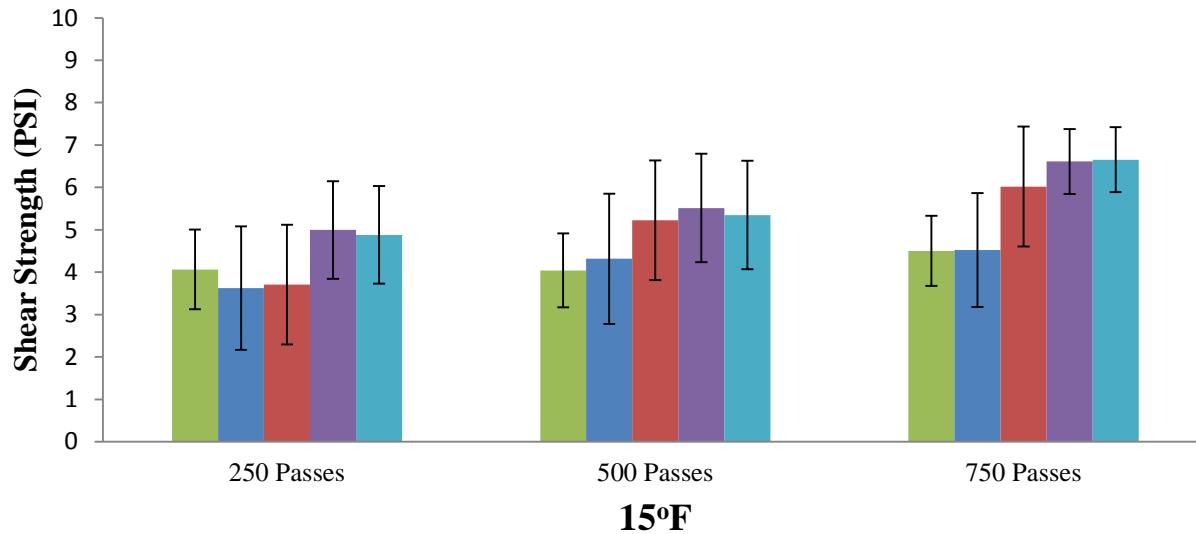
Weakening of ice bond to pavement

- CCM based products
 - bond strength between ice and pavement is slightly reduced compared to NaCl at 25°F and 15°F
- Agro-based products
 - bond strength between ice and pavement compared to salt brine (NaCl, liquid) was significantly reduces at 25°F, 15°F and 5°F when used as anti-icer.
 - the addition of agro-based products to salt brine increased the overall viscosity of the products.
 - agro-based products with higher viscosity than salt brine may have slower grain boundary penetration than the salt brine with lower viscosity.
 - This may result in more product spread on the pavement surface resulting in reduction in bond strength between ice and pavement surface.

Results – Laboratory Testing

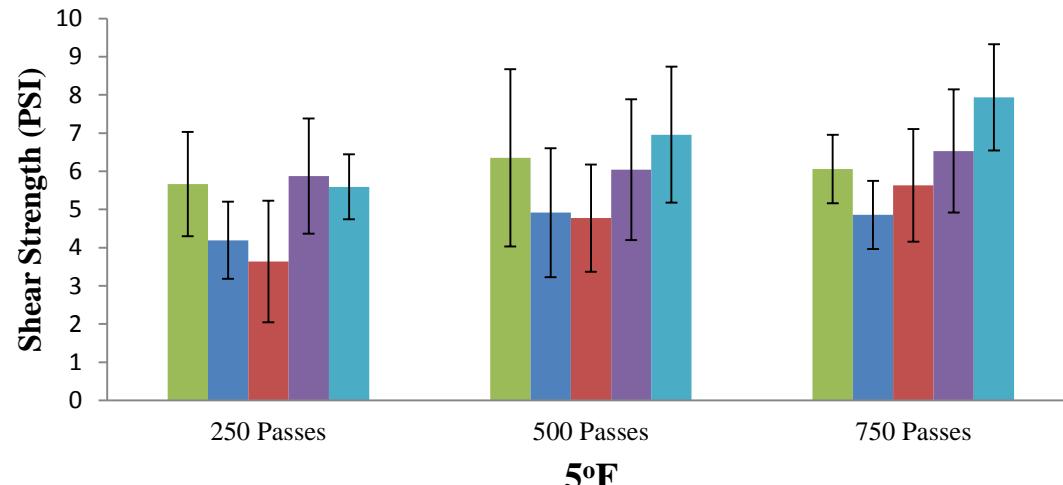
Improving product longevity on the pavement

■ Product B4 ■ Product C1 ■ Product C4 ■ Salt Brine ■ No product

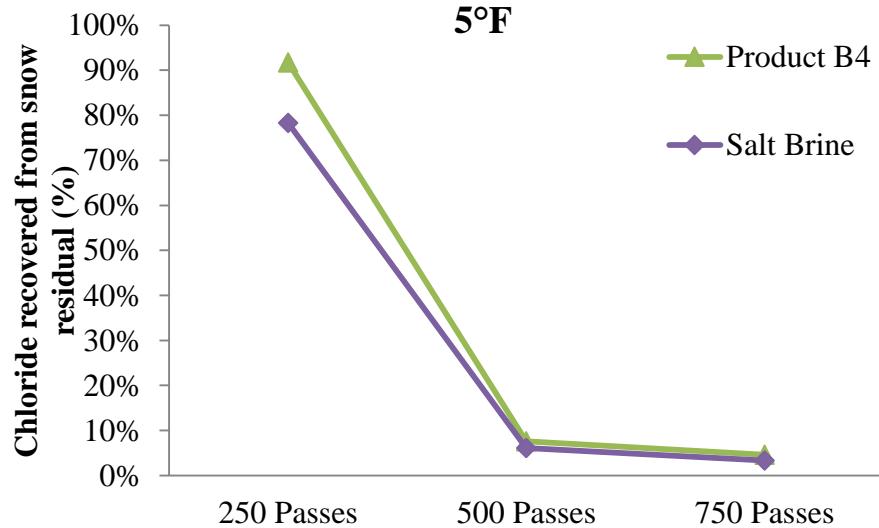
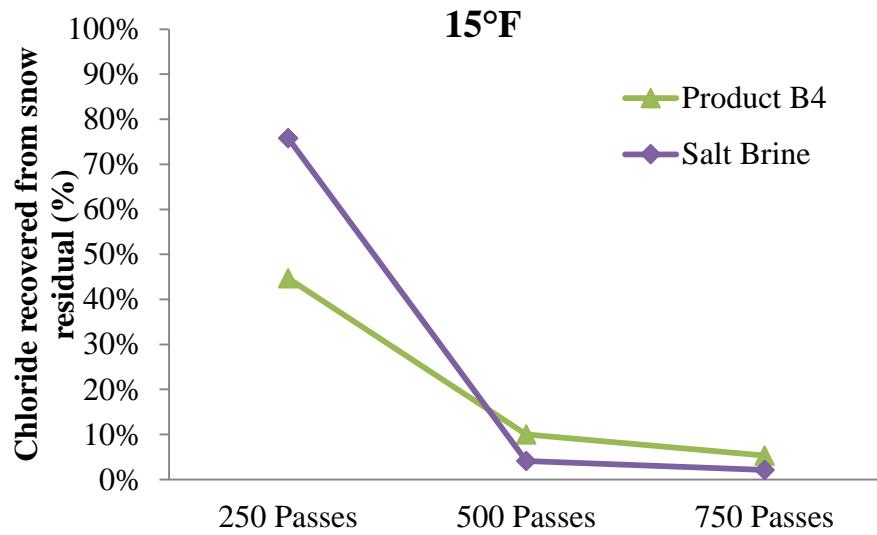


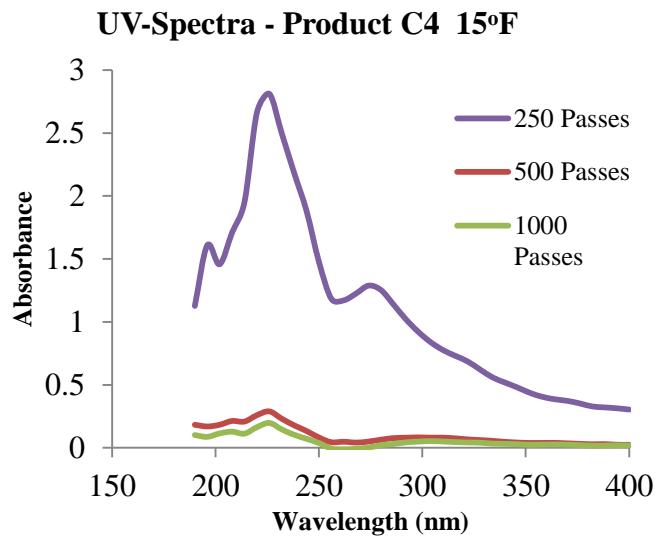
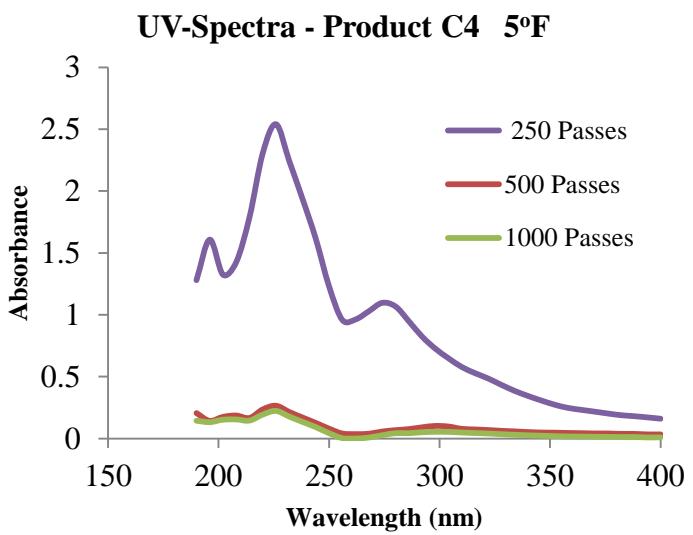
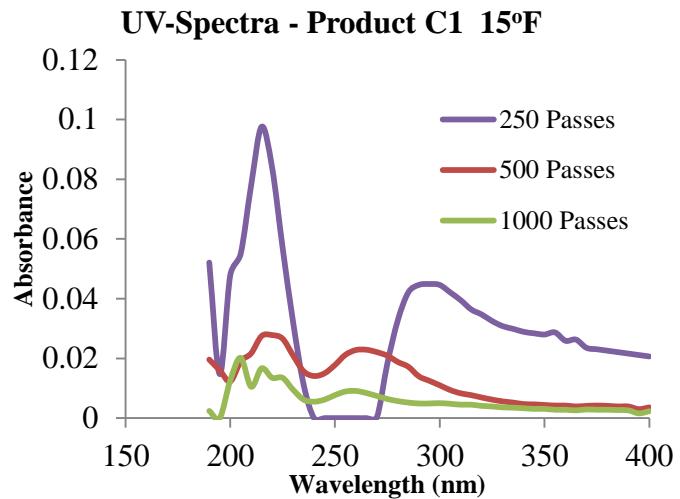
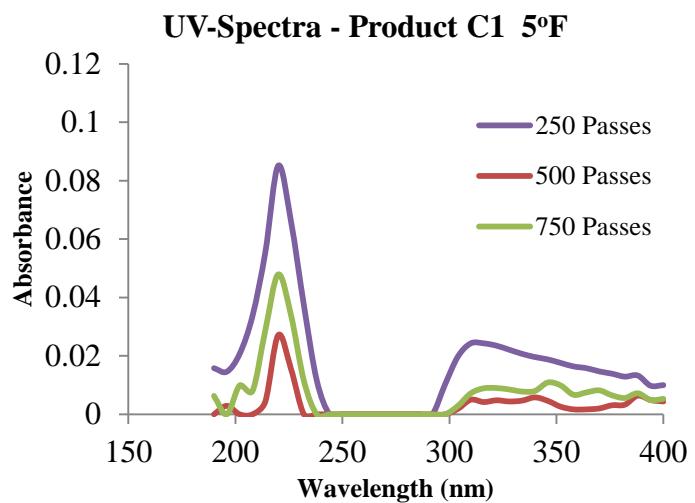
15°F

■ Product B4 ■ Product C1 ■ Product C4 ■ Salt Brine ■ No product



5°F





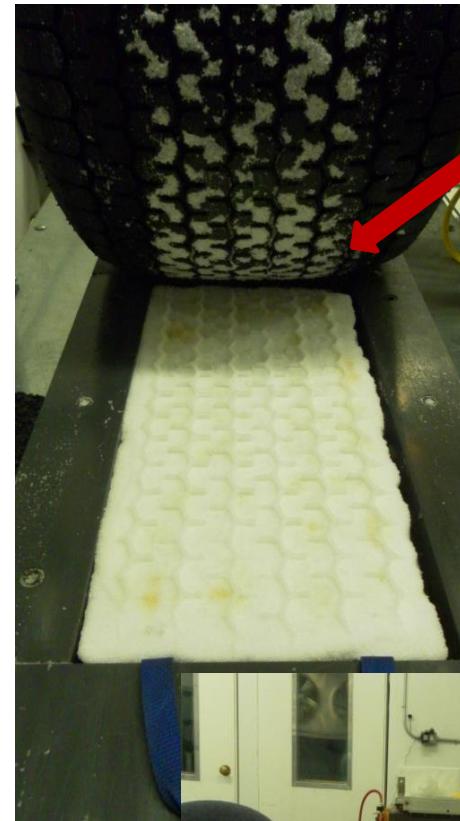
Results – Laboratory Testing

Improving product longevity on the pavement

- Agro-based products (B4, C1, C4) tend to stay on the road surface longer than salt brine.
- Longevity of the product on the road surface depends on the amount of product dissolved in to the snow before each cycle of plowing.
- Agro-based products tend to wick less into the snow when compared to salt brine when used as anti-icers.

Results – Laboratory Testing

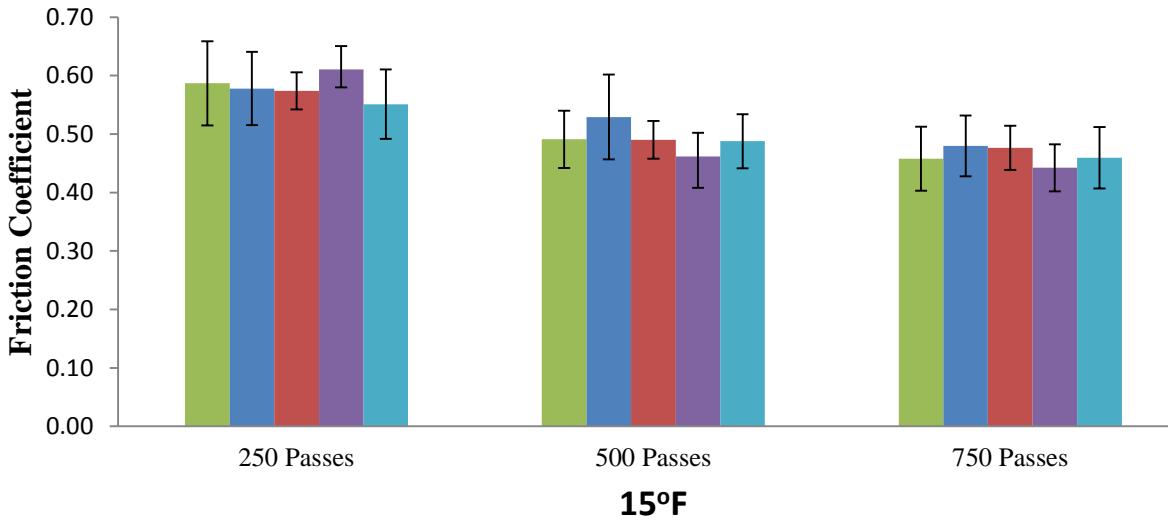
Prevention of ice formation/refreezing



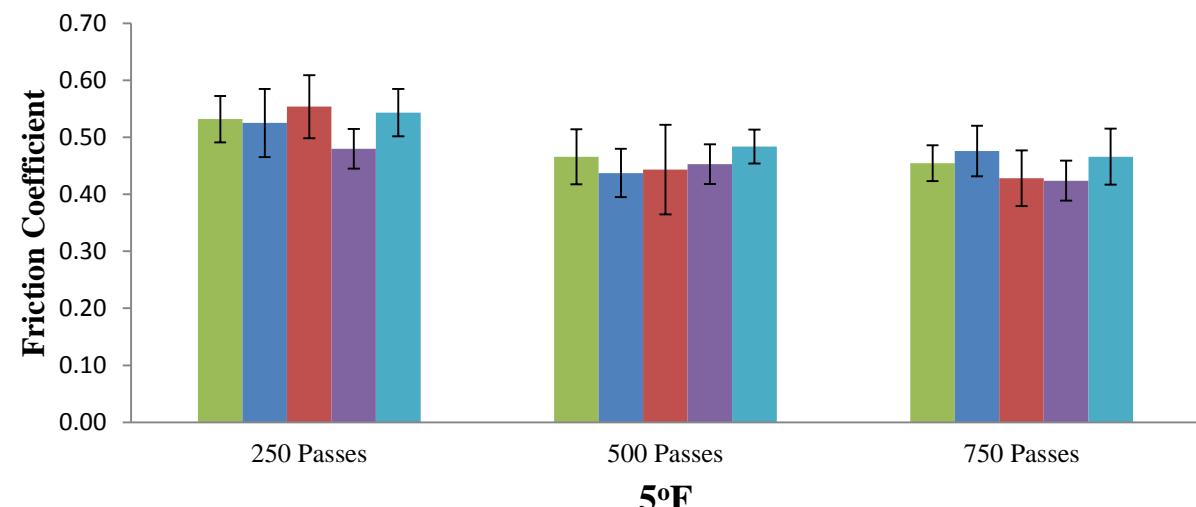
Results – Laboratory Testing

Prevention of ice formation/refreezing

■ Product B4 ■ Product C1 ■ Product C4 ■ Salt Brine ■ No product



■ Product B4 ■ Product C1 ■ Product C4 ■ Salt Brine ■ No product



MONTANA
STATE UNIVERSITY

College of
ENGINEERING

Results – Laboratory Testing

Prevention of ice formation/refreezing

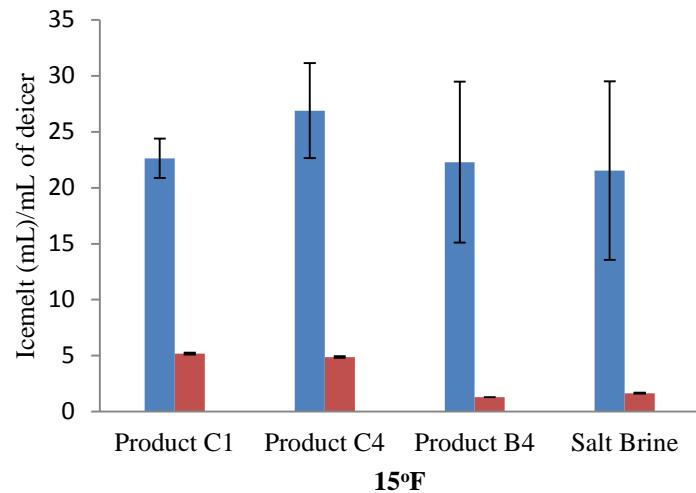
- Agro-based products (B1, C1, C4) tend to have better friction values during extreme cold snow events (around 5°F) and during repeated warm snow events (25°F and 15°F).
- Agro-based products act as ice crystal nucleation point inhibitors, delaying the formation of ice compared to salt brine.
 - Cryoprotectants are substances that prevent ice nucleation.
 - The agro-based products significantly reduce the freezing point of water, therefore could act as cryoprotectants, delaying the freezing point of water.

Results – Laboratory Testing

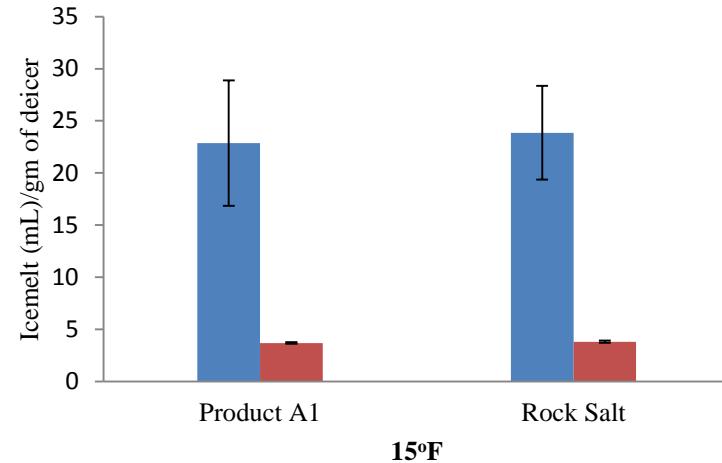
Absorbance of sunlight



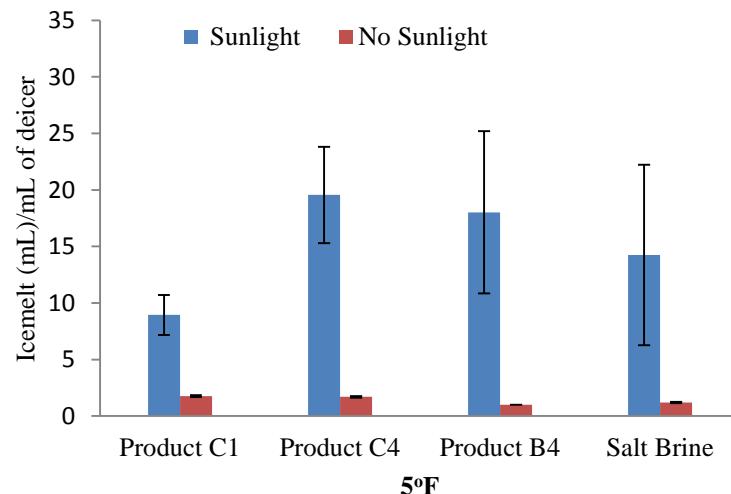
■ Sunlight ■ No Sunlight



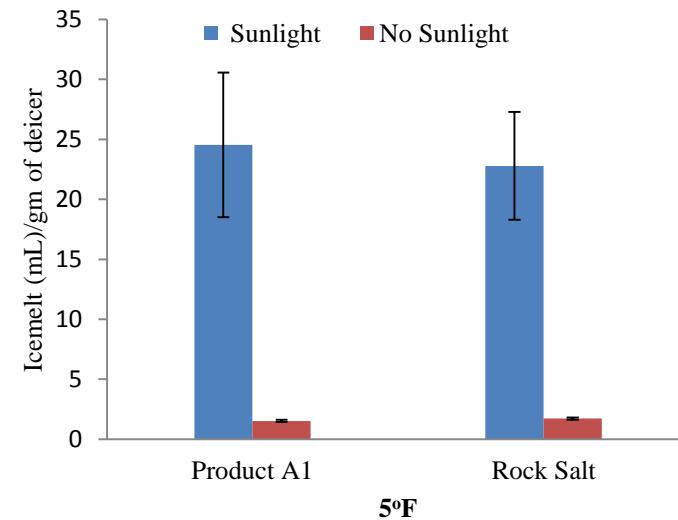
■ Sunlight ■ No Sunlight



■ Sunlight ■ No Sunlight



■ Sunlight ■ No Sunlight



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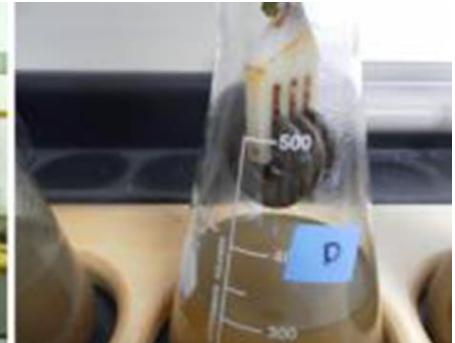
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Results – Laboratory Testing

Absorbance of sunlight

- For CCM (A1) based products, at higher intensity sunlight, ice melting capacity was similar irrespective of the product type at 15°F and 5°F.
- For CCM (A1) based products, at medium intensity sunlight, ice melting capacity of CCM based product is slightly higher than NaCl at 15°F and 5°F.
- For agro-based products (B4, C1, C4), at higher intensity sunlight, ice melting capacity was similar irrespective of the product type at 15°F and 5°F.
- At colder temperatures, darker colored agro-based products had higher ice melting capacity than lighter color agro-based products and salt brine.

Results - Corrosion



Results - Corrosion

Deicer	Original state	PNS Dipping Test		Electrochemical Test		
		Average Corrosion Rate (MPY)	Percentage Corrosion Rate (%)	E_{corr} (mV, SCE)	I_{corr} ($\mu\text{A}/\text{cm}^2$)	Average Corrosion Rate (MPY)
3% Product A1	Solid	50.5	82.0	-683.0	7.2	32.8
3% Product A2	Solid	46.2	74.1	-709.0	8.3	37.8
3% Product B1	Liquid	42.8	80.2	-508.0	5.4	24.6
3% Product B2	Liquid	15.1	30.8	-656.0	8.5	38.8
3% Product B3	Liquid	20.3	34.0	-704.0	7.6	34.7
3% Product B4	Liquid	29.5	52.9	-638.0	11.3	51.5
3% Product C1	Liquid	16.8	31.2	-556.0	6.3	28.7
3% Product C2	Liquid	18.1	38.7	-521.0	4.5	20.5
3% Product C3	Liquid	21.2	45.4	-685.0	8.9	40.6
3% Product C4	Liquid	14.3	30.6	-524.0	5.5	26.2
3% NaCl	Solid	56.3	100	-751.0	12.8	58.4
DI Water	Liquid	5.0	0	-	-	-

Results - Corrosion

- The PNS dipping test revealed that the CCM deicers feature slightly lower corrosivity to carbon steel than solid 3% NaCl control.
- Most agro-based deicers in both category B and category C (except product B1) feature much lower corrosivity to carbon steel than both solid NaCl and 23.3% NaCl brine controls.

Best Practices Manual

- Developed based on the results from laboratory investigation and literature review.
- Components of the best practices manual include:
 - summary of findings from laboratory testing already presented
 - storage guidelines,
 - material handling and loading,
 - storage and mixing,
 - brine production equipment,
 - application methods and guidelines,
 - anti-icing and direct liquid application,
 - and identified issues with agro-based products.



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Best Practices – Material Handling and Loading

- Loading trucks with buckets that are too large can lead to loss of material.
 - Smaller buckets can be used to avoid this but may increase load times.
- Loading equipment should have a way to track the quantities loaded.



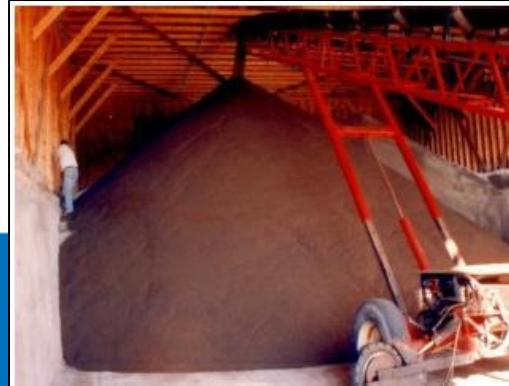
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Best Practices – Storage and Mixing

- Use blending ratios that work!
 - Either vendor recommended blending ratios,
 - Or if deviating from these have a good reason (track it, study it, identify what worked and what did not).
- Blending materials on the apron is not recommended – inaccurate and inefficient.
 - Instead used metered supply lines to blend at the pile or on the truck.



Best Practices – Solids Storage Guidelines

- Solid material should be stored on an impervious surface and covered.
- Storage facility should be design to:
 - accommodate typical runoff
 - Provide sufficient space for indoor loading and unloading
 - Consider prevailing wind direction to limit snow drifts and precipitation indoors
- Storage areas should be routinely:
 - Inspected and maintained
 - Kept clean and orderly
 - Well labeled



Best Practices – Liquid Storage Guidelines

- All liquids should have secondary containment.
 - Double walled tanks will not protect against broken fittings or hoses.
 - Indoor tanks should have a berm at all ground level exits to prevent loss of liquids.
 - Consult with local environmental regulators regarding siting and containment requirements.
- To avoid spills routine inspection and maintenance should be performed.
- Spills should be captured, cleaned up, and disposed of as soon as is possible.



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Best Practices – Application Methods and Guidelines

- Recommended practices include:
 - Pre-wetting,
 - slurry/high ratio pre-wetting,
 - anti-icing
 - direct liquid application.
- Reduces loss of solid material to bounce and scatter.
- Keeps product on the road longer.
- Product activates quicker.

Best Practices – Identified Issues with Agro-based Products

- Road slickness has been reported
 - avoid over application which may cause this.
- Clogging of spray equipment
 - Flush system with water between use of various products, agitate or stir products periodically if stored for long periods.
- Bacterial growth
 - Some products have inhibitors to prevent this, products may have a shelf life, and proper long term storage may be needed (no sun exposure, cool temperatures, periodic mixing, etc.)
- Attractant to wildlife on roadways
 - Additional research is needed to confirm this.

Thank you!

Questions?

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research for winter highway maintenance

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