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Field Usage of Alternative Deicers for Snow and Ice Control

Prepared by The Western Transportation Institute

Introduction

In the last two decades, potassium acetate (KAc), sodium acetate (NaAc), potassium formate (KFm), and sodium formate (NaFm) have gradually replaced urea as the freezing-point depressant in airport pavement deicing products (Shi 2008). (Urea imparts relatively large impacts on the environment. For this reason we will not include urea in this discussion of non-chloride deicers for use in roadway winter maintenance operations.) Additionally, the use of non-chloride based deicers and anti-icers have become more common in roadway winter maintenance operations due to the impacts that chloride based deicers exert on infrastructure and the environment. For example, acetates are commonly used to deice bridge decks as a part of FAST (Fixed Automated Spray Technology) systems that are remotely triggered by temperature sensors, and in some states acetates are used in designated no salt zones. While non-chloride based deicers are used on roadways, they have not been employed as extensively as they are at airports for many reasons, including higher cost, impacts to various pavement and metal types, environmental impacts, and runoff capture and treatment requirements.

Other non-chloride based deicers available include glycol based products and succinate based deicers. Glycols are commonly used at airports, but generally speaking all of these are less commonly used, if at all in roadway winter maintenance. Yet, these deicers could be viable options for roadway winter maintenance operations if the cost, ease of application, and impacts to infrastructure and environment can be justified, as compared to chloride based deicers.

This Transportation Research Synthesis (TRS) summarizes non-chloride based deicers available on the market at this time, including acetate, formate, glycol, and succinate based deicing products. This report explores their feasibility for use as alternatives to chloride based deicers, and identifies next steps to determine if a non-chloride based deicer is a viable option for implementation in winter maintenance operations by the Minnesota Department of Transportation (MnDOT) and local snow and ice removal providers.

Summary Methods

An extensive literature review was conducted targeting information on non-chloride deicers for use in snow and ice control operations, the feasibility of using of these products in Minnesota, information on functional temperature range and cost for each identified product, and information on known impacts to infrastructure and the environment imparted by these products. A summary of the literature review findings can be found in the next section, and the detailed literature review can be found in Appendix A, followed by the references.

An agency survey was then administered to state department of transportation (DOT) winter maintenance personnel, specifically those in Minnesota and snow belt states, to gain information on the use of non-chloride deicers. A second product manufacturer/vendor survey was sent to companies known to make and or sell non-chloride deicers. A summary of the survey findings can be found in the next section. The detailed survey responses from agencies and manufacturers can be found in Appendix B and the survey questionnaires can be found in Appendix C. Follow-up interviews were conducted as needed to gain additional information from survey respondents and from individuals, agencies, and organizations identified in the literature review process. Information gained from these follow-up conversations has been added to the relevant sections in this document.

This Transportation Research Synthesis summarizes all pertinent information gained in the research process.

Literature Review

Acetate and formate deicers and anti-icers have not changed much in the last decade, and there are many of these products on the market in both liquid and solid form. They are good quality deicing products with low corrosivity compared to chlorides, but they do exert impacts to concrete and asphalt, and cause elevated Biochemical Oxygen Demand (BOD) in waterways. Additionally, these products are significantly more expensive than chloride based deicers, but the additional cost may be justified in specific locations to protect infrastructure or where chloride loading to the environment has led to impacts.

Glycols are considered a newer deicing technology for roadway winter maintenance, but have been used at airports for some time, and there are a few products available on the market specifically formulated for use on roads. These products work very well in cold climates, but have been shown to have elevated toxicity to aquatic species. These products cost significantly more than chlorides, but their use may be justified in specific locations to increase safety and reduce impacts to infrastructure compared to other products.

Succinates are considered a newer deicing technology that is currently marketed primarily towards use at airports, due to the extremely low corrosivity compared to chlorides, acetates, and formates. The viability of using potassium succinate (KSu) as a roadway deicer is unknown but shows promise. There is a company (BioAmber) working toward producing KSu as a roadway deicer. The cost of KSu is expected to be comparable to formates, which is significantly more than the cost of chlorides. Impacts caused by succinates are limited to elevated BOD, similar to that of formates and acetates. Contrary to acetates and formates, succinates are a non-corrosive option for all pavement and metal types, instead functioning as a corrosion inhibitor. For this reason the higher cost and BOD impacts maybe justifiable in specific locations where corrosion is a primary concern or where chloride loading to the environment has led to impacts.

By switching from chloride based deicers to acetates, formates, glycols, glycerols, or succinates, there is a shift in the conversation of potential impacts. Chloride and sodium (from sodium chloride (NaCl), or magnesium choride ($MgCl_2$), or calcium chloride ($CaCl_2$)) are conservative, which means they do not break down beyond these chemical elements, and can accumulate over time, posing risks to human health, water quality, aquatic flora and fauna, as well as the near road environment. The alternative non-chloride deicers do not accumulate in the environment but exert a higher BOD as they are broken down in the environment, and some of these products are toxic to aquatic species.

The consideration of the tradeoff of impacts from using chloride based deicers to non-chloride deicers should consider the impacts of elevated BOD. The temporary impact of elevated BOD from the breakdown of the non-chloride deicers will likely have limited, to no long-term impacts on water quality and aquatic species. However, products that exert a higher BOD or that are used in significant quantities may cause extremely high BOD (acute exposure) or high BOD values for extended periods of time (chronic exposure). In these instances, these products have the potential to have serious impacts on water quality and aquatic species.

Table provides a high-level summary of the non-chloride deicers under consideration, providing information on functional temperature range, relative cost, relative toxicity, and impacts to the environment and infrastructure. Based on this table, there are no clear “stand out” deicers that are a best-case alternative to chloride base deicers, but acetates appear to be the most moderate option because of function temperature range, moderate cost and impacts. However, the succinate-based products deserve consideration based on their potentially equal or similar performance to acetates and formats. Additional testing of KSu is recommended to confirm the findings reported in the BioAmber patent and to determine additional information such as relative performance for KSu compared to typical deicers.

Table 1. Summary of non-chloride deicer working temperature range, relative cost and toxicity, key environmental impacts, and known impacts to infrastructure. Boxes highlighted in orange are rated high which is this case is negative.

Deicer Type	Lower Functional Temperature	Relative Cost	Relative Toxicity	Environmental Impacts	Infrastructure Impacts
Chlorides	NaCl: 15°F $MgCl_2$: -5°F $CaCl_2$: -15°F	Low	High	Accumulate in the environment. Impact water quality, aquatic and terrestrial flora and fauna.	Pavements and metals
Acetates	KAc: -26°F NaAc: 0°F CMA: 0°F	Moderate	Moderate	Moderate BOD	Pavements and galvanized steel
Formates	NaFm: 0°F KFm: -20°F	High	Moderate	Moderate BOD	Pavements and galvanized steel
Glycols	-20°F	Moderate	High	High BOD	Limited
Succinates	-4°F (unknown)	High (Unknown)	Moderate	Moderate BOD	None known

Survey Results

Among survey respondents, acetates are the most commonly used non-chloride deicer. They are used in many winter weather conditions (such as snow, sleet, and ice) and in a wide range of temperatures (0 to 40°F) [We assume from 32ºF to 40ºF the products are used to prevent ice formation, such as anti-icing]. Respondents indicated that non-chloride deicing products are used in typical winter maintenance operations and in fixed automated technologies on roads and bridges. Typical application rates were similar to application rates used for anti-icing. Prices for liquid non-chloride products ranged from $3.75 to $5.00 per gallon, including delivery costs. These products require special storage, handling, application, and equipment, such as separate storage tanks, mixing the product before use if stored over summer, and using automated spray systems to apply the product.

Limited useful information was gained from the vendor/manufacturer survey. The companies stated that they are happy and willing to work directly with the DOT to determine product cost and shipping rates for their products.

Next-Steps

To move forward beyond the recommendations made in this TRS, the Center for Environmentally Sustainable Transportation in Cold Climates (CESTiCC) University Transportation Center (UTC) is sponsoring laboratory testing of the KSu deicing product. The Western Transportation Institute (WTI) is conducting the research at Montana State University (MSU) in the Sub Zero Facility. This research project will evaluate the feasibility of KSu performance as a snow and ice control product for roadways. Based on the recommendation in this TRS, the research effort will include ice melting tests, determination of eutectic curve, DSC (thermo-graphing) for the KSu product, as well as product performance testing comparing KSu, Acetate-based deicer (likely potassium acetate (KAc)), and salt brine (NaCl).

Appendix A – Detailed Literature Review

Acetates

Commonly used acetate based deicers include potassium acetate (KAc), sodium acetate (NaAc), and calcium magnesium acetate (CMA). Potassium acetate (KAc) is an attractive alternative to chlorides because it is has a low effective temperature, is less corrosive to metals than salts, and imparts minimal impacts on surrounding soils and ecosystems. However, some of the disadvantages include higher cost, corrosivity to galvanized steel, and damaging impacts on concrete and asphalt pavements (Fay et al. 2008, Shi 2008, Shi et al. 2009). Acetate based deicers are predominantly used to deice airport pavements and in selected areas such as highway bridges where corrosion to metal is a primary concern (Shi 2008, Gerbino-Bevins 2011). A summary of information on acetate based deicers can be found in Table 1.

Relative Performance Compared to Chlorides

KAc was found to produce more ice melt and to be effective at very low temperatures compared to chloride based products. Fischel (2001) reported that KAc (CF7®) has a eutectic temperature of -72°F and effective temperature of about -26°F. A recent study conducted by Xie et al. (2016) compared the ice-melting capacities of sodium chloride (NaCl) and KAc using SHRP ice melting test methods at about -25°F. The study found that KAc exhibited a higher melting capacity than NaCl. The volume of ice melt increased from 0.2 to 1.4 mL for KAc, whereas for NaCl ice melt only increased from 0 to 0.8 mL in 60 minutes as shown in Figure 1 (Xie et al. 2016). Similarly, Gerbino-Bevins (2011) compared the performance of KAc and NaCl using the Shaker Test and found that KAc melted about twice as much ice as NaCl at 20°F and almost three times as much at 10°F.

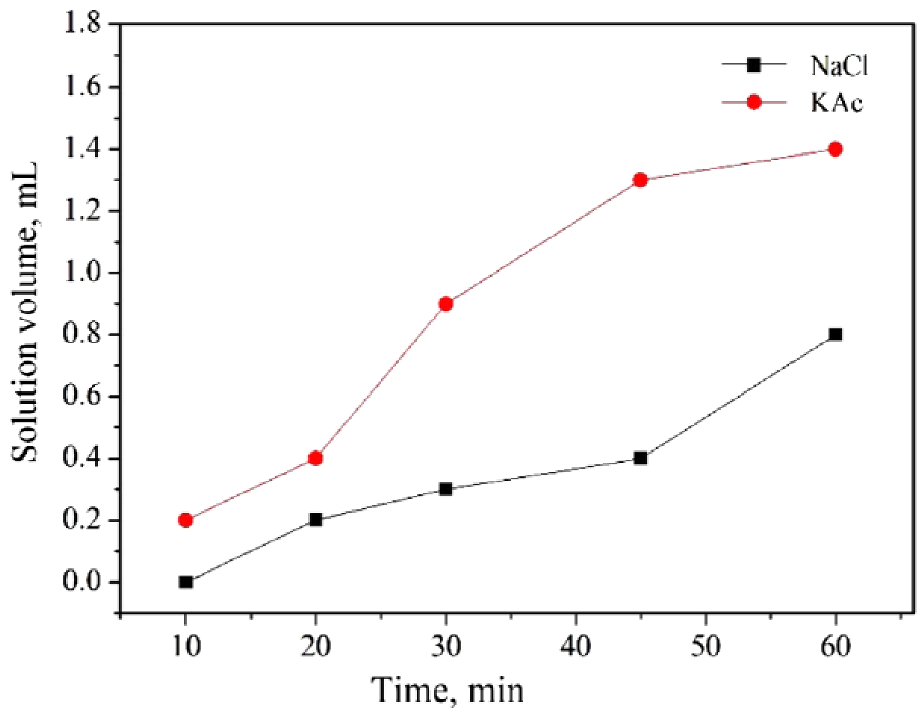

Figure 1: Laboratory testing results of the deicing capabilities of NaCl and KAc deicers at about -25°F (Xie et al. 2016)

CMA works similarly to NaCl, yet it can require 30-50% more product by weight than NaCl to achieve the same results (Wegner and Yaggi, 2001), especially as temperatures drop below 20°F (Fay et al., 2015). Relative to NaCl, CMA is "slower acting and less effective in freezing rain, drier snowstorms, and light-traffic conditions" (Ramakrishna and Viraraghavan, 2005) and performs poorly in thick accumulations of snow and ice (Fay et al. 2015).

Cost

In general, acetate based deicers are very expensive compared to chloride based deicers. Fischel (2001) reported that NaCl prices range from about $32 to $150/ton (Minnesota: $76/ton) (Clear Roads 2016) whereas acetate based deicers on average cost about $600 to 1000/ton (Fischel 2001; Kelting and Laxson 2010; Fay et al. 2015). Fortin Consulting, Inc. (2014) identified the cost of acetates as $4.50 per gallon for KAc, and $1900 per ton for NaAc and CMA. A cost analysis performed by Montana Department of Transportation (MDT) indicated that, compared to $MgCl_2$, KAc would cost 12 times more (Williams 2001). The Environmental Protection Agency (EPA) estimates the cost of using acetates to be 10 to 20 times higher than salts (EPA 1999). The high cost of acetates has limited their use by highway agencies. In fact, less than 10% of the 28 state and provincial highway departments surveyed used acetates for snow and ice control, and these agencies used them very sparsely (Kelting and Laxson 2010). In another study, only about 25% of the survey respondents indicated they have or are currently using KAc for snow and ice control (Shi et al. 2009).

Impacts to Infrastructure

Acetate based deicers are known to be non-corrosive to mild steel compared to chloride based deicers. However, acetates have been found to be as corrosive as chlorides to galvanized steel (Shi et al. 2009). In addition, KAc based deicers can pose deleterious effects to asphalt pavement through emulsification of the asphalt binder (Pan et al. 2008). In concrete pavements, KAc can induce alkali-silica reactivity (ASR) on susceptible aggregates (Shi et al. 2009) and in concrete (Balachandran et al. 2011; Bérubé et al. 2002; Math et al. 2011).

Impacts to Water and Soil

A test used in the environmental assessment of deicers is the Biochemical Oxygen Demand (BOD), also known as biological oxygen demand. The biochemical oxygen demand measures the amount of oxygen consumed in the biological processes that break down organic matter in water, and is a standard test for measuring the amount of dissolved oxygen (DO) utilized by aquatic organisms. BOD is generally reported as a quantity in mg/L. Non-chloride based deicers that break down in the environment often exhibit elevated BODs because oxygen is consumed as microbes break down these materials. The most pronounced environmental issue associated with acetate-based deicers is the increased BOD that reduces available oxygen for organisms in soil and aquatic environments (LaPerriere and Rea 1989).

Dissolved oxygen (DO) is the available oxygen dissolved in water. Oxygen is consumed by aquatic systems during microbial activity, and produced from the atmosphere, photosynthesis from plants, and running water churning in more dissolved oxygen (EPA, 2012). Dissolved oxygen levels fluctuate seasonally and over a 24-hour period. DO varies with water temperature and altitude, such that colder water holds more oxygen than warmer water, and water holds less oxygen at higher altitudes (EPA, 2012). "Aquatic species are most vulnerable to lowered DO levels in the early morning on hot summer days when stream flows are low, water temperatures are high" (EPA, 2012).

"The rate of oxygen consumption in a stream is affected by a number of variables: temperature, pH, the presence of certain kinds of microorganisms, and the type of organic and inorganic material in the water" (EPA, 2012). Research has shown that BOD is generally lower in the winter due to colder temperatures suppressing biological activity, and higher in summer when biological activity increases with warmer water temperatures (Gillies et al., 2012). "BOD directly affects the amount of dissolved oxygen in rivers and streams. The greater the BOD, the more rapidly oxygen is depleted. The consequences of high BOD are the same as those for low dissolved oxygen: aquatic organisms become stressed, suffocate, and die." (EPA, 2012)

The acetate ion is the most abundant organic acid metabolite in nature, and its biodegradation could lead to anaerobic soil conditions or localized DO depletion in surface waters (TRB 1991; D'Itri 1992). With a half-life of less than two days at 45°F (7°C), the acetate ion can be easily degraded by soil microorganisms (Defourny 2000). But in those two days, acetate concentrations of 100 ppm could completely deplete the DO in water, whereas an acetate concentration of 10 ppm would only temporarily reduce oxygen supplies (Cheng and Guthrie 1998). Data pertaining to sodium acetate/formate (Ice Shear) suggests that during the spring thaw runoff, short periods of oxygen depletion in receiving waters may occur, with potential danger in warmer weather (Hellsten et al., 2005). Work by Pilgrim (2013) ranked deicers by toxicity and in this paper KAc was ranked as more toxic than any of the chloride based deicers when considering BOD and impacts to aquatic organisms.

Vendors

There are many commercially available options for acetate based deicing products. Below is a list of some of the available vendors and products.

- Cryotech
  - Potassium acetate (KAc), Sodium acetate (NaAc), Calcium Magnesium Acetate (CMA)
  - http://www.cryotech.com/cryotech-cf7-commercial
  - http://www.cryotech.com/runway
- Chemical Solutions, Inc.
  - Potassium acetate (KAc), Sodium acetate (NaAc), Calcium Magnesium Acetate (CMA)
  - http://meltsnow.com/products/acetates/
- NASi,
  - Potassium acetate (KAc)
  - http://www.nasindustrial.com/alpine-ice-melt.html
- Hawkins, Inc.
  - Potassium acetate (KAc)
  - http://www.hawkinsinc.com/groups/oil-field-chemicals/liquid-potassium-acetate-60/
- Midwest Industrial
  - Potassium acetate (KAc)
  - http://midwestind.com/enviro-mlt/

Table 1. Summary of information on acetate based deicers. Modified from Fay et al. (2015).

Product Type	Liquid/Solid	Application Rate	Conditions and Pavement Temp. range	Cost	Performance
NaAc (Sodium Acetate)	Solid/Liquid	Near 32°F (thin ice) = 190-320 lbs/l-m 10°F (1in ice) = 600-1500 lbs/l-m	Works in temps down to 0°F. Commonly used at airports and parking garages.	\$1000-\$1500 per ton	Excellent melting properties, works faster and at lower temperatures than NaCl.
CMA (Calcium Magnesium Acetate)	Solid/Liquid	250-400 lbs/l-m, heavier initial application, followed by lighter applications	Works in temps down to 0°F. CMA does not work well below 20°F.	\$600-\$2000 per ton	CMA performs similarly to NaCl but requires more by weight to achieve the same results. Slow acting, not as effective in freezing rain and light traffic as NaCl.
KAc (Potassium Acetate)	Solid/Liquid	60-80 gal/l-m (deicing), 25-60 gal/l-m (anti-icing)	32°F to -26°F, performs quicker than CMA at lower temps. Commonly used at airports.	\$600-\$1200 per ton	KAc activates quickly, and works quicker than glycol and is less slippery.

<u>Formates</u>

Formates are a family of non-chloride deicers of which the most common are sodium formate (NaFm) (CHO_2Na) and potassium formate (KFm) (CHO_2K). Formates are available commercially and are commonly used at airports. Formates typically work in temperatures ranging from -20°F to 15°F. Like acetates, some of the disadvantages include higher cost (even more so than acetates), corrosivity to galvanized steel, and damaging impacts on concrete and asphalt pavements (Fay et al. 2008, Shi 2008, Shi et al. 2009). A summary of information on formate based deicers can be found in Table 2.

Relative Performance Compared to Chlorides

Formate based products have shown similar ice melting performance to acetates. At this time there is limited data directly comparing deicing performance between formates and chlorides.

Impacts to Infrastructure

Similar to acetates, formates have little to no corrosive impact on steel. Potassium formate was reported to cause serious corrosion to landing gear and associated wiring of some airplane models and the corrosion risk of acetate/formate-based deicers to cadmium-plated steel has raised concerns by aircraft manufacturers and airlines (Shi 2008). Studies have identified corrosion issues with mixed metal types. This issue is not isolated to acetate/formate deicers and also occurs in the presence of chlorides.

A sodium acetate-sodium formate (NaAc/F) blend and a potassium formate (KF) deicer were found to cause fewer impacts to Portland cement concrete than salt (NaCl) (Shi et al., 2009), but similar to acetates, KFm and NaFm can induce alkali-silica reactivity (ASR) on susceptible aggregates (Shi et al. 2009) and in concrete pavements (Balachandran et al. 2011; Bérubé et al. 2002; Math et al. 2011). Additionally, durability of concrete at airports exposed to formates has been reported (Shi 2008).

Impacts to Water and Soil

Similar to acetates, formates degrade in water, but while doing so exert a high BOD, reducing the amount of available oxygen for aquatic species. The elevated BOD appears to be of greatest concern during spring thaw runoff and during warmer weather (Bang and Johnston, 1998). Acetate and formate blended deicers can decrease water quality through increased turbidity, water hardness, and alkalinity. Limited research specifically on formate deicers has been completed, but one study found formates do not cause any impact to groundwater chemistry as they frequently breakdown in the topsoil (Horner and Brener, 1992).

At low concentrations acetate and formate blended deicers demonstrated positive impacts on plants in the near road environment, but at higher concentrations the presence of formates becomes detrimental (Bang and Johnson 1998; Hellsten et al. 2005). Acetate and formate blended deicers can also impact aquatic species (Bang and Johnston 1998).

Cost

Reported costs for NaFm were $200-300 per ton and for KFm were $1000-1600 per ton (2015 US dollars) (Fay et al. 2015). Fortin Consulting, Inc. (2014) identified the cost of formates as $400 per ton for NaFm and $70 per gallon for KFm.

Vendors

There are many commercially available options for formate based deicing products. Below is a list of some of the available vendors and products.

- Hawkins, Inc.
    - Potassium formate (KFm)
    - http://www.hawkinsinc.com/groups/oil-field-chemicals/liquid-potassium-formate-53/
- Five Star, Inc.
    - Sodium formate (NaFm)
    - http://www.fyvestar.com/sodiumformatesafeway.html
- NASi
    - Sodium formate (NaFm), Potassium formate (KFm)
    - http://www.nasindustrial.com/nasi-sf.html
    - http://www.nasindustrial.com/airfieldrunway.html
- Seneca Mineral
    - Potassium formate (KFm)
    - http://senecamineral.com/potassium-formate-deicer/

Table 2. Summary of information on formate based deicers. Modified from Fay et al. (2015).

Product Type	**Liquid/Solid**	**Application Rate**	**Conditions and Pavement Temp. range**	**Cost**	**Performance**
NaFm (Sodium Formate)	Solid/liquid	Near 32°F (thin ice) = 125-25- lbs/l-m 10°F (1in ice) = 400-1000 lbs/l-m	Working temp down to 0°F. Commonly used at airports.	$200 - $350 ton	Fast acting
KFm (Potassium Formate)	Solid/liquid		Working temp below -58°F. Commonly used at airports.	$1000 - $1600 ton	Efficient at deicing.

<u>Glycol</u>

Glycol based deicers represent a family of deicers that include glycol, glycerol, and glycerin[1]. This report generally refers to these products as glycols unless specified. Glycols are non-chloride based products that are more commonly used at airports. The two most common forms of glycols are propylene glycol and ethylene glycol. They work in temperatures ranging from -20 °F to 15 °F (Fortin, Consulting, Inc. 2014), but have a very low eutectic temperature of -74°F. A summary of information on glycol based deicers can be found in Table 3.

Glycerol can be sourced as a by-product, making it a sustainable option. For each gallon of biodiesel produced, approximately 0.35 kg (0.76 lbs) of crude glycerol is also produced. Glycerol represents an opportunity to better utilize this by-product with added value (Pachauri and He, 2006; Thompson and He, 2006).

Glycerin (also called glycerol) is also an effective anti-freezing agent. Glycerin has a relatively low freezing point when mixed with water (Chauhan et al. 2012), and is often used as an anti-freeze or ice inhibiting constituent (Kormann 1937; Keenoy 1941). Contrary to some glycols (e.g., propylene glycol), glycerin is less expensive and has the advantage of being an anti-caking agent that can enhance melting. It has been discovered that glycerin added in a small percentage as an exterior coating will decrease the caking of salt in both bulk storage and bag storage, and will increase the ice melting capability (Ossian 2007; Ossian 2012).

Relative Performance Compared to Chlorides

At this time there is limited data directly comparing deicing performance between glycols and chlorides.

Impacts to Infrastructure

Glycol and glycerol are non-corrosive to steel.

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[1] *Glycol* refers to any organic compound that belongs to the alcohol family, such that two hydroxyl (-OH) groups are attached to two different carbon atoms. Two examples are ethylene glycol and propylene glycol. *Glycerol* (or glycerin) belongs to the alcohol family of organic compounds (Merriam-Webster's Encyclopedia, 2000).

Impacts to Water and Soil

Once applied these products are not recoverable and may be transported to surface and ground water. However, these products do not accumulate over time; instead they break down, and this process can lead to elevated BOD (Fortin Consulting, Inc. 2014).

<u>*Glycol Impacts*</u>

The predominant impacts of glycol-based (ethylene and propylene) deicers include the observed elevated BOD due to oxygen consumption during its breakdown in aquatic systems, with propylene glycol exerting a higher *BOD* (U.S. Navy, 2010). Ethylene glycol has high degradation rates by aerobic microorganisms with low bioaccumulation potential (Hartwell et al. 1995), as well as low adsorption into soils, and high mobility. Essentially ethylene glycol will be consumed by bacteria, will not accumulate, and likely will not impact the soil structure.

Carcinogenic effects to aquatic fauna have been observed, such that Kent et al. (1999) found that glycol-based deicers used at airports are more toxic to aquatic species than deicers commonly used on roadways. This may in part be due to the concentrations present as the result of frequent applications. Corsi et al. (2006) found endocrine disrupting properties in both ethylene and propylene glycol deicers at airports, which have been attributed, in part, to additives.

Ethylene glycol is acutely toxic to mammals when consumed and has led to death by depressing the central nervous system. Ethylene glycol is also considered a hazardous air pollutant and is subject to reporting requirements under the Comprehensive Environmental Response, Compensation and Liability Act (Fortin Consulting, Inc. 2014). Because of these findings ethylene glycol will not be considered as a viable non-chloride option. By contrast, propylene glycol is essentially non-toxic.

Glycols can inhibit plant growth, but only slightly more than salt (Kawaski et al. 1983). If impacts to protected plant species or sacred native plant species are of concern, then selecting a glycol based deicing product may not be the best option.

<u>*Glycerin Impacts*</u>

Generally glycerin deicers are less toxic than chloride deicers due to the inherent non-toxic property of glycerin. For instance, glycerin deicers have minimal adverse influence on soil structure and permeability, and some components of glycerin (e.g. carbon (C) and nitrogen (N)) can be absorbed by vegetation (Wang et al., 2014). However, glycerin may be slightly harmful to some species of animals and plants under certain conditions. It was reported that glycerin has multiple effects on plant cell metabolism (Aubert et al., 1994) and could inhibit the activity of some enzymes at elevated concentrations, especially for organisms that are not salt tolerant (Heimer, 1973). If glycerin were ingested by an animal, potential impacts may include hemolysis, hemoglobinuria, renal failure, fatty liver, and convulsion (Tao et al., 1983). For fish, glycerin is a contraceptive and has adverse consequences on fertility (Alvarenga et al, 2005). The cellular effects caused by glycerin include changes in cytoplasmic events due to increased viscosity by intracellular glycerol, altered polymerization of tubulin, alteration of microtubule association, effects on bioenergetic balances, and direct alteration of the plasma membrane and glycocalyx (Hammerstedt and Graham, 1992).

Cost

Crude glycerol is inexpensive at $0.02 per gallon (Fortin Consulting, Inc. 2014), while costs for ethylene glycol were $14-40 per gallon and propylene glycol were $10-20 per gallon (Fay et al. 2015). Fortin

Consulting, Inc. (2014) identified the cost of glycerol as $50 per gallon, and ethylene and propylene glycol as $40 per gallon.

Vendors

There are many commercially available options for glycol based deicing products. Below is a list of some of the available vendors and products.

- Cryotech
    - Propylene glycol, Ethylene glycol
    - http://www.cryotech.com/aircraft
- Dow
    - Propylene glycol, Ethylene glycol
    - http://www.dow.com/en-US/aircraft
- Octagon Process
    - Propylene glycol, Ethylene glycol
    - http://www.airport-technology.com/contractors/deicing/octagon/

Table 3. Summary of information on glycol and glycerin based deicers. Modified from Fay et al. (2015).

Product Type	Liquid/Solid	Application Rate	Conditions and Pavement Temp. range	Cost	Performance
Ethylene glycol	Liquid	50-2000 gal/l-m	Glycols work down to -74°F. Commonly used to deice airplanes.	$14-$40 per gal	Very effective at deicing.
Propylene glycol	Liquid			$10-$20 per gal	
Glycerin	Liquid	Typically used as an additive. Application rates vary depending on the blend ratio.	Glycerin has a relatively low freezing point when mixed with water and is used as an anti-freeze or ice inhibiting constituent.	$10-$30 per gal	Low freezing point, used as an ice inhibiting additive. Less expensive than glycols and acts as an anti-caking agent.

Succinates

Succinate salts have been shown to aid in deicing and corrosion inhibition, specifically in the work by Berglund et al. (2001). Succinate salts exist naturally and are manufactured in what is considered to be an environmentally sustainable process that utilizes existing co-products, such as from corn processing, and carbon dioxide. One gram of succinate is generated from a biological fermentation process of one gram of glucose from biomass such as cornstalks, corn fiber, and sugarcane (Potera 2005). This process uses carbon dioxide to make the succinate, and for this reason, is considered a greenhouse-friendly fermentation process. 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 glycols, 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).

Succinate salts consist of potassium succinate (KSu), ammonium succinate, sodium succinate, and combinations of these (Berglund et al., 2001). For the purpose of this work, the discussion will focus on KSu, because this succinate salt out performed all other forms of succinate salts as a deicer and corrosion inhibitor. While succinates are more commonly used as corrosion inhibitors, research has been conducted to explore the functionality of deicers blended with succinates for anti-corrosion and deicing effects (Berglund et al. 2001; Seo 2007; Taylor et al. 2010).

Relative Performance Compared to Chlorides

Berglund et al. (2001) found that potassium succinate "penetrates ice at temperatures as low as -20°C" (-4°F) (Alizadeh and Berglund 2015). It should be noted that this was determined using a modified ice penetration test, not the standard eutectic curve or ice melting test. Ice melting test results were not as conclusive for this product. The Researcher Team recommend that the ice melting capability of potassium succinate be determined using any or all of the various methods: eutectic curve, SHPR ice melting test, and/or DSC.

Data reported by BioAmber[2] on the ice melting capacity of potassium succinate shows relatively low ice melting capacity at 20°F (about 1.75 ml/g deicer) compared to the other products tested, while at 5°F KS shows average to low ice melting (about 1 ml/g deicer) compared to the other products tested (BioAmber Inc. 2011). This is in stark contrast to ice penetration data BioAmber reports on the performance of potassium succinate, which implies that the product out performs all products at 20°F and 5°F (5.5 mm of penetration, and 3 mm of penetration, respectively). Interestingly, in the patent application, BioAmber reports the ice penetration data, and not the ice melting data, which seems to suggest that potassium succinate out melts other deicer products. Based on these contrary findings the researchers recommend conducting performance testing on this product to determine if it can perform as well or better than other non-chloride deicers.

The ice undercutting results for potassium succinate show mixed results, where at 20°F KS performance is average, while at 5°F KS performed well (about 20 cm^2/g deicer and 10 cm^2/g deicer, respectively) (BioAmber Inc. 2011).

Potassium succinate has been shown to depress the freezing point of water (-12°C, or 10.4°F), while a mix of water, potassium succinate, potassium acetate, and potassium formate at a ratio of 50:30:10:10, respectively provided the lowest depression of freezing point to -19°C (-2.2°F) (BioAmber Inc. 2011). Based on these findings, the use of a blended product warrants consideration.

Impacts to Infrastructure

Alizadeh and Berglund (2015) found that potassium succinate imparts no corrosion to steel and aluminum, and when mixed with salt brine at 2% by weight reduces the corrosion rate of salt brine by 40%. Further reduction of corrosion rates was not observed with increased amounts of potassium

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[2] BioAmber is the only potential manufacturer of a succinate based deicer in the US at this time. We have been in communication with BioAmber and have set up a testing agreement with them.

succinate added to salt brine beyond the 2% by weight. Potassium succinate also imparts no significant signs of corrosion pitting to galvanized steel (BioAmber Inc. 2011).

Potassium succinate causes minimal to no concrete scaling (BioAmber Inc. 2011). Experimental succinate based deicer formulations have been certified for use on airport runways (BioAmber Inc. 2011, from reference SMI, Inc. Miami, FL).

Impacts to Water and Soil

Limited information on the impacts of succinates is available, however the BOD of KSu was analyzed by BioAmber. BioAmber reported the following BOD values shown in Table 4. This shows that BOD values for succinates are similar to those for acetates.

Table 4. BOD values reported by BioAmber.

Deicer	BOD (g O_2/g fluid)
Succinate Formula	0.15
Potassium Acetate	0.14[3]
Potassium Formate	0.12
Ethylene Glycol	1.0[2]

Cost

Succinates were reported to cost less than $1 a pound[4] for biosuccinate (Potera 2005). Recent input from BioAmber suggests that a price cannot be determined at this time due to the fact that the product manufacturing has not yet been scaled up for mass production, but the company suggests the price of a 50% KSu solution would be on par with those of formate based products (P. Petersen February 23, 2017). Fortin Consulting, Inc. (2014) identified the cost of succinates as $2.50 per gallon, and up to $75 per lane-mile.

Vendors

- BioAmber Green Technologies (Formerly DNP Green Technologies)
    - Potassium succinate
    - http://www.bio-amber.com/ignitionweb/data/media_centre_files/606/Deicer_Overview_BA_2011.pdf

Succinates have been suggested as options for use in winter maintenance operations on roadways by multiple studies (Shi 2008; Akin et al. 2013; Fortin Consulting, Inc. 2014), but at this time appear to be marketed for use at airports due to the low corrosivity to many metal types and limited to no impacts to pavements. Because of the similar performance of KSu compared to many of the acetate, formate, and chloride based deicers, and outstanding performance as a corrosion inhibitor, the researchers recommend this product for additional testing. In addition to this, the Research Team have suggested that BioAmber consider additional testing, including toxicity testing, eutectic curve, and various methods to determine ice melting capacity and the functional temperature range for use of this product.

[3] While this data is reported by BioAmber they use the follow reference for this data – Cryotech Deicing Technology, “Cryotech E36® Environmental Impact,” and the linked web address no longer works.

[4] When oil prices were around $25 a barrel.

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Appendix B. DOT and Practitioner Survey Results

A total of 32 respondents participated in the survey, of which 25 indicated their location (displayed in Figure 1). Survey responses were received from state DOTs, local transportation agencies, airports, and private applicators. The following section provides a summary of the survey results provided by DOTs and practitioners.

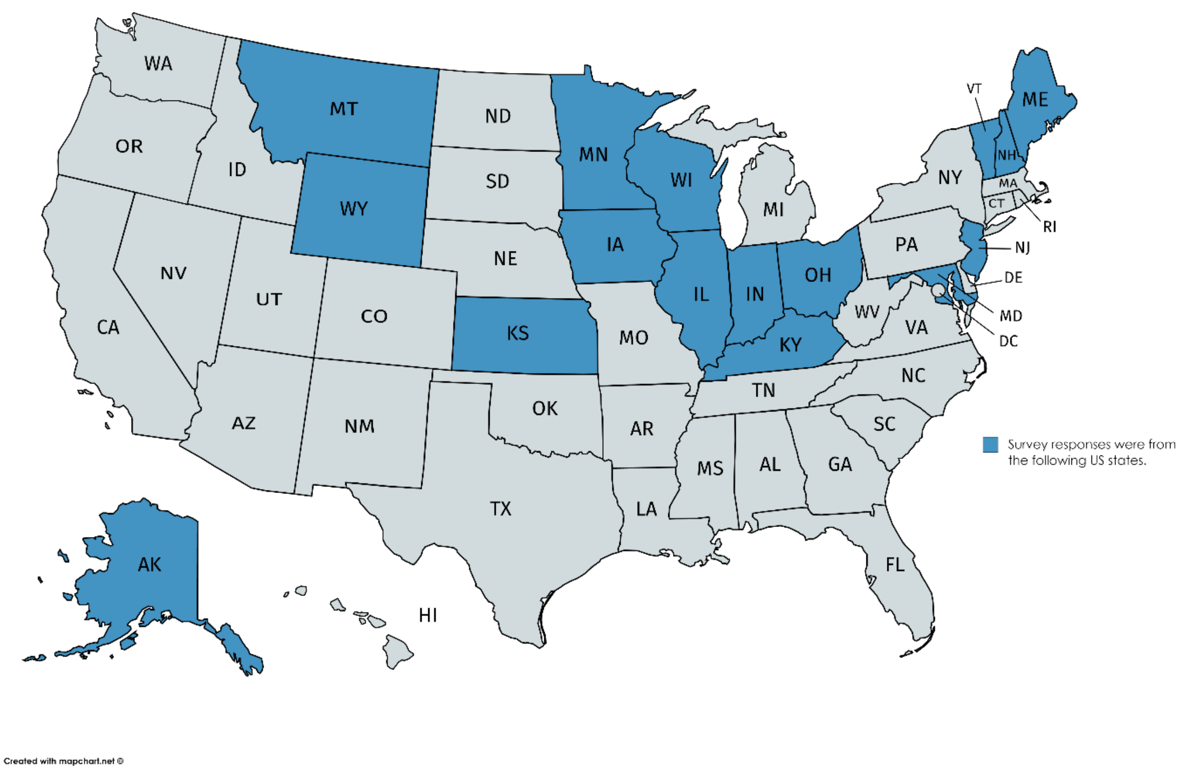

Figure 2. Survey responses from states highlighted in blue included responses from state DOTs, local transportation agencies, airports, and private applicators.

Of the 32 survey respondents, 47% (n=15) indicated that they have experience using non-chloride deicers in their current position; whereas 53% (n=17) indicated they do not. Survey respondents who indicated they do not have experience using non-chloride deicers were excused from taking the remainder of the survey. From this point forward, survey responses will be discussed for the respondents who indicated they do have experience using non-chloride deicers.

Non-chloride deicers used by respondents are shown in Table 5. They reported using acetate based deicers sodium acetate (NAAc) and Potassium Acetate (KAc) most frequently. Responses for the Other category included blended potassium acetate and glycol (n=1), beet juice (n=2), and agricultural by-product deicers (n=2). A total of 10 responses were received for this question.

Table 5. Non-chloride deicers used by survey respondents.

Answer Options	Response Percent	Response Count (n)
Acetates - Sodium Acetate (NAAc), Potassium	70%	7
Formates - Sodium Formate (NaFm), Potassium	20%	2
Glycols - Propylene glycol, glycerol, glycerin	20%	2
Succinates - Potassium Succinate (KSu)	10%	1
Other (please specify)	50%	5

Survey respondents were asked how often they use these non-chloride deicers and provided the following information shown in Table 6. The frequency of use of the non-chloride deicers was highly variable, with equal number of responses for rarely used and used often.

Table 6. Frequency of use of non-chloride deicers by survey respondents.

Answer Options	Response Percent	Response Count (n)
Rarely, a couple times season	20.0%	2
Often, a couple times a month	20.0%	2
Every storm	10.0%	1
Other (please specify)	50.0%	5

The Other category included the following responses:

- They are used in automated bridge deicing systems (n=2).
- Almost every storm (n=1).
- Airports (n=1).

The respondents were asked about the conditions present when they use non-chloride deicers. Table 7 lists and categorizes the information provided. This question received nine responses. The temperature ranges in which the non-chloride deicers were used was highly variable. This may be due in part to the varying functional temperature ranges of the various non-chloride products discussed in this survey. The non-chloride deicers were used to treat the following precipitation types: snow, sleet, ice, and as pre-treatment for anticipated precipitation. The non-chloride deicers were used to treat snow from ¼ to 30 inches, and for sleet and ice up to ¼ inch. The non-chloride deicers were used on bridge systems or fixed automated systems on hills (n=4), on highways (n=3), on pavements and parking decks, and around sensitive plantings or “fancy” streetscapes. Respondents indicated that non-chloride deicers are generally used for all storm types that do not begin with rain. One respondent provided additional comments that potassium acetate (KAc) is used in the bridge deicing system when ice is forming. This respondent also commented that airports regularly use non-chloride deicers prior to Air Carrier Operations.

Table 7. Survey responses for the storm type and conditions for which the non-chloride deicers are used.

Temperature range (°F)	Precipitation type/amount	Locations used (highway, shaded areas, with the FAST system, etc.)	Storm type
All temps		Bridge systems and Fixed systems on hills	
0°F to 20°F	varied	Highway, non-shaded, open	All types of snow & ice, wind
Below 20°F	snow, ice	Highway	Snow and ice storms
32 °F to - 17 °F	1/4 inch to 30 inches	All pavements	If the storm is coming in as rain and ground temps are above 33 °F we wait until the temperatures drop.
40 °F to 0°F	snow up to 1 inch; sleet up to 1/4 inch; ice up to 1/4 inch	Pavement; parking decks, around sensitive plantings or fancy streetscapes	Snow; freezing rain/sleet; anticipated black ice
		Fast system	
16°F to 32°F	snow; used as a pre-treatment	Highways	Those that do not begin as rain.
Above 13 °F		Bridge decks with automated systems	

Survey respondents were asked what application rates they use for the non-chloride deicers. This question received 10 responses. All respondents indicated they use liquid products, with application rates ranging from 15 to 50 gallons per lane mile (gal/l-m). Detailed responses on application rates include:

- Anti-icing at 25 to 35 gal/l-m, deicing at 40 to 45 gal/l-m
- 30 to 50 gal/l-m
- Automated based on primarily road temperature.
- 16 to 20 gal/l-m
- Unknown (n=3)
- 15 to 17 gal/l-m
- Depends on conditions and location.

Survey respondents were asked to provide information on the cost of purchase and delivery of non-chloride deicers. This question received eight responses. The reported cost to purchase the non-chloride deicer is provided below:

- Cryotech CF7 $4.20 - $4.58 (reported without units)
- Geomelt Gen3 $3.80 - $3.87 (reported without units)
- $3.75 a gallon in bulk
- KAc $5.00 per gal., CMA $1.75 per lb
- $4.00 per gal
- $1.50 per gal on average

When respondents were asked to provide information on shipping costs, most indicated that the cost of shipping is folded into the purchase price. Respondents also noted that the cost will vary based on location, and that shipping cost may vary between $0.17 - $0.46 per gal.
Survey respondents were asked if the non-chloride deicers they use require any special storage, handling, application or equipment. This question received nine responses, which are shown in Table 8. In general the respondents indicated that non-chloride deicers require special storage, handling, application and equipment.
Table 8. Survey responses on whether non-chloride deicers require special storage, handling, application or equipment.

Answer Options	Response Percent	Response Count (n)
Special Storage	78%	7
Special Handing	56%	5
Special Application or equipment	67%	6
Other (Please explain)	22%	2

Specific comments from survey respondents regarding special storage of non-chloride deicers include the need for separate tanks for storage. Specific comments from survey respondents regarding special handling of non-chloride deicers include use of standard protective gear, and the need to flush and conduct routine maintenance of the system. One respondent noted that mixing of the product before November is key. Specific comments from survey respondents regarding special application and equipment of non-chloride deicers include the use of automatic (fixed) spray systems (n=3).

Survey respondents were asked to provide in detail their experience using non-chloride deicers. The following information was provided by eight respondents, with relevant comments shown below.

- Our Metro District and Duluth District (District 1) have had Fixed systems in place for over 10 years. We started with magnesium chloride ($MgCl_2$) and migrated to various vendors of Potassium Acetate (KAc) products over the years. Presently the bulk of systems use Cryotech CF7. One site in District 1 is doing a trial of GeoMelt Gen3 which have been performing well but have less experience with GeoMelt Gen3.

- Beet juice - used mostly on bridges to cut ice and keep the road wet. The product tracks and is sticky, resulting residue lasting a long time. The product appears to attract moisture, [preventing] future ice buildup. Mag chloride is used with salt during very cold temps to melt compact[ed snow] ice. [The Mag chloride is] used mostly in shaded areas. Resulting residue did attract moisture in days following event.
- The non-chloride products are used as an enhancement to brine use for application at colder temperatures.
- The only place we use non-chloride deicers is in a FAST (Fixed Automated Spray Technology) system on a new bridge deck. The project is only partially completed and has been used for one season primarily because of new concrete. Time will tell if we will continue with this product.
- The non-chloride deicing product lowers the effective operating temperature of our chloride-based anti- and de-icing materials, and has longer residual effects due to its naturally adhesive nature.
- Overall good performance when used appropriately.

Survey respondents were asked if in their opinion there are any other promising non-chloride deicing options that were not included in this survey. This question received five responses, of which three indicated that they are not aware of any other products. Other comments included:

- Agricultural by-products
- Continued research should be done
- We have started some preliminary development on mobile systems and associated evaluation.

Finally, survey respondents were asked if they can provide any lessons learned or other information on the use of non-chloride deicers. This question received three relevant responses which are provided below:

- I think we have lost much of the momentum in the industry [to use non-chloride deicers] because of retirements and budget cuts in government. The 'next' generation employee seldom has the commitment or drive to maintain the technology much less push it forward. The fall back becomes: 'just blast it with salt, repairing damage is not my problem, it comes out of someone else's budget'
- Non-chloride deicers can be less corrosive than chloride products.
- Be very cautious with their use and side effects.

<u>Vendor and Manufacturer Survey Results</u>

Seven vendors or manufacturers of non-chloride deicing products participated in this survey, of which four provided contact information.

Bio-Amber, Paul Petersen, Montreal, QC, Canada
Email: paul.petersen@bio-amber.com
Phone: (508) 769-5159

Duchess Marketing, Steven Kaar, Geneva, Illinois
Email: steve.duchessmarketing@gmail.com
Phone: (630) 845-1909

Winter Equipment, Marty Emnett, Willoughby, Ohio
Email: memnett@winterequipment.com
Phone: (330) 714-3283

US Environmental Resources, Frank Garber, St. Paul, Minnesota
Email: 060749@COMCAST.NET
Phone: (612) 889-9171

Of the seven respondents to this survey, five indicated they sell or make non-chloride deicing products. These products include:

- Acetates - Sodium Actetate (NAAc) and Potassium Acetate (KAc) (n=2)
- Formates – Sodium Formate (NaFm) and Potassium Formate (KFm) (n=1)
- Glycols – Propylene glycol, glyercol, glycerin (n=2)
- Succinates – Potassium Succinate (KSu) (BIOA-4055) (n=1)
- Geomelt Gen3 (agricultural by-product) (n=1)

Recommended application rates were provided for the following products:

- CMA (Calcium Magnesium Acetate) - 500 to 1000 lbs/l-m
- Acetate liquid – 30 to 50 gal/l-m
- Geomelt Gen3 – pre-wetting 4 to 10 gal/ton at the spinner, anti-icing 20 to 40 gal/l-m, deicing 50 to 70 gal/l-m

Survey respondents were asked who their products are typically marketed to, the results of which are shown in Table 9. The Other product in the Answer Options category is the Geomelt Gen 3 product, and the Other audiences the products are marketed too include parking decks and LEED facilities.

Table 9. Survey responses of whom products are typically marketed to.

Answer Options	Airport	DOT, local transportation agency	Other
Acetates - Sodium Acetate (NAAc), Potassium			X
Formates - Sodium Formate (NaFm), Potassium			
Glycols - Propylene glycol, glycerol, glycerin			X
Succinates - Potassium Succinate (KSu)	X	X	
Other (please explain)		X	

One respondent indicated that the manufacturer/vendor currently supplies non-chloride deicers to the State DOT, local transportation agencies, and private contractors in the state of Minnesota. Two vendors indicated they are willing to provide cost data to DOT personnel upon request as prices vary greatly with shipping. Two vendors indicated that if significant quantities of their non-chloride products are purchased the cost may change (i.e., decrease). One respondent clarified that cost reductions are determined by the number of full truckloads of material purchased. Two respondents indicated that scaling up production of their product to meet the needs of larger orders will lead to reduced product costs.