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# **EVALUATION OF ALTERNATIVE ANTI-ICING AND DEICING COMPOUNDS USING SODIUM CHLORIDE AND MAGNESIUM CHLORIDE AS BASELINE DEICERS - PHASE I**

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**COLORADO DEPARTMENT OF TRANSPORTATION  
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16. Abstract  This project aims to evaluate potassium acetate, sodium acetate/formate-blend deicers, and potassium formate as alternative anti-icing and deicing compounds relative to sodium chloride (NaCl), salt-sand mixtures, and magnesium chloride (MgCl <sub>2</sub> ) currently used by CDOT. Based on the literature review, deicers may pose detrimental effects to portland cement concrete infrastructure and asphalt pavement, cause corrosion damage to the transportation infrastructure, or have significant impacts on the environment. We conducted laboratory tests to evaluate the performance of several alternative deicers compared with traditional chloride-based deicers, including: SHRP ice melting, penetration and undercutting tests, differential scanning calorimetry test, and tribometer tests. The negative effects of deicers on metals and concrete were investigated both in the laboratory and in the field. It was estimated that even for high-quality concrete, the implications of chloride-based deicers on the service life of steel-reinforced concrete might be significant. At the three field locations, water samples were collected periodically and the data showed no immediate impact from chloride-based deicers following application adjacent to waterways. We described a deicer composite index that would allow winter maintenance managers to numerically evaluate deicers based on their agency priorities or local needs and constraints.  <u>Implementation:</u> <ul style="list-style-type: none"> <li>• Continue the use of inhibited NaCl and inhibited MgCl<sub>2</sub> deicers until better deicer alternatives are identified;</li> <li>• Explore new technologies to minimize the salt usage while maintaining the desired levels of service;</li> <li>• Optimize deicer application rate;</li> <li>• Provide maintenance practitioners with sufficient training/learning opportunities;</li> <li>• Explore new technologies/methods to minimize the negative side effects of NaCl, MgCl<sub>2</sub>, and other deicers;</li> <li>• Encourage environmental compliance; Explore options for infrastructure preservation;</li> <li>• Routinely clean out the liquid-holding tanks prior to introducing different liquid deicer products;</li> <li>• Fund more research related to winter maintenance best practices in a proactive manner; and</li> <li>• Determine whether an additional two-year project is warranted to further investigate corrosion-inhibited chlorides, agricultural byproduct-based deicers, and other proprietary brands of deicers.</li> </ul>					
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# **Evaluation of Alternate Anti-icing and Deicing Compounds Using Sodium Chloride and Magnesium Chloride as Baseline Deicers – Phase I**

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## EXECUTIVE SUMMARY

Maintenance agencies are continually challenged to provide a high level of service (LOS) on winter roadways and improve safety and mobility in a cost-effective manner while minimizing corrosion and other adverse effects to the environment. The overall goal of this project was to evaluate potassium acetate (KAc), sodium acetate (NaAc)/formate (NaFm)-blend deicers, and potassium formate (KFm) as alternative anti-icing and deicing compounds relative to sodium chloride (NaCl), salt-sand mixtures, and magnesium chloride ( $MgCl_2$ ) currently used by CDOT.

All deicers<sup>1</sup> available on the market have various impacts, the level of which depends on many factors including the application rate of deicers, the winter precipitation rate, the specific road environment of the application, the traffic volume, etc.

Based on the literature review, deicers may pose detrimental effects to portland cement concrete (PCC) infrastructure and thus reduce concrete strength and integrity (as indicated by expansion, mass change and loss in the dynamic modulus of elasticity). The proper use of air entrainment, high-quality cementitious materials and aggregates, and mineral admixtures is promising in mitigating the deicer impact on PCC.

Second, deicers may pose detrimental effects to asphalt pavement. While their impact on skid resistance is still inconclusive, deicers are known to affect pavement structure and cause loss of the strength and elasticity of asphalt concrete (i.e., mixture of asphalt binder and aggregates). Formate/ acetate-based deicers were found to significantly damage asphalt pavements, through the combination of chemical reactions, emulsifications and distillations, as well as generation of additional stress inside the asphalt concrete. In order to manage deicer effects on asphalt concrete, it is recommended to: 1) follow best

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<sup>1</sup> For simplicity, the term *deicer* will be used to refer to all chemicals for anti-icing, deicing, and pre-wetting operations.

possible practices in asphalt mix design and paving (e.g., low void contents); 2) use binders with high viscosity or polymer-modified binders; 3) use alkaline aggregates or high-quality (sound) aggregates (avoid limestone filler or heavily-contaminated recycled asphalt pavement when acetates/formats are used as deicers); and 4) test the compatibility of the materials in advance.

Third, deicers may cause corrosion damage to the transportation infrastructure such as reinforced or pre-stressed concrete structures and steel bridges. The relative corrosivity of deicers is dependent on many details related to the metal/deicer system; and it is important to note the test protocol employed, the metal coupons tested, the deicer concentrations, the test environment, etc. There are many ways to manage the corrosive effects of deicers, such as: selection of high-quality concrete, adequate concrete cover and alternative reinforcement, control of the ingress and accumulation of deleterious ions or molecules from deicers, injection of beneficial ions or molecules into concrete, and use of non-corrosive deicer alternatives and optimal application rates.

Finally, deicers can have significant impacts on the environment, and the impacts are dependent on a wide range of factors unique to each formulation and the location of application. Abrasives mainly contribute to suspended solids in water runoff and reduced air quality, while deicers become dissolved in runoff. The removal of suspended solids is best accomplished through settling, which is very efficient at removing sand-sized particles but less effective for clay- to silt-sized particles usually absent in sand used for road traction. Structural Best Management Practices (BMPs) include detention and settling ponds, chambers, wetland type environments, infiltration trenches and basins, sand traps and filters, wet and dry swales and vegetation filter strips, few of which can effectively remove deicing products that have dissolved. Non-structural BMPs are preventative measures designed to reduce the amount of deicers and abrasives applied to roadways, which can reduce the need for or dependence on structural BMPs. They are procedures, protocols, and other management strategies including but not limited to: utilizing environmental staff in construction and maintenance practices; proper training of

maintenance professionals; utilizing tools like MDSS and other computer- and simulator-based training systems; passive snow control through snow fences and living fences; designing proper snow storage facilities; utilizing street sweeping; and improving deicing and anti-icing practices via better road weather forecasts and appropriate application rates. Among four typical deicers tested (NaCl, CMA, CaCl<sub>2</sub>, and MgCl<sub>2</sub>), CaCl<sub>2</sub> was the only product that was both irritating to the eyes and skin on contact, and toxic if inhaled. NaCl and CMA were slight eye irritants, but only CMA was a skin irritant. MgCl<sub>2</sub> proved to be the least harmful, being only a slight eye irritant and non-toxic if inhaled. To minimize the environmental impacts of deicer, it is crucial to make informed decisions by utilizing available resources including existing test methods and the PNS-approved deicer list. By identifying sensitive areas and species and setting limits for air and water quality, minimum impact requirements can be established which all deicers must meet, so that a toolbox approach may be implemented. Despite the potential damaging effects, the use of deicers for snow and ice control can reduce the need for applying abrasives, and thus pose less threat to the surrounding vegetation, water bodies, aquatic biota, air quality, and wildlife.

Our survey of deicer users in 2007 indicated that solid NaCl was most frequently used, followed by abrasives, then MgCl<sub>2</sub>, agricultural-byproduct-based (agr-based)<sup>2</sup>, calcium chloride (CaCl<sub>2</sub>), and then other deicers (Table 6). It is interesting to note that less than 25% of the survey respondents used alternative deicers such as acetates and formates whereas conventional deicers such as abrasives and chlorides are still most widely used. The agr-based products were perceived by users to be the most advantageous, with abrasives being the least and no significant difference between chlorides and acetates/formates. Acetates and formates were perceived by users to have the least impacts and chlorides the most (Tables 7 & 8).

Lessons learned by practitioners that were provided in the survey include:

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<sup>2</sup> Agricultural-based deicers must contain some quantity of bio-based product, for example corn or sugar beet co-products and may also contain chlorides, acetates, and/or formates.



- Don't panic if magnesium chloride gets slick. Just add water. Never apply magnesium chloride when road temperatures are above 32°F and rising. Don't apply magnesium chloride until you are sure that a storm is on its way.
- No matter how good the product is, the supplier is the key to your success. If they cannot provide accurate, consistent blends, this can create many problems for your agency.
- Equipment calibration should be done routinely (twice per year); otherwise you can be applying much higher rates of deicer than is needed.
- Proper training on application rates is important.
- Hotter mixes (2:1 or 3:1) instead of the standard 5:1 or 7:1 will reduce the amount of salt and sand applied to the roadway to maintain a bare road policy.
- Finding the value of corrosion inhibitors and identifying the realities of performance between chemicals will allow your DOT to become more strategic in your approach to buying, storing and applying the correct product at the correct time. Different geographic, demographic and climatic regions in our state require different approaches and eventually different products to maintain roads in the winter.
- The high cost of CMA and no alternative at present to match the environmental expectations, has driven us to introduce ice prediction technology to provide a "just-in-time, in-the-right-place" level of service. This also applies to abrasive use which will reduce the exposure to the hazards this can bring if applied on a "just-in-case" basis.
- Pre-wetting sand extends its life time on the road surface.
- Depending on the snow and ice event details (air temperature, wind, ground temperature, previous applications, future events forecasted, etc.) we will use a combination of anti-icing and/or deicing techniques. We will anti-ice with salt brine alone, or with a salt brine and De-ice<sup>®</sup> mixture. Mixing ratio depends on conditions. Every event is different in some way and we adjust accordingly.

- Only use calcium chloride in the liquid form (for deicing). (Note: the same respondent also had a comment: don't use CaCl<sub>2</sub> for anti-icing.).
- A ground temperature sensor installed for decision making during a storm is a must.
- We do see a need for an enhanced salt product that can be delivered pre-mixed to our maintenance sites. This can eliminate our on-board pre-wet systems, which are difficult to maintain in the harsh winter environment on the back of a spreader.

According to our 2007 survey of CDOT winter maintenance practices, NaCl (s) cost \$20.00 to \$42.00 per ton delivered to all regions in Colorado, whereas MgCl<sub>2</sub> (l) cost \$0.53 to \$0.84 per gallon delivered. These two deicers were mostly used and also consistently the most affordable. The application rate for NaCl (s) generally ranged from 100 to 500 lb/l-m, whereas that for MgCl<sub>2</sub> (l) ranged from 20 to 100 gallons/l-m. The application rates were reported to increase with the traffic volume and the intensity of the storm.

The hidden costs of road salts to the infrastructure and surrounding environment can be substantial; such costs are often ignored in formulating highway winter-maintenance strategies. Some products for snow and ice control may cost less in regard to materials, labor and equipment, but cost more in the long run as a result of their corrosion and environmental impacts.

According to our 2008 survey of CDOT deicer priorities, CDOT personnel rankings for deicer performance attributes varied greatly, most likely due to the difference in their job descriptions. The high ice melting capacity, low material cost per lane mile, ease of application, and low cost of application equipment were ranked as having the greatest relevance. The deicer corrosion to metals were consistently ranked as highly relevant, with the low corrosion effect on rebar or dowel bars and slow penetration into concrete

ranked as the highest. Deicer impacts on concrete and asphalt pavements were ranked by survey respondents as having great relevance. Survey respondents also ranked some deicer impacts on the environment, including impact to water quality and air quality as highly relevant.

We conducted laboratory tests to evaluate the performance and impacts of several alternative deicers compared with traditional chloride-based deicers. The SHRP ice melting, penetration and undercutting tests together identified four best performing deicers that were all liquids, including the CDOT  $MgCl_2$  blend,  $MgCl_2$ -based Apex Meltdown,  $MgCl_2$ -and-*agr*-based IceBan, and KAc-based CF7. At this time we do not recommend the SHRP ice penetration test as useful tool for solid deicers, modification to the test method may be necessary to allow for consistent results between liquid and solid samples. This is also true for the SHRP ice undercutting test, modifications may be necessary to obtain similar results between liquid and solid deicers.

The differential scanning calorimetry (DSC) test showed that CF7 had the coldest effective temperature, followed by Apex Meltdown (Table 12A). The comparison between DSC and ice melting capacity data validated that more powerful deicers require less external energy to melt ice. The tribometer test revealed that IceBan led to the lowest friction coefficients on both the ice and the deiced concrete. Based on the gravimetric and macroscopic observations of freeze/thaw specimens following the SHRP H205.8 freeze/thaw laboratory test, de-ionized water, CMA solid deicer, and the CDOT  $MgCl_2$  blend were benign to the PCC durability, whereas KFm and the NaAc/NaFm blend deicer (NAAC/Peak SF) showed a moderate amount of weight loss and noticeable deterioration of the concrete. NaCl, IceSlicer, and CF7 were the most deleterious to the concrete. In addition to exacerbating physical distresses, each investigated chemical or diluted deicer chemically reacted with some of the cement hydrates and formed new products in the pores and cracks, the composition of which may be determined by the thermodynamics of the chemical reactions. Some new reaction products were identified as oxychloride crystals, which according to previous research can be expansive. This work provides new

insights into the deicer/concrete interactions and highlights the need for bridging the gap between the laboratory data with the field experience. The physiochemical changes of the cement paste induced by the deicers pose various risks for the concrete durability, the level of which depends on the kinetics of the chemical reactions.

The corrosive effects of deicers to metals were investigated both in the laboratory and in the field. For deicers diluted at 3% by weight or volume (for solid and liquid deicers respectively), electrochemical polarization test results showed that acetate-based deicers (CF7 and NAAC) were much less corrosive to mild steel than chloride-based deicers (the CDOT MgCl<sub>2</sub> blend, IceSlicer, and IceBan) while comparably corrosive to galvanized steel. Gravimetric PNS/NACE test results showed that (non-inhibited) Iceslicer, Peak SF, NAAC/Peak SF, and the CDOT MgCl<sub>2</sub> blend were very corrosive to mild steel and failed to pass the PNS specification of being 70% less corrosive than NaCl(r,s). We would suggest that if CDOT continues to use IceSlicer a corrosion-inhibited IceSlicer product should be used. Apex Meltdown and IceBan barely passed the PNS specification, whereas CF7 and NAAC demonstrated to be non-corrosive to mild steel. At three field locations where chloride-based deicers were applied (Aspen, Greeley, and Castle Rock, Colorado), the mild steel samples generally lost weight over time and galvanized steel generally gained weight over time, both at an average rate of 0.09 MPY (0.05±0.06 g/m<sup>2</sup>/day). Based on the electromigration test of chloride diffusion coefficients in portland cement mortar, it was estimated that even for high-quality concrete, the implications of chloride-based deicers on the service life of steel-reinforced concrete might still be significant. The diffusion coefficient of acetates and formates in concrete were not measured, since they are not corrosive to the rebar whereas chlorides are. Over the course of more than one year of exposure at the field locations, concrete samples showed no surface scaling or cracking and little presence of chloride on the surface and little diffusion into the concrete.

At the three field locations where chloride-based deicers were applied (Aspen, Greeley, and Castle Rock, Colorado), water samples were collected periodically to assess potential

impacts of deicers on surface water adjacent to highways. All relevant water quality parameters were below Environmental Protection Agency (EPA) and Colorado State standards (for chloride both are currently 250 mg/l), with the exception of the Greeley chloride concentration from March 2008 (250 mg/l). The field data also showed no immediate impact from chloride-based deicers following application adjacent to waterways. Values of pH were observed outside the acceptable range.

We also conducted laboratory experiments to study the potential interactions between deicers. When allowed to sit without stirring at room temperature, the  $\text{MgCl}_2+\text{NaAc}$  (NAAC),  $\text{MgCl}_2+\text{NaFm}$  (Peak SF),  $\text{MgCl}_2+\text{KAc}$  (CF7), and  $\text{MgCl}_2+\text{KFm}$  deicer blend solutions formed precipitates on the bottom of the beaker. Precipitates did not form when the CDOT  $\text{MgCl}_2$  liquid deicer was mixed with NAAC/ Peak SF or CF7/KFm, though the solutions were milky in appearance. To determine whether a physical or chemical reaction occurred to form the precipitates, samples of each solution were collected and FTIR was performed to provide insight on the potential reaction products. The precipitates were most likely  $\text{Mg}(\text{Ac})_2$  and/or  $\text{Mg}(\text{Fm})_2$  formed by the reaction of  $\text{MgCl}_2$  with NaAc, NaFm, KAc, or KFm. The nitrogen and sulfur based functional groups observed in the  $\text{MgCl}_2+\text{KFm}$  and  $\text{MgCl}_2+\text{NaFm}$  precipitates may be derived from corrosion inhibitors and additives added to the deicers for enhanced performance.

The literature reviews and laboratory data both shed light on the complexity and challenges in evaluating various deicers. To facilitate scientifically sound decision-making, we propose a systematic approach to integrate the information available regarding various aspects of deicers and to incorporate agency priorities, which is expected to help transportation agencies in selecting or formulating their snow and ice control materials. We described a *deicer composite index* that would allow winter maintenance managers to numerically evaluate deicers based on their agency priorities or local needs and constraints. The *deicer composite index* for each deicer product is calculated by multiplying the relevant *decision weights* by the *attribute values* indicating where the product's cost, performance or impacts fall in the specific category or

subcategory. The *deicer composite index* was calculated to be 46.6, 57.1, and 46.5 for non-inhibited NaCl, inhibited liquid MgCl<sub>2</sub>, and K- or Na-acetate/formate deicers, respectively. This illustrates the challenges still faced by the highway maintenance agencies, given that none of the deicers evaluated is close to being perfect (which would have a *deicer composite index* of 100). With the CDOT user priorities, the inhibited liquid MgCl<sub>2</sub> deicer products present a better alternative than either the non-inhibited NaCl or the K- or Na-acetate/formate deicers.

### **Implementation Statement**

In light of the research findings from this project, we provide the following recommendations for implementation:

1. Continue the use of inhibited NaCl and inhibited MgCl<sub>2</sub> deicers until better deicer alternatives are identified.
2. Explore new technologies such as MDSS, automatic vehicle location (AVL), in-place anti-icing pavement, fixed automated anti-icing technology (FAST), and thermal deicing to minimize the salt usage while maintaining the desired levels of service.
3. Optimize application rates through anti-icing practices, AVL, vehicle-based sensor technologies, MDSS, and road weather information systems (RWIS).
4. Provide maintenance practitioners with sufficient opportunities for training in and continuous learning of winter maintenance best practices.
5. Explore new technologies and methods to minimize the negative side effects of NaCl, MgCl<sub>2</sub>, and other deicers.
6. Encourage environmental compliance through the training in winter maintenance best practices and provide resources on region-specific BMPs that will meet compliance standards.
7. Explore options for infrastructure preservation including mix design specifications, cathodic protection, concrete sealers, overlays, etc.

8. Routinely clean out the liquid-holding tanks prior to introducing different liquid deicer products to prevent precipitates from forming and clogging equipment.
9. Fund more research related to winter maintenance best practices in a proactive manner. Given the millions of dollars spent by CDOT for snow and ice control each winter season, such CDOT-sponsored research is expected to lead to implementable results addressing CDOT priorities and generate great return on investment. In addition to cost savings for the agency, benefits to the road users can be expected as a result of improved LOS, while environmental and infrastructure benefits can be expected as a result of reduced salt usage.
10. Determine whether a second round (an additional two-year project) is warranted to further investigate corrosion-inhibited chlorides, agr-based products, and other proprietary brands of deicers.

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# CHAPTER 1. INTRODUCTION

## 1.1. Problem Statement

In the northern United States, Canada, and other parts of the world, snow and ice control operations are essential to ensure the safety, mobility and productivity of winter roadways, where driving conditions are often worsened by the inclement weather. These maintenance activities offer direct benefits to the public such as fewer accidents, improved mobility, and reduced travel costs. They also offer indirect benefits such as sustained economic productivity, reduction in accident claims, and better access to emergency services. Depending on the road weather scenarios, resources available and local rules of practice, maintenance agencies use a combination of tools for winter road maintenance and engage in activities that include anti-icing, deicing, sanding and mechanical means (e.g., snowplowing).

Large amounts of solid and liquid chemicals, known as deicers<sup>3</sup>, and abrasives are applied onto winter highways to keep them clear of ice and snow. Chlorides, mainly sodium chloride (NaCl), magnesium chloride (MgCl<sub>2</sub>), and calcium chloride (CaCl<sub>2</sub>), can be found in a wide variety of snow and ice control products used on winter highways to either prevent the bonding of ice to the roadway (anti-icing) or break the bond between ice and the roadway (deicing). Prior to application onto roadways, liquid salts are also added to abrasives or solid salts to make them easier to manage, distribute, and stay on roadways (pre-wetting). Transportation agencies are under increasing pressure to maintain high levels of safety and mobility even during the winter months, while working with limited financial and staffing resources and recognizing the corrosion and environmental challenges related to chemical and material usage (1, 2, 3, 4, 5, 6). The

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<sup>3</sup> For simplicity, the term *deicer* will be used to refer to all chemicals for anti-icing, deicing, and pre-wetting operations.

United States spends \$2.3 billion annually to keep roads clear of snow and ice (7); in Canada, more than \$1 billion is spent annually on winter maintenance (8).

In recent years, transportation agencies across North America have been shifting from reactive strategies to proactive strategies, such as anti-icing, for snow and ice control. Compared with traditional methods for snow and ice control (e.g., deicing and sanding), anti-icing leads to decreased applications of chemicals and abrasives, decreased maintenance costs, improved level of service, and lower accident rates (9). Reliable weather forecasts are crucial to a successful anti-icing program, as the pavement surface temperature dictates the timing for anti-icing applications and the appropriate application rate. When conducted properly, anti-icing can reduce the amount of plowing required and decrease the quantity of chemicals required (10). In many conditions, anti-icing eliminates the need for abrasives because it eliminates the cause of slipperiness (11).

New deicing chemicals, additives or mixtures are continually introduced into the market by manufacturers for use in snow and ice operations. Currently users do not have access to a robust set of performance-testing procedures that would enable them to make informed decisions on which products to purchase. Research is needed to help users understand how a product may work in their operations, and to help with matching better deicing substances with their specific roadway environment (road weather conditions, or financial, political, and environmental constraints, etc.) and level-of-service requirements. This will lead to best practices by transportation agencies that *deliver the right type and amount of materials in the right place at the right time* for snow and ice control, providing a high level of service on winter roadways in a cost-effective and environmentally responsible manner.

The Pacific Northwest Snowfighters (PNS, <http://www.wsdot.wa.gov/partners/pns/>) Association has become a recognized pioneer in establishing and standardizing chemical products for snow and ice control, consisting of professionals from transportation

agencies in Washington, Oregon, Montana, Idaho, Colorado and British Columbia. The PNS conducts extensive testing on various deicing chemicals, with a focus on corrosion of bare steel and environmental impacts. Corrosion-inhibited deicer products must prove to be at least 70% less corrosive than NaCl to be qualified for sale in the PNS states.

Clear Roads (<http://www.clearroads.org>) is a pooled fund research project aimed at rigorous testing of winter maintenance materials, equipment and methods for use by highway maintenance crews, with member states of Colorado, Illinois, Indiana, Iowa, Massachusetts, Michigan, Minnesota, Missouri, New York, Ohio, Utah, Virginia, Wisconsin, Wyoming, and FHWA partners. Launched in 2004 by seasoned winter maintenance engineers, Clear Roads responds to a need for research based on practical experience. By conducting structured field testing and evaluation across a range of winter conditions and highway maintenance organizational structures, Clear Roads projects aim to deliver immediately useful data and recommendations on the effectiveness, ease of use, optimum application rates, durability, and other aspects of many advanced winter operations technologies.

As a participant of both the PNS and Clear Roads, CDOT has been constantly examining best practices for snow and ice control. A 2001 CDOT report entitled “Evaluation of Selected Deicers Based on a Review of the Literature” suggests additional studies to resolve some of the outstanding issues related to components present in deicers, environmental effects, human health effects, corrosion, and other topics related to the use of deicers (12). To this end, research efforts such as this project are needed in order to identify non-corrosive, environmentally friendly, and cost-effective deicers with good performances in anti-icing and deicing.

## 1.2. Background

### *1.2.1. Snow and Ice Control Materials*

Deicers applied onto highways often contain chlorides because of their cost-effectiveness. NaCl traditionally has been abundant and inexpensive. It can be used as either rock salt (for deicing) or as salt brine (for anti-icing). However, its effectiveness is minimal below pavement temperatures of  $-12^{\circ}\text{C}$  ( $10^{\circ}\text{F}$ ). The possible presence of harmful substances and additives may render the use of salt-sand mixture impractical due to their adverse impacts on roadway structures, pavements, vehicles, soil, terrestrial flora and fauna, and water and air quality (13). An example is the common use of ferric ferrocyanide (Prussian blue), which has been listed as a toxic material by the U. S. Environmental Protection Agency, as an anti-caking agent mixed with NaCl.  $\text{CaCl}_2$  or  $\text{MgCl}_2$  is often used by many DOTs in a brine solution for anti-icing. Both of them work at lower temperatures than salt brine but cost more. At low relative humidity, their chloride residue on roads can attract more moisture than salt, resulting in potentially slippery conditions under certain circumstances (14).

Currently, CDOT maintenance personnel utilize two primary compounds for anti-icing and deicing operations—NaCl mixed with sand, and  $\text{MgCl}_2$  liquid deicer (13). In addition to  $\text{MgCl}_2$ , another liquid deicer used by CDOT is  $\text{MgCl}_2$  with corn-based agricultural additives to enhance its performance (15). According to the field experience of CDOT personnel,  $\text{MgCl}_2$  outperformed the salt-sand mixture as a deicer. Compared with the salt-sand mixture,  $\text{MgCl}_2$  has proved to be more effective, less toxic and less corrosive, and to significantly decrease the amount of sediment entering Colorado's streams and particulates entering its air (13, 16, 17). CDOT has thus shifted from using primarily NaCl and sand to using  $\text{MgCl}_2$  liquid deicers for wintertime operation and maintenance of state and national highway systems over the past several years. However, some local governments have banned the use of  $\text{MgCl}_2$  and returned to using salt-sand mixtures. Consequently, in order to bolster current suitability, acceptability, and the good

performance record demonstrated by  $\text{MgCl}_2$  and the continued use of salt-sand mixtures, additional research studies on alternate deicers are deemed necessary (13).

The use of chloride-based salts has raised concerns over their corrosion impact on motor vehicles and highway bridges. DOTs have begun to voice a preference for acetate-based deicers such as potassium acetate (KAc), calcium magnesium acetate (CMA), or calcium-magnesium-potassium acetate (CMAK), because they tend to decompose quickly and do not contain chloride (3). Electrochemical and weight loss tests of 14- to 17-month duration indicated that bridge structural metals, including steel, cast iron, aluminum, and galvanized steel corroded considerably less in CMA solutions than in NaCl solutions (18). CMA and KAc offer attractive alternatives to chloride-based chemicals due to their non-corrosive characteristics, benign impacts on surrounding soils and ecosystems, and minimized adverse human health effects. CMA works as a deicer similar to salt, yet it can require 50% more by weight than salt to achieve the same results. Both CMA and CMAK have been reported to react with cement and thus cause deleterious effects on concrete pavement (3). Other disadvantages of CMA include the air quality impacts, high cost of applications, and poor performance in thick accumulations of snow and ice and in temperatures below 23°F. New technologies have been developed to reduce the cost of CMA through a gasification/fermentation process to produce CMA from domestic wastes (19), or through a cheese-whey fermentation process to produce acetic acid that then reacts with dolomitic lime to produce CMA (20). Potassium acetate performs more quickly than CMA at lower temperatures, but is more costly than CMA; few studies have been done to examine its impacts on the environment (21). Acetate-based deicers have been used on some winter roadways. Formates (sodium formate and potassium formate) have also emerged as potential alternative deicers. However, these non-conventional deicers have not been widely used, mainly due to concerns over their high cost.

In addition, bio-based products have begun to offer new options for snow and ice control applications since the late 1990s, and they often come from the fermentation and processing of beet juice, molasses, corn, and other agricultural products (22, 23, 24).

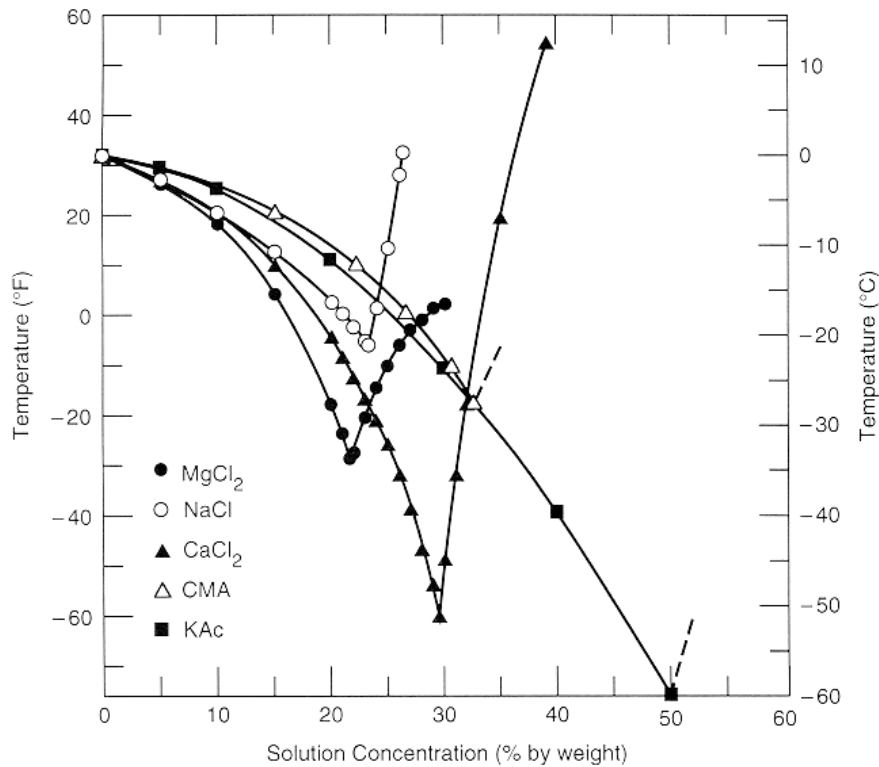
Recently glucose/fructose and unrefined sugar have been mixed in sand to prevent freezing and added in salt brine for anti-icing (25). Bio-based products are generally non-corrosive and offer great performance by significantly lowering the freezing point and enhancing the melting capacity of brine solutions. However, the deployment of commercially available bio-based products has been hindered by their high cost and concerns over their toxicity to the aquatic ecosystems adjacent to highways due to high phosphate, nitrogen, or total organic content. Such products can be very expensive if used alone; however, they are frequently mixed with other common deicers to lower their freezing point and inhibit their corrosivity (26). One product thoroughly studied is IceBan, a mix of  $MgCl_2$  and an agricultural byproduct. In an evaluation report, IceBan was found to exceed the PNS specifications for copper, zinc, and sulfate. IceBan was also found to have a pH less than 4.0, which could result in acidification of soils and cause leaching of metals into surrounding waters (12). Another concern when using biobased products is oxygen depletion. The organic materials of byproducts when broken down may cause temporary anaerobic soil conditions as well as oxygen depletion in surface waters. Oxygen depletion may also occur in waterways if too much phosphorus is present. Phosphorus spurs the growth of algae, reducing oxygen for other aquatic biota (8). In addition, biobased products often contain high concentrations of nitrates that may contaminate groundwater (8). The common bio-based products are proprietary products and include trade names such as IceBan, Caliber, and Dow Armor, all of which contain chloride salts and low molecular-weight carbohydrates derived from sugar beet, molasses, or corn, and there are user concerns over their possible attraction to wildlife or high phosphorus content (per the discussions on the Snow-Ice Listserv in 2005).

### ***1.2.2. Performance Measures for Deicers***

Roadway maintenance agencies need unbiased information for snow and ice control operations, especially when it comes to the selection, pricing and quality assurance of deicer products. As summarized in a recent report by Levelton Consultants (2), various performance measures have been established for evaluating the physical, chemical and

environmental attributes, and time-dependent performance measures of deicers, such as standard tests developed or adopted by the Strategic Highway Research Program (SHRP), PNS, American Society for Testing and Materials (ASTM), and American Association of State Highway and Transportation Officials (AASHTO).

To predict deicer performance in the field environment, laboratory experiments of ice melting (SHRP H-205.1 and H-205.2), ice penetration (SHRP H-205.3 and H-205.4), and ice undercutting (SHRP H-205.5 and H-205.6) have to be conducted under given temperatures, as described in SHRP test methods (27). Not only are such experiments time-consuming and labor-intensive, but it is also difficult to generate reproducible results. Other drawbacks include the differences between actual and theoretical performance and, more importantly, the difficulty “to predict or design for the optimum combination of deicer and associated practices” (2). Other SHRP tests are developed for evaluating the corrosive effects of deicers on metals (SHRP H-205.7, weight loss method); effects of deicer formulations and freeze/thaw cycling on the structural integrity of small test specimens of non-air-entrained concrete (SHRP H-205.8); scaling effects on horizontal concrete surfaces exposed to freezing-and-thawing cycles in the presence of deicers (SHRP H-205.9); frictional characteristics of deicers (SHRP H-205.10); ecological effects of deicers (SHRP H-205.11); and corrosive effects of deicing chemicals on steel reinforcement in concrete (SHRP H-205.12). The SHRP materials compatibility tests generally take advantage of ASTM test methods in quantifying the deicer effect on metals, nonmetals, concrete and pavement. There are additional SHRP tests used to characterize the physiochemical properties of deicers, such as moisture content, solubility, pH, and viscosities.



**Figure 1 Eutectic curves of five chemical solutions (33).**

Usually the theoretical melting capacities of a deicer product are characterized by its eutectic curve, or freezing point-concentration relationship. The *eutectic temperature* corresponds to the point at which the liquid phase borders directly on the solid phase; for a binary deicer-water phase diagram, this defines the lowest temperature at which a deicer can melt ice or snow. Figure 1 shows the eutectic curves of five chemical solutions (28). The eutectic temperature, however, does not provide a reliable forecast of the effective temperature range of chemicals for snow and ice control.

The PNS currently characterizes various deicer products using a large number of tests as listed in the 2006 Pacific Northwest Snowfighters Snow and Ice Control Chemical Products Specifications and Test Protocols (29): Percent Concentration of Active Ingredient in the Liquid; Weight per Gallon; Corrosion Control Inhibitor Presence and Concentration; pH; Corrosion Rate; Percent Total Settleable Solids and Percent Solids



Passing a 10 Sieve; Total Phosphorus; Total Cyanide; Total Arsenic, Barium, Cadmium, Chromium, Copper, Lead, Selenium and Zinc; Total Mercury; Milliequivalents or "meq"; Moisture Content of Solid Chemical Products; Gradation; Visual Inspection and Field Observations; Toxicity Test; Ammonia—Nitrogen; Total Kjeldalh Nitrogen; Nitrate and Nitrite as Nitrogen; Biological Oxygen Demand; Chemical Oxygen Demand; Frictional Analysis; Insoluble Material.

Notably, the recent report by Levelton Consultants anticipated the trend towards “performance-based methodologies” in determining procedures and how this can accommodate technical advances in measurement science (2), which is consistent with the tests completed in this research, such as the use of differential scanning calorimetry to assess effective temperature and ice-melting capacity of deicer products.

### **1.3. Objectives**

The overall goal of this project is to evaluate potassium acetate, sodium acetate/formate-blend deicers, and potassium formate as alternative anti-icing and deicing compounds relative to NaCl, salt-sand mixtures, and MgCl<sub>2</sub> (baseline deicers), based on various criteria specified by the CDOT RFP No: HAA 05-06/BL.

The project focused on the comparison of potassium acetate and sodium acetate/formate blends with NaCl, salt-sand mixtures (10%–25% salt by weight) and with MgCl<sub>2</sub> (27%–29% brine), in terms of their deicing performance and impacts on infrastructures and the environment. Potassium acetate and blends of sodium acetate/formate, and potassium formate were investigated as substitute experimental deicers.

In the first year of the two-year study, the research team collected data on potassium acetate, sodium acetate/formate blends, and potassium formate, and compared the data

with the two baseline deicers. Depending on the funding availability and the research findings from this project, CDOT will determine whether a second round (an additional two-year project) is warranted to further investigate acetate and formate, calcium chloride ( $\text{CaCl}_2$ ), and other proprietary brands of deicers.

This project collected data from literature reviews, laboratory tests and field investigations based on the following concerns and interests:

1. Advantage and disadvantage of using  $\text{NaCl}$  salt-sand mixtures and  $\text{MgCl}_2$  brine in the state of Colorado;
2. The reaction of the mixture of  $\text{KAc}$  and  $\text{MgCl}_2$  and how it will impact and be prevented on Colorado roads and highways;
3. The possible chemical reaction of  $\text{KAc}$  with concrete and asphalt pavements and the evaluation of how this reaction impacts public safety, the environment, and infrastructures;
4. The environmental impacts of  $\text{KAc}$  and the comparison with  $\text{MgCl}_2$  baseline deicers. The study includes the investigation of COD, BOD and other parameters in the receiving streams and reservoirs, both instantaneous and residual, from the deicing application;
5. The same assessment of  $\text{KAc}$  will be extended to investigate newly introduced deicers such as blends of sodium acetate/formate, potassium formate, and potassium acetate/formate blends.

To achieve the objectives of this project, the proposed research consisted of a synthesis of relevant literature coupled with laboratory tests and field investigations to evaluate potassium acetate, sodium acetate/formate-blend deicers, and potassium formate relative to  $\text{NaCl}$ , salt-sand mixtures, and  $\text{MgCl}_2$  brine.

## 1.4. How This Report Is Organized

The following chapter will discuss the methodology used in gathering and synthesizing information from the laboratory and field investigations as well as the surveys. Chapters 3–5 are literature review chapters that present a synthesis of information on how winter maintenance practices affect pavements, metals in transportation infrastructure, and the environment. Chapter 6 provides a synthesis of survey results. Chapters 7 and 8 present the laboratory and field data regarding the performance and impacts of deicers, respectively. Chapter 9 looks into potential interactions between mixed deicers. In general, each chapter is dedicated to a single theme. Finally, Chapter 10 summarizes the key findings from the previous nine chapters, presents research needs identified from this project, and concludes with suggestions and recommendations for implementation by CDOT. Appendices conclude this report.

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## CHAPTER 2. METHODOLOGY

### 2.1. Deicers or Other Materials Tested

The reagent-grade sodium chloride, NaCl (99%, solid) was purchased from ScienceLab.com (Houston, TX). The non-inhibited IceSlicer, distributed by EnviroTech Services (Greeley, CO), was provided by the Colorado Department of Transportation (CDOT) from its solid stockpile, consisting of naturally occurring complex chlorides (mostly NaCl) and more than 40 trace minerals. The MgCl<sub>2</sub>-based deicer was provided by the CDOT from its liquid tank, with active ingredient concentration of 27% to 29%. The solid CMA deicer was obtained from Cryotech (Fort Madison, IA) with 96% of hydrated calcium magnesium acetate. The reagent-grade potassium formate, KFm (99%, solid), was purchased from Alfa Aesar (Ward Hill, MA). The liquid deicer CF7<sup>TM</sup> was obtained from Cryotech (Fort Madison, IA) with 50% KAc. The NaAc/NaFm deicer was a blend made from NAAC<sup>TM</sup> (solid, 97% anhydrous NaAc, from Cryotech, Fort Madison, IA) and Peak SF<sup>TM</sup> (98% granulated NaFm, from the BlackFoot Company, Toledo, OH) at 50:50 weight ratio. The IceBan deicer provided by CDOT was an agr-based product of Earth Friendly Chemicals with MgCl<sub>2</sub> as active ingredient. It should be noted that the test solution of CMA, CF7, NAAC, Peak SF and IceBan deicers contained 18.4mM, 0.2mM, 6.6mM, 11.4mM, and ~200mM of chloride, respectively, based on chloride sensor measurements. The deicers and reagent-grade chemicals used in various laboratory tests are listed in Table 1. This research was intended to focus on testing NaCl and MgCl<sub>2</sub> compared to sodium and potassium acetate/formate based deicers. Additional deicers were tested when available. Not all deicers listed in Table 1 were used in each test due to time and funding constraints.

An ASTM specification C150-07 Type I/II low-alkali portland cement (ASH Grove Cement Company, Clancy, MT) was used in this study. The chemical composition and physical properties of the cement are listed in Tables 2 and 3, respectively.

**Table 1 Deicers or chemicals tested in this study.**

Deicer	Reagent grade (r) /Commercially available (c)	Distributor	Liquid (l) / Solid (s)	Active Ingredient	Active Ingredient concentration	Tests used in
sodium chloride	r	ScienceLab.com	s	NaCl	99%	SHRP 205.1,3,5,8, Chloride Diffusion, Electrochemistry, PNS/Nace Corrosion test, Tribometer, DSC
sodium chloride-sand*	c	Colorado DOT	s	NaCl	10-25%**	SHRP 205.8, Electrochemistry
calcim chloride	r	Acros Organics	s	CaCl <sub>2</sub> dihydrate	99%	Chloride Diffusion
potassium formate	r	Alfa Aesar	s	K(CHOO) <sub>2</sub>	99%	SHRP 205.8,
IceSlicer*	c	EnviroTech Services	s	NaCl	100%	SHRP 205.1,3,5,8, Electrochemistry, PNS/Nace Corrosion test, Tribometer, DSC
CDOT blended Magnesium chloride*	c	Colorado DOT	l	MgCl <sub>2</sub>	27-29%	SHRP 205.2,4,6,8, Chloride Diffusion, Electrochemistry, PNS/Nace Corrosion test, Tribometer, DSC
Apex Meltdown*	c	EnviroTech Services	l	MgCl <sub>2</sub>	27-29%	SHRP 205.2,4,6, PNS/Nace Corrosion test, DSC
Geomelt C	c	America West Environmental Supplies, Inc.	l	CaCl <sub>2</sub>	32.4%	DSC
Geomelt 55	c	SNI Solutions	l	CaCl <sub>2</sub>	NA	DSC
NAAC	c	Cryotech	s	Na(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub>	97%	SHRP 205.1,3,5,8, Electrochemistry, PNS/Nace Corrosion test, Tribometer, DSC
Peak SF	c	The Blackfoot Company	s	Na(CHOO) <sub>2</sub>	98%	SHRP 205.1,3,5, PNS/Nace Corrosion test, Tribometer, DSC
CF7	c	Cryotech	l	K(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub>	50%	SHRP 205.4,6,8, Electrochemistry, PNS/Nace Corrosion test, Tribometer, DSC
CMA	c	Cryotech	s	CaMg(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub>	96%	SHRP 205.1,5,8, DSC
IceBan*	c	Earth Friendly Chemicals	l	MgCl <sub>2</sub>	26%	SHRP 205.2,4,6, Electrochemistry, PNS/Nace Corrosion test, Tribometer, DSC

\*Provided by CDOT out of stockpiles or tanks.

\*\*CDOT generally uses 5-18% salt-sand blend.



**Table 2 The chemical composition of the type I/II portland cement.**

<b>Item</b>	<b>Specification Limit</b>	<b>Test Result</b>
SiO <sub>2</sub> (%)	N/A	20.4
Al <sub>2</sub> O <sub>3</sub> (%)	6.0 max	3.7
Fe <sub>2</sub> O <sub>3</sub> (%)	6.0 max	3.2
CaO (%)	N/A	63.3
MgO (%)	5.0 max	3.2
SO <sub>3</sub> (%)	3.0 max	2.6
Loss on Ignition (%)	3.0 max	2.7
Na <sub>2</sub> O (%)	N/A	0.1
K <sub>2</sub> O (%)	N/A	0.4
Insoluble Residue (%)	0.75 max	0.43
CO <sub>2</sub> (%)	N/A	1.7
Limestone (%)	5.0 max	4.0
CaCO <sub>3</sub> in Limestone (%)	70 min	98
Tot. Alkalies (% as Na <sub>2</sub> O)	0.60 max	0.37
<b>Potential Compound Composition (%)</b>		
C <sub>3</sub> S	N/A	56
C <sub>2</sub> S	N/A	16
C <sub>3</sub> A	8.0 max	4.5
C <sub>4</sub> AF	N/A	10
C <sub>4</sub> AF+2(C <sub>3</sub> A)	N/A	19
C <sub>3</sub> S+4.75(C <sub>3</sub> A)	100 max	78

**Table 3 The physical properties of the type I/II portland cement.**

<b>Item</b>	<b>Test Method</b>	<b>Specification Limit</b>	<b>Test Result</b>
Air Content of Mortar(%)	C185	12.0 max	7.9
Blaine Fineness,m <sup>2</sup> /Kg	C204	280 min	397
Air Permeability Test		420 max	
Autoclave Expansion(%)	C151	0.80 max	0.03
Normal Consistency(%)	C187	N/A	26.6
Compressive Strengths, psi (MPa)	C109		
1-Day		N/A	1998 (13.8)
3-Day		1740(12.0)min	3472 (23.9)
7-Day		2760(19.0)min	4600 (31.7)
Setting Times(minutes)	C191		
Vicat Initial		45 min	111
Vicat Final		375 max	240
Pass 325 Mesh(%)		72 min	98.7
Heat of Hydration (cal/g)-7days		N/A	70.7
False set(%)	C451	50 min	85

## **2.2. Lab and Field Data Collection**

### ***2.2.1. Ice Melting Capacity of Deicers***

Laboratory measurements of ice melting capacity of various deicers were conducted following the SHRP (Strategic Highway Research Program) H205.1 and H205.2 test methods (1). The SHRP H205.1 test measures the ice melting capacity of solid deicer pellets spread randomly across an ice surface of uniform thickness. The results of the test provide a measurement of the ice melting capacity of the deicer relative to the generated brine, or melted ice. The test utilized 25 ml of de-ionized water to form a sheet of ice of uniform thickness in a 3.5 cm (radius) Petri<sup>®</sup> dish. Once frozen, ice extrusions protruding from the ice surface were melted. The sample was then refrozen for 24hrs to equilibrate. After equilibration at the desired temperature, 1g of solid was broadcast over the ice specimen. At 10, 20, 30, 45, and 60 minutes after application of deicer, the generated brines were removed from the specimen dish, and weighed. The generated brine was then reintroduced to the same specimen dish. The process of brine removal, weighing, and

reintroduction was completed within one minute for each sample. The process was completed at 0°C, -5°C, -18°C (32, 23, -0.4°F). Special consideration was taken to use separate weighing dishes for each deicer to avoid cross-contamination.

For liquid deicing solutions (SHRP H205.2), similar procedures were followed except that 0.9g of liquid deicer was pipetted onto the ice surface. The liquid MgCl<sub>2</sub>-based product was applied at 27% to 29% concentration, and liquid IceBan was applied at the vendor-mixed concentration.

### ***2.2.2. Ice Penetration of Deicers***

Laboratory measurements of ice melting capacity of various deicers were conducted following the SHRP H205.3 and H205.4 test methods. The SHRP H205.3 test measures the penetration behavior of solid deicer pellets on a cylinder of ice. The results of this test provide a measure of the penetration rate of the selected deicer over time. A 0.50in thick (1.3cm) plexi-glass with dimension 2in × 8in (5cm × 20cm) had 10 cavities drilled vertically along the margin using a 5/32in (0.4cm) drill bit to a depth of 3.5cm with 1.7cm spacing between cavities. The cavities were then enlarged at the top with a countersink bit, to create a surface cone. These cavities were filled with de-ionized water and then frozen for 12-24 hours. The solid deicers were placed in the same freezer to ensure equilibration to the test temperature. Once completely frozen, any extrusions of ice were melted. The top of the ice surface was then wiped with an absorbent tissue to remove all liquid water and the apparatus was replaced in the freezer for an additional 1-2 hours to re-equilibrate. A pellet of solid deicer was weighed and placed on the surface of the ice specimen along with a dye solution (McCormick®, red) and was placed in the freezer. The penetration depth of each pellet was measured using a ruler at 10, 20, 30, 45, and 60 minutes. The process was carried out at 0°C, -12°C, and -20°C (32, 10.4, and -4°F) in triplicate.

For liquid deicing solutions (SHRP H205.4), similar procedures were followed except that 25 ml of liquid deicer were mixed with two drips of dye (McCormick®, red). The dyed liquid deicer solution was mixed and allowed to equilibrate to the given test temperature during the freezing of the ice specimen. Three drops of dyed liquid deicer solution were pipetted onto the ice specimen. The liquid MgCl<sub>2</sub>-based products were applied at 27% to 29% concentration, the liquid CF7 was applied at 45% to 50% concentration, and the liquid IceBan was applied at the vendor-mixed concentration.

### ***2.2.3. Ice Undercutting of Deicers***

Laboratory measurements of ice melting capacity of various deicers were conducted following the SHRP H205.5 & H205.6 test methods. The SHRP H205.5 test measures the ice undercutting ability of a solid chemical deicer. The results of the test provide an area where the ice-cement bond has been broken by the deicer as a function of time. Portland cement concrete blocks were made 6in × 9in × 2in (15.2cm × 22.8cm × 5.1cm) and allowed to cure in the mold for 48 hours in a wet chamber. The concrete blocks were then de-molded and placed in a saturated lime solution for 28 days to cure. Once removed from the lime solution, the substrate was washed and allowed to dry. A 1in-wide (2.54cm) rubber strip was affixed to the exterior of the concrete block forming a wall around the substrate. The interface between the substrate and the rubber wall was sealed using silicon sealant.

Subsequently, 150ml of de-ionized water were allowed to freeze on top of a concrete block for 12 to 24 hours. The solid deicers were placed in the freezer to equilibration to the test temperature. Two drops of dye (McCormick®, red) were deposited at three equally spaced locations across the ice surface and were allowed to freeze for 3-4 hours. Two weighed deicer pellets were placed at the center of each frozen red dye stain. Photographs were taken at 10, 20, 30, 45, and 60 minutes. The process was carried out at 0°C, -6°C, -10°C, and -16°C (32°F, 21.2°F, 14°F, and 3.2°F) in triplicate. The digital

pictures taken of the undercut area were imported into Adobe Photoshop™ CS2. The magic wand, polygon selection, lasso selection, and pixel count tools were used to select the extent of undercut area. A pixel count was obtained of the given selection and an area of undercut substrate was calculated for each photo. For liquid deicing solutions (SHRP H205.6), similar procedures were followed with the exception that when the ice specimen was completely frozen, a 0.5in metal rod was heated and pressed vertically at three evenly spaced locations across the specimen. The resulting liquid was wiped clean, leaving a shallow cylinder free of ice terminating at the concrete surface. Three drops of dyed deicer liquid solution were pipetted into the center of the three shallow holes. The liquid MgCl<sub>2</sub>-based products were applied at 27% to 29% concentration, the liquid CF7 was applied at 45% to 50% concentration, and liquid IceBan was applied at the vendor-mixed concentration.

#### ***2.2.4. Freeze-Thaw Testing of PCC in the Presence of Deicers***

Laboratory measurements of changes to PCC (portland cement concrete) through freeze/thaw testing in the presence of deicers were conducted following the SHRP H205.8 test method. The SHRP H205.8 test evaluates the effects of chemical deicing formulations and freeze/thaw cycling on the structural integrity of concrete test specimens of non-air-entrained concrete. The method quantitatively evaluates degradation of the specimen through weight-loss measurements. This test method is not intended to be used in determining the durability of aggregates or other ingredients of the concrete. An ASTM specification C150-07 Type I/II low-alkali portland cement (ASH Grove Cement Company, Clancy, MT) was used in this study. The fine aggregates used were river sand sifted to allow a maximum aggregate size of 0.05in (1.18mm) before proportioning and admixing. The coarse aggregates used had a maximum size of 0.375in (0.95cm). The concrete mix design had a water-to-cement ratio ( $w/c$ ) of 0.51, a coarse-aggregate-to-cement ratio of 2.36, and a fine-aggregate-to-cement ratio of 1.75. The fresh concrete featured a slump of nearly zero and air content of 3%. Concrete specimens were made in 1.5in diameter  $\times$  1.875in height (3.8cm  $\times$  4.8cm) poly(vinyl chloride) piping

with a volume of 54cm<sup>3</sup>. Concrete specimens were cured to the standards set forth by the SHRP H205.8 testing protocol in a moist cure room. The 28-day compressive strength of test cylinders was 6619 psi, well above the recommended 4000 psi.

Once fully cured the samples were allowed to dry overnight and then weighed. The samples were then placed on a sponge inside a dish containing 310ml of deicer solution. The specimens were then covered with plastic wrap. The deicer solutions were 3% by volume for liquids and 3% by weight solution for solids using de-ionized water. Four concrete specimens were tested in each deicer solution. The test specimens were placed in the freezer for 16 to 18 hours at  $-17.8 \pm 2.7^{\circ}\text{C}$  ( $-0.04^{\circ}\text{F}$ ). The specimens were then placed in the laboratory environment at  $23 \pm 1.7^{\circ}\text{C}$  ( $73.4^{\circ}\text{F}$ ) and with a relative humidity ranging from 45 to 55 percent for 6 to 8 hours. This cycle was repeated 10 times. The test specimens were then removed from the dish and rinsed under running water to remove any scaled off material. The test specimens were air dried overnight before the final weight was recorded.

#### ***2.2.5. SEM/EDX Measurements***

Following the SHRP H205.8 freeze-thaw test, the concrete specimens were used for FESEM and EDX testing. For surface analyses, a 0.2in-thick (0.5cm) slice sample was cut from the bottom of each remaining concrete specimen, using a concrete saw with a diamond crusted blade. These samples were then washed with de-ionized water before being desiccated for seven days prior to surface analyses.

The newly cut concrete surface was subjected to field emission scanning electron microscopy (FESEM) and energy-dispersive X-ray spectroscopy (EDX), in order to examine its localized morphology and elemental distributions at the microscopic level. We used a Zeiss Supra 55VP PGT/HKL system coupled with the energy dispersive X-ray analyzer. The EDX data were obtained using a micro-analytical unit that featured the

ability to detect small variations in trace element content. We used FESEM/EDX under a pressure of typically of  $10^{-5}$ - $10^{-4}$  torr to investigate the effect of deicers on the morphology and chemistry of cement hydrates by collecting data from multiple selected sites from the cement paste.

### ***2.2.6. Thermal Properties of Deicers***

Laboratory testing was conducted using differential scanning calorimetry (DSC) to quantify the thermal properties of deicers. The DSC (TA Instruments Q200) was set to run from 25 to  $-60^{\circ}\text{C}$  ( $77$  to  $-76^{\circ}\text{F}$ ) with cooling/heating rates of  $2^{\circ}\text{C}$  per minute. All samples were run as liquids. Solid samples were made into a saturated liquid solution with de-ionized water. Samples were run at 1.5:1 dilution. Ten  $\mu\text{l}$  of each sample were pipetted into the aluminum test chamber and sealed, and then weighed. All samples were run in triplicate.

### ***2.2.7. Friction Coefficient of Deiced Pavement***

Concrete samples were made 1.2in diameter x 0.4in thick ( $3\text{cm} \times 1\text{cm}$ ) with a water-to-cement ratio of 0.46 and sand and aggregate sizes no greater than 0.07in (0.17cm). Samples were cured in the moist cure room for 28 days at approximately 100% humidity. The compressive strength of the concrete at seven days was 4929 psi.

Concrete samples and the deicers were brought to the CSM Instruments Laboratory (Needham, MA) where 1.7 ml of de-ionized water was allowed to freeze (approximately 30 minutes) on the concrete surface to a thickness of approximately 0.08in (0.2cm). Samples were prepared at freezer temperature  $-16.5 \pm 1.5^{\circ}\text{C}$  ( $2.8 \pm 3.0^{\circ}\text{F}$ ) and humidity  $50.6\% \pm 11.6\%$ . Testing was conducted at lab temperature  $24^{\circ}\text{C}$  ( $74.8^{\circ}\text{F}$ ) and 30% humidity. Deicers were then applied to ice surface and allowed to sit for five minutes in

the freezer. Samples were then loaded onto the tribometer and run for 100 laps at 3 cm/s with a 0.4in (1cm) diameter and 5 Newtons of force applied. The pin was cleaned between each sample using water and isopropyl alcohol. The liquid deicers were diluted to 3% by volume and two drops were pipetted onto the surface. Solid deicer was weighed and applied so that by weight the deicer did not exceed 3% concentration if all the ice on the sample was melted. Each deicer was run at least in triplicate.

#### ***2.2.8. PNS/NACE Corrosion Test***

This test method is based on the National Association of Corrosion Engineers (NACE) Standard TM0169-95 as modified by the Pacific Northwest Snowfighters (PNS). It measures the weight loss of steel coupon samples that are cyclically immersed in deicer solutions. The metal coupons were purchased from Ad-Tek, Inc., and were 0.5in flat steel washers (0.38in x 0.56in x 0.11in or 0.97cm x 1.42cm x 0.28cm) with an average density of 7.85 g/cm<sup>3</sup>. The metal coupons were cleaned by placing in 1+1 hydrochloric acid for 2-3 minutes. The coupons were rinsed in tap water, then de-ionized water, then wiped dry and placed in chloroform. The coupons were then placed in the fume hood and were allowed to dry for 15 minutes. The coupons were then weighed and placed on the corrosion testing machine (Corrosion Testing Machine CTM10- 10/50, AD-TEK, Inc.).

The corrosion testing machine cyclically lowered the three metal coupons for 10 minutes into a 3% deicer solution and then raised the metal coupons into ambient air for 50 minutes. This cycle continued every hour for 72 hours. The solid deicers were 3% weight-to-volume solutions were made and for liquid deicers were 3% volume-to-volume solutions. The final weight of the coupons was recorded after 72 hours of cyclic testing and cleaning. Room temperature and humidity readings were recorded three times each day.



### ***2.2.9. Deicer Corrosivity Test using Electrochemical Techniques***

Corrosion of mild steel (ASTM A36) and galvanized guardrail steel (Trinity Highway Products) was measured using a Gamry Instruments® Potentiostat with an 8-channel Electrochemical Multiplexer ECMB. Deicer solutions were 3% by weight for solid and by volume for liquid samples, made with de-ionized water. Prior to testing, the metal samples were cleaned with acetone, de-ionized water, and were then dried. Four samples of each metal type were placed in the deicer solution and the open circuit potential (OCP) was monitored for 48 hours.

Electrochemical techniques provide an attractive alternative to the gravimetric method (e.g., PNS/NACE test) in terms of allowing for rapid determination of corrosion rates of metals and revealing information pertinent to the corrosion mechanism and kinetics. As such, at 48 hours of immersion in the deicer solution, the weak polarization curve of each metal sample was taken to rapidly measure the corrosivity of the deicers. Weak polarization is an experimental technique that measures the current-potential relationship of a metal in the electrolyte when an external potential signal (perturbation) is applied within  $\pm 120\text{mV}$  range of its corrosion potential ( $E_{\text{corr}}$ ) at a given sweeping rate.

Such a current-potential plot, known as a potentiodynamic polarization curve, provides information on the corrosion mechanisms occurring at the metal/electrolyte interface as well as the instantaneous corrosion rate of the metal, based on which the corrosivity of various deicers can be evaluated.

### ***2.2.10. Corrosion of Metals in the Field***

Metal samples of mild steel (ASTM A36) and galvanized guardrail steel (Trinity Highway Products) were cut by CDOT at the Greeley, Colorado machine shop to 1in x

2in (2.5cm × 5.1cm), and brought back to the WTI Corrosion and Sustainable Infrastructure Laboratory (CSIL) for labeling, cleaning, and weighing prior to field deployment. Samples were washed with de-ionized water, rinsed with acetone, and dried. The average weight of the mild steel and galvanized guardrail samples was  $33.6578 \pm 0.6428\text{g}$  and  $31.1101 \pm 1.1512\text{g}$ , respectively. Samples were placed on wood boards and fixed in place with plastic coated wire, so that there was no metal-on-metal contact avoiding galvanic corrosion issues. Samples were placed in the field at the three selected sites: at the junction of Hwy 34 and Business Route 34 in Greeley, on Hwy 25 at mile 167 (north bound) in Castle Rock, and on Hwy 82 at the irrigation station (north bound) in Aspen. A total of 12 samples, six each of mild steel and galvanized guardrail, were deployed at each site.

Greeley has an approximate elevation of 4642ft and average annual snowfall of approximately 55in. Castle Rock has an elevation of 6210ft and average annual snowfall of 62.2in. Aspen has an elevation of 7908ft and average annual snowfall of approximately 300in.

The original samples were deployed at the field sites on March 21, 2007. The metal samples were stolen from the Greeley and Castle Rock field sites at some point after their deployment. On July 8, 2007, new metal samples were re-deployed at all three field sites.

Pictures were taken in the field at each site visit. The initial samples were removed from the field the week of March 10-14, 2008 and the remaining samples were removed July 23, 2008. In the CSIL weight loss was determined by three methods: 1) metal samples were weighed once upon arrival, 2) metal samples were rinsed with de-ionized water and then acetone, and 3) mild steel samples only were cleaned with acid to remove all rust and were then rinsed with de-ionized water. The acid cleaning method was not used on the galvanized steel because it would have removed the zinc layer and given an

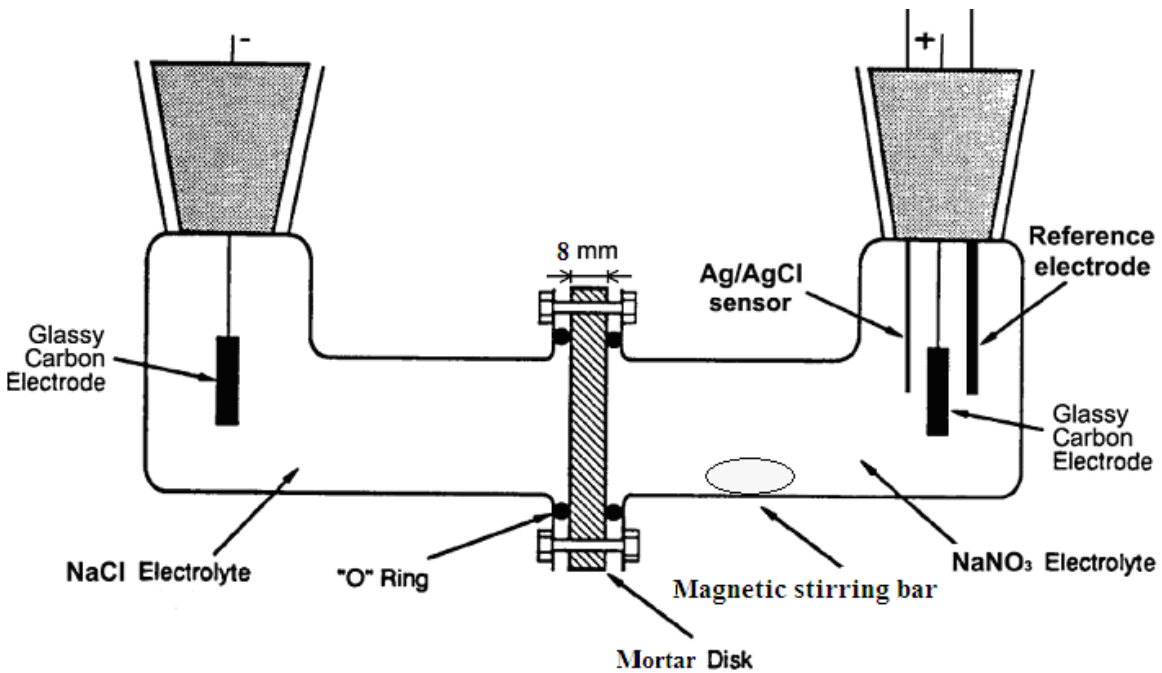
artificially high weight loss value. All samples were allowed to air dry for 15 minutes and were then weighted. Visual observations were noted as well.

### ***2.2.11. Electrically Accelerated Test of Chloride Diffusion Coefficient in Cement Mortar***

Mortar samples were made using a bench top mixer (Kitchen Aid) with a 0.45 water-to-cement ratio and a fine-aggregate-to-cement ratio of 1.75. Samples were 1in in diameter  $\times$  0.3in thick (2.5cm  $\times$  0.8cm). The fine aggregates used were river sand sifted to allow a maximum aggregate size of 0.05in (1.18 mm) before proportioning and admixing. They were oven dried for 24 hours before cooling to room temperature, and then 3% additional water was added to bring the sand to surface-saturated-dry (SSD) conditions. Samples were prepared on a vibrating table to remove air pockets and cured for 28 days prior to use in a moist cure room. Samples were de-molded after 28 days and polished with 40-grit sand paper to a uniform surface thickness and roughness.

The chloride ion permeability of the PCC mortars was determined through electromigration experiments, conducted using the glass cell shown in Figure 2. The glass cell featured a disc-shaped mortar sample that separates the chloride anion source (25ml 3% deicer solution) and the chloride anion destination (25ml 4.3% NaNO<sub>3</sub> solution). Each of the two compartments contained one glassy carbon electrode with an exposed surface area of 0.16in<sup>2</sup> (1cm<sup>2</sup>). Once the mortar disc, electrolytes, and electrodes were in place, an 8-volt DC electric field was maintained across the disc through the two carbon electrodes in the two compartments. During the test, readings of chloride concentration were taken using a computerized chloride sensor (WQ Chloride ion selective sensor, Nexsens, Beavercreek, OH), on a five minute interval. In addition, the electric current passing through the disc was monitored using a Potentiostat/Galvanostat (Model 263A). Prior to running the experiment, the chloride sensor was calibrated using known solutions

and this calibration was checked on a daily basis. The readings from the chloride sensor were converted to units of molarity and plotted versus time.



**Figure 2 Experimental setup for the electro-migration tests. The Ag/AgCl sensor was an ion selective chloride sensor (WQ-Cl, Nexsens).**

### *2.1.12. Modeling of Chloride Diffusion through PCC*

Chloride penetration into concrete is the main cause of steel deterioration in concrete structures exposed to chloride-laden environments. Through the use of deterioration models, cost-effective decisions can be made concerning the time to repair or replace existing structures, and the most effective corrosion abatement systems. Khatri and Sirivivatnanon (2) proposed a model for predicting the service life of reinforced concrete structures, where the acceptable level of deterioration is related to the presence of chloride ions on the rebar surface. As such, the service life is defined as the time required for transport processes to raise the chloride content at the depth of the rebar to the threshold level for pitting corrosion. It should be mentioned that the service life is not a

fixed value as calculated by a deterministic model, but instead it is a range of values determined by material characteristics, cover depth, and severity of service environments.

The diffusion of chloride ions in water-saturated cement is a complex process involving various physical and chemical interactions. The chloride ions can be bound either physically or chemically by cement paste, thereby lowering the fraction of free chlorides that can diffuse freely in the pore solutions. In addition, the internal electric field formed by the cations and anions will speed up the ions that have low diffusion coefficients and slow down the ions that have high diffusion coefficients to maintain the electro-neutrality condition. If we ignore such complex internal processes and treat the diffusion problem phenomenologically, the temporal and spatial evolution of chloride-ion concentration can be calculated based on Fick's second law in Eqn. (1) (3,4), which has been used extensively by many researchers to calculate the chloride concentrations for various concrete cover depths at different exposure time intervals:

$$\frac{\partial C}{\partial t} = D_c \frac{\partial^2 C}{\partial x^2} \quad (1)$$

where  $C$  is the concentration ( $\text{mol m}^{-3}$ );  $t$  is the time (s);  $D$  is the diffusion coefficient ( $\text{m}^2 \text{s}^{-1}$ );  $\chi$  is the position (m). In this work, the service life or the length of the corrosion initiation stage is approximated with the following simplified assumptions:

- The concrete is initially chloride-free, and the concrete acts as a physical barrier to protect the rebar. The rebar corrosion is triggered only when the concrete in contact with the steel becomes contaminated with chloride ions exceeding a threshold concentration value.
- Chloride ions progress inward from the external surface of the concrete, which is covered by aqueous solutions of chlorides from deicers and precipitation. Therefore, the concrete immediately below the surface acquires a surface chloride concentration that remains unchanged in the simulation.

- Chloride ions progress inward by simple diffusion, driven by the gradient of the concentration of chloride ions in the concrete. The effective diffusion coefficient is constant with time and space, and is a property of the concrete between the concrete surface and the steel rebar.

Based on these assumptions, an analytical solution exists to predict the spatial and temporal evolution of chloride concentration profiles, which is given by (2,3,5):

$$C_t = C_s [1 - \operatorname{erf}(\frac{x}{2\sqrt{D_c t}})] \quad (2)$$

where  $x$  is the concrete cover depth;  $C_t$  is the chloride concentration at cover depth;  $C_s$  is the surface chloride concentration;  $t$  is time;  $D_c$  is the effective diffusion coefficient in concrete;  $\operatorname{erf}$  is the Gaussian error function as below (3):

$$\operatorname{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-t^2} dt \quad (3)$$

Eqn. (2) can be used to calculate the service life of a concrete cover, provided that  $C_t$ ,  $C_s$ ,  $D_c$  and  $x$  are known.

Concrete is a multiphase porous composite consisting of cement paste and aggregates, in both of which phases pores exist. Chloride ions can only diffuse in the pore solutions. Effective diffusion coefficients of chloride, characterizing the resistance of concrete to diffusive ingress of chlorides, are therefore considered to be a function of the characteristics of the cement paste and the aggregates. The rate at which chloride ions ingress into water-saturated concrete depends on the diffusion coefficients in cement

paste and aggregates as well as the aggregates fraction. Additionally, the rate of ingress is also influenced by the cement paste/aggregate interfacial (ITZ) zones and internal cracks. Prediction of effective chloride diffusion coefficients in concrete based on its mixture proportions is needed for service life evaluation. If the roles of ITZ and internal cracks on chloride ingress can be ignored, the effective diffusion coefficient of chloride in water-saturated concrete can be calculated by (6):

$$D_c = \frac{[(D_a - D_p)V_a + (D_p + D_a)]D_p}{(D_p + D_a) + (D_p - D_a)V_a} \quad (4)$$

where  $D_p$  and  $D_a$  are the chloride ion diffusion coefficients in the cement paste and aggregates, respectively, and  $V_a$  is the aggregate volume fraction.

If the aggregates have a lower diffusion coefficient than the cement paste, the concrete will have a lower diffusion coefficient than the cement paste. Therefore, chloride ion ingress will decrease with the increase in the aggregate volume, and controls are necessary on the quantity of cement paste and aggregate in order to achieve a specified service life. The diffusion coefficient of chloride ions in aqueous solutions (7), cement paste (8) and marble (6) has the order of  $10^{-9}$  m<sup>2</sup>/s,  $10^{-12}$  m<sup>2</sup>/s and  $10^{-15}$  m<sup>2</sup>/s, respectively. Accordingly, it can be assumed that diffusion of chloride ions in aggregates of concrete is negligible, leading to:

$$D_c = \frac{(1 - V_a)}{(1 + V_a)} D_p \quad (5)$$

Thus, at  $V_a = 0.7$ , the effective diffusion coefficient predicted from Eqn. (5) is:

$$D_c = 0.1765 D_p \quad (6)$$

The chloride threshold value is required in the assessment of service life when chloride-induced corrosion is the failure mechanism. Choosing an accurate value for  $C_t$  is a great challenge as this parameter varies over a wide range of reported values. The chloride threshold level is commonly presented as total chloride content expressed relative to the weight of cement, which is favored because of the availability of relatively simple means to derive data. A summary of chloride threshold levels inferred from extensive published data was given by Glass and Buenfeld (9) as well as Alonso et al. (10), where the critical chloride levels ranged from 0.17% to 2.4%. Evidently, despite such abundant data in the literature, no agreement among the obtained values is found. This lack of accordance is due to the existence of several processing parameters, such as concrete mixing proportions, moisture content in the concrete, temperature, and types of cations, which may affect the cement binding ability and, therefore, the amount of free chlorides able to depassivate the steel. Recently, it has been shown that corrosion initiation is more dependent on the chloride and hydroxyl ratio or free chloride concentration in the concrete pore solutions than the chloride threshold value (10), from which the corrosion initiation criterion can be given by:

$$\frac{[\text{Cl}^-]}{[\text{OH}^-]} \geq 0.6 \quad (7)$$

where  $[\text{Cl}^-]$  and  $[\text{OH}^-]$  are the concentration for free  $\text{Cl}^-$  and  $\text{OH}^-$ , respectively.

In concrete, the typical pH value in pore solutions is 13.5, which corresponds to the  $\text{OH}^-$  concentration of 0.3162 M in the pore solutions. As such, it follows from Eqn. (7) that the minimum chloride concentration for steel to initiate pitting corrosion,  $C_t$ , is 0.1897 M.



### ***2.1.13. Chloride Penetration and Weight Loss of Field Concrete***

The concrete samples were made in Greeley with the help of CDOT personnel. Materials (type I portland cement and aggregates with maximum size 0.375in (1cm) from the CDOT stockpiles were used to fabricate the samples. Nine samples were made based on the SHRP H205.8 (reference Freeze/Thaw Testing of PCC in the Presence of Deicers). Samples were mixed by hand because of the small batch size and carefully compacted to minimize the amount of entrapped air. The samples sat covered for 24 hours and were then removed from their molds and placed in lime water for curing for 28 days. Concrete samples were placed in the field at the three sites, with three concrete blocks deployed at each site.

The original samples were deployed at the field sites on March 21, 2007. Concrete samples were stolen from the Greeley and Castle Rock field sites at some point after their deployment. On July 8, 2007, new concrete samples were re-deployed at the Greeley and Castle Rock field sites.

Pictures were taken in the field at each site visit. The initial samples were removed from the field the week of March 10-14, 2008 and the remaining samples were removed July 23, 2008. Collected samples were weighed and visually inspected for scaling, cracking, and other defects. Samples were sliced into four equal sections and the spatial distribution of chloride was determined through the application of  $\text{AgNO}_3$  and then  $\text{K}_2\text{CrO}_4$  on the concrete surface, which was cut and wiped clean, revealing a brown-red color in the areas where chloride is not present, and turning the concrete bright yellow where chloride is present (11).

#### ***2.1.14. Water Quality***

Water sampling was conducted at three field sites in Colorado (Greeley, Aspen, and Castle Rock) with the intention of observing the effect of deicers on water quality over time. Water quality parameters of interest include: ambient air temperature, relative humidity, water temperature, flow rate, pH, turbidity, dissolved oxygen (DO), biological oxygen demand (BOD), chemical oxygen demand (COD), chloride (Cl<sup>-</sup>) concentration, total Kjeldahl nitrogen (TKN), and PO<sub>4</sub><sup>3-</sup>. Data related to meteorological conditions, average daily traffic (ADT), and winter maintenance treatments of the roadways during the storm events were also collected. Water samples were tested by the Colorado Department of Public Health and Environment for the relevant parameters.

#### ***2.1.15. Effects of Mixing Deicers***

To test the potential interactions between different deicers, we mixed selected deicing products at equal concentration (e.g., 50:50, MgCl<sub>2</sub>+KAc). The starting deicer concentrations were vendor-mixed (e.g., MgCl<sub>2</sub> 27-29% and KAc ~50%), or vendor recommended if the deicer was reagent grade, to simulate the observed reactions at ambient conditions.

Solutions of de-ionized water (DI), MgCl<sub>2</sub>, NAAC, NaFm (reagent grade), CF7, KFm (reagent grade), NaAc/NaFm (NAAC and Peak SF) (50:50 blend), and KAc/KFm (CF7 and reagent grade) (50:50 blend) were made. All acetate- and formate-based deicers were mixed at a 50:50 ratio with MgCl<sub>2</sub> in 100ml beakers and agitated with magnetic stir bars for the length of the experiment. Data were collected on day 1 every hour for eight hours, and then after that once a day at the same time each day for a total of seven days. Photographs were taken throughout the experiment. The average ambient air temperature was 22.6 ± 1.0°C (72.7°F) and average deicer solution temperature was 24.8 ± 1.1°C (76.6°F). The relative humidity ranged from 35% to 52% with an average of 44%.

At the end of the experiment precipitated material was extracted from the sample solution and transferred to 100mL beakers. Samples were placed in the oven to dry at 35°C (95 °F). Solids were then crushed with a mortar and pestle and combined with pre-dried Fourier Transform Infrared (FT-IR) grade potassium bromide using KBr/sample mass ratio of 100, and were then pressed into pellets. The FTIR spectra of prepared samples were collected and analyzed in order to determine whether a chemical reaction occurred after the mixing of two different deicers. The infrared spectra of the prepared samples were collected using a Thermo Nicolet Nexus 670 FT-IR spectrometer over the wavelength range of 4,000 to 400  $\text{cm}^{-1}$ . Each sample was scanned 64 times. Sample spectra were baseline corrected to account for instrument and atmospheric effects.

FTIR spectroscopy is an analytical technique that measures the infrared intensity versus wavelength (wavenumber ( $\text{cm}^{-1}$ )) of light. Infrared spectroscopy detects the vibration characteristics of chemical functional groups in a sample as they stretch, contract and bend when exposed to infrared light. As a result, a chemical functional group adsorbs infrared radiation in a specific wavenumber range regardless of the structure of the rest of the molecule, the effect of temperature, pressure, sampling, or change in the molecular structure in other parts of the molecules. Therefore the presence of specific functional groups can be monitored by signals in certain wavenumber ranges (12).

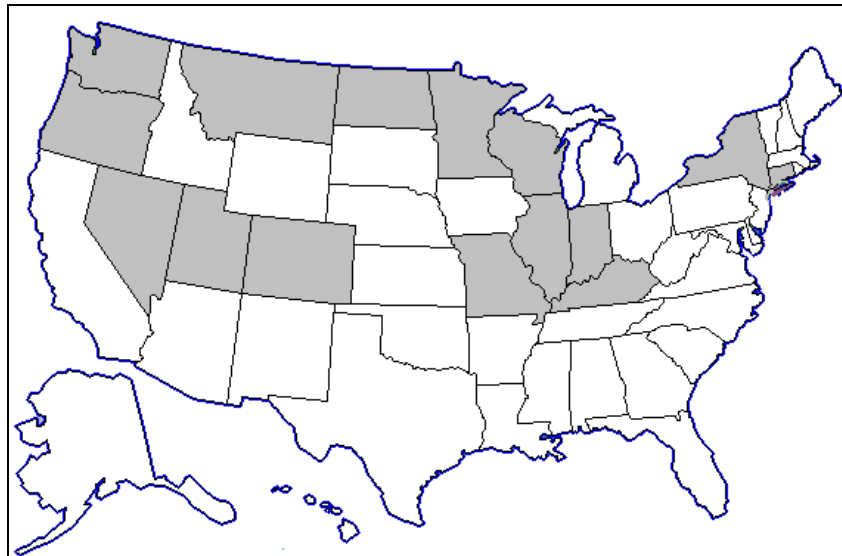
## **2.3. Agency Surveys**

### ***2.3.1. Survey of Deicer Performance and Impacts***

The purposes of this survey were to gain insight on the deicing and anti-icing (deicer) products currently available and used by road maintenance agencies, and to highlight successes and lessons learned from professionals in the snow and ice control community. The survey was designed to help CDOT personnel determine which compounds they

should further evaluate as possible alternatives to NaCl salt-sand mixtures and MgCl<sub>2</sub> for deicing and anti-icing.

The survey consisted of four multipart questions and was developed to document the user-perceived ranking of the deicers in terms of performance and impacts. Respondents were notified about the survey via the Snow and Ice List Serve where it was posted for one month and some individuals were provided with an electronic copy of the survey. The List Serve is operated under the Snow and Ice Pooled Fund Cooperative Program (<http://www.sicop.net/>), which has hundreds of subscribers including state and local DOT professionals, researchers and private sector specialists in highway winter maintenance issues.



**Figure 3 Map of the United States with the survey respondents states highlighted in gray. Not included here are the countries of New Zealand and Finland, each of which had one respondent.**

A total of 24 deicer users participated in the survey with one from Finland, and one from New Zealand, and the rest from the United States representing agencies in 15 different states (see Figure 3). In some cases, participants did not answer all of the questions, often due to the lack of available data or experience. As a result, the summaries of some questions have information provided by fewer than 24 respondents.

### ***2.3.2. Survey of CDOT Winter Maintenance Practices***

The survey was conducted to provide insight on what procedures, equipment, and deicing products are being employed on the roadways of Colorado for snow and ice control. Fifteen questions were asked about the cost of deicers, application rates, the methods of application, equipment used and storage, and any other issues they might have encountered. The survey was provided to the CDOT Environmental & Planning Research Manager, and was then internally disseminated. Survey responses were provided via fax and email. We received input from all six DOT regions in Colorado. A total of 13 people responded to the survey ranging from the regional superintendant to the maintenance supervisor. The most frequently skipped question referred to the modification of equipment to introduce other deicers.

### **2.3.3. Survey of CDOT Deicer Priorities**

The survey was conducted to gain insight on how CDOT personnel prioritize various aspects of deicers including deicer performance, corrosion of metals, and impacts to pavements and the environment. Personnel were asked to rank deicers based on 10 general categories and 40 subcategories. These data were then applied to a Multi-Criteria Decision Making (MCDM) framework. The product of the MCDM is a generated numerical evaluation that can be used to compare deicers.

The survey was provided to the CDOT Environmental & Planning Research Manager, and was then internally disseminated to stakeholders in the six CDOT regions. Survey responses were provided via fax and email.

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## **CHAPTER 3. DEICER IMPACTS ON PAVEMENT MATERIALS**

### **3.1. Introduction**

The deleterious effect of chloride-based deicers on reinforcing steel bar (rebar) in concrete structures is well known (1). Deicers may also pose detrimental effects on concrete infrastructure through their reactions with cement paste and/or aggregates and thus reduce concrete integrity and strength. This in turn may foster the ingress of moisture, oxygen and other aggressive agents onto the rebar surface and promote rebar corrosion.

This literature review presents a synthesis of the impacts of common deicers on cement and asphalt pavements, respectively, detailing the various mechanisms found to cause deterioration. Of the common deicers, NaCl (liquid and solid) with or without sand, and MgCl<sub>2</sub> are currently used in Colorado. The following sections document the impacts NaCl, CaCl<sub>2</sub> and MgCl<sub>2</sub> have on pavement materials, compared with those of alternative deicers such as calcium magnesium acetate (CMA) and potassium acetate (KAc).

### **3.2. Deicer Effects on Portland Cement Concrete**

Previous studies on deicer/concrete interactions focused mostly on concentrated deicer solutions. A Transportation Pooled Fund study investigated the effects of concentrated brines of NaCl, CaCl<sub>2</sub>, MgCl<sub>2</sub> and CMA on portland cement concrete (PCC) and concluded that both physical and chemical interactions occur within concrete when it is exposed to freeze/thaw conditions and deicers (2). Based on the ASTM C 666 freeze/thaw test results, concrete prisms of 4 in diameter × 2 in height (10cm × 5cm) subjected to 300 freezing/thawing cycles in 14% MgCl<sub>2</sub> and 15% CaCl<sub>2</sub> reported considerable expansion (0.17% and 0.18% length change, respectively), mass change



(3.5% and -3.5%, respectively) and loss in the dynamic modulus of elasticity (50% and 40%, respectively). In contrast, those exposed to 18% NaCl did not expand more than 0.04% and reported 0.5% mass gain and approximately 5% loss in the dynamic modulus of elasticity. Significant evidence existed that  $MgCl_2$  and  $CaCl_2$  chemically reacted with hardened cement paste, as indicated by the dissolution of the cement paste and formation of expansive oxychloride phases. These mechanisms were assumed responsible for the observed expansive cracking, increased permeability, and significant loss in compressive strength of the concrete (2). Exposure to NaCl, however, did not result in noticeable chemical interaction or related distress in concrete mortar or concrete (2).

As detailed in Chapter 8, the recent study in our laboratory investigated the effects of diluted deicers on PCC, assuming a 100-to-3 dilution ratio<sup>4</sup> for all liquid and solid deicers (3). Based on the gravimetric and macroscopic observations of freeze-thaw specimens following the SHRP H205.8 laboratory test, de-ionized water, the CMA solid deicer, and the  $MgCl_2$  liquid deicer were benign to the PCC durability, whereas potassium formate and the sodium acetate/sodium formate blend deicer showed moderate amount of weight loss and noticeable deterioration of the concrete. NaCl, the NaCl-based deicer, and the KAc-based deicer were the most deleterious to the concrete. In addition to exacerbating physical distresses, each investigated chemical or diluted deicer chemically reacted with some of the cement hydrates and formed new products in the pores and cracks, the composition of which may be determined by the thermodynamics of the chemical reactions. Some new reaction products were identified as oxychloride crystals, which according to previous research can be expansive. This work provides new insights into the deicer/concrete interactions and highlights the need for bridging the gap between the laboratory data with the field experience. The physiochemical changes of the cement paste induced by the deicers pose various risks for the concrete durability, the level of which depends on the kinetics of the chemical reactions.

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<sup>4</sup> A 100-to-3 dilution ratio is equivalent to three percent of liquid deicer added by volume or three percent of solid deicer added by weight to make a 100 percent solution.

Yet another laboratory study investigated the effects of both diluted and concentrated deicers on PCC. Concrete specimens were exposed to weekly cycles of wetting and drying in distilled water and in solutions of NaCl, CaCl<sub>2</sub>, MgCl<sub>2</sub>, and CMA with either a 6.04 molal ion concentration (equivalent to a 15% solution of NaCl), or a 1.06 molal ion concentration (equivalent to a 3% solution of NaCl), for periods of up to 95 weeks. At lower concentrations, NaCl and CaCl<sub>2</sub> showed a relatively small negative impact on the properties of concrete, whereas MgCl<sub>2</sub> and CMA caused measurable damage to concrete. At high concentrations, NaCl showed a greater but still relatively small negative effect, whereas CaCl<sub>2</sub>, MgCl<sub>2</sub> and CMA caused significant loss of material and a reduction in stiffness and strength of the concrete (4).

In addition to chlorides, the detrimental effects of CMA on PCC have also been confirmed. In a recent laboratory study, cement mortar samples (water-to-cement ratio ( $w/c$ )=0.485) were reported to lose cohesiveness and disintegrate completely after 30-day exposure to 28% CMA solution at room temperature, and the formation of calcium acetate hydrate phases were confirmed by X-ray diffraction results (2). In another laboratory study (5), eight-month continuous exposure of good-quality concrete ( $w/c$ =0.45 and air-entrained) to concentrated CMA solutions (25%) caused a significant decrease in load capacity, mass loss and severe visual degradation of the concrete. The use of 40% blast furnace slag along with a portland clinker was found effective in mitigating such impacts of CMA (5). The deleterious effects of CMA were also reported in earlier studies (6-7), involving a delamination process of the cement matrix likely associated with leaching of the calcium hydroxide.

In light of these studies, it appears that deicers may pose a risk for the durability of PCC structures and pavements through three main pathways: 1) physical deterioration of the concrete through such effects as salt scaling; 2) chemical reactions between deicers and concrete; and 3) deicers aggravating aggregate-cement reactions.

### ***3.2.1. Deicer Scaling—A Physical Process***

Physical mechanisms of attack by deicers can lead to damage of PCC in the common forms of scaling, map cracking, or paste disintegration (2). Scaling refers to the local peeling of the hardened concrete surface, often as a result of cyclic freezing and thawing (8). Scaling can occur on concrete surfaces independent of deicer application, as the aqueous solution in the concrete pores near the surface freezes and thaws due to temperature fluctuations. Freezing of water in saturated concrete exerts tremendous expansive forces that consequently lead to scaling off of concrete surfaces, especially when the concrete surface is not adequately protected with entrained air.

Many research studies have shown that chloride-based deicing salts can exacerbate the scaling problem as concrete experiences freeze/thaw cycles. Moisture tends to move toward zones with higher salt concentrations via osmosis. Accordingly, the osmotic pressure adds to the normal hydraulic pressure if salts are present in the pore solution, which increases the risk for physical deterioration of concrete. In addition, the application of deicing salts to pavements increases the rate of cooling, which increases the number of freeze/thaw cycles and thus the risk for freeze/thaw deterioration. However, the presence of deicers can be beneficial as it widens the temperature range in which phase transitions occur. These opposing effects define the physical distress in concrete caused by deicers, and a pioneering laboratory study revealed the worst conditions at a low deicer concentration (5% NaCl) and optimum conditions at a moderately high concentration (13% NaCl) (9). Another study suggested that concrete containing relatively high concentrations of dissolved salts can provide better resistance to scaling than concrete with plain water in its pores (10).

The scaling of concrete in the presence of deicers, referred to as “salt scaling,” has been recognized as the main cause of frost-related concrete deterioration, and has been found closely related to concrete quality (e.g., air entrainment level), weather conditions, and

the number of freeze/thaw cycles (11-14). Concrete damage from salt scaling was found to be significantly dependent on the salt type (sodium, potassium, magnesium or calcium chloride) and salts containing potassium seemed to cause more scaling damage for unknown reasons (15). Potassium acetate was reported to cause minor scaling associated with alkali carbonation of the surface layer of concrete (16).

Recently, however, the treatment of PCC with sodium acetate solutions was claimed to be a promising technology to grow crystals inside the pores to reduce water penetration into concrete and thus extend the service life of concrete (17). Such beneficial effect was demonstrated in the treatment of a poor-quality concrete ( $w/c=0.65$  and non-air-entrained).

Early research argued that the best protection against "salt scaling" would be reduction of porosity (9). It is now generally believed that the use of properly cured, air-entrained portland cement concrete would prevent physical damage by the freeze/thaw cycles. For instance, high-quality concrete with 5–7% entrained air has been found more resistant to freeze/thaw cycles and scaling (18). Entrained air provides spaces within the concrete mass for expanding water to move into, thereby reducing the potential stress and associated deterioration. For an air-entrained concrete, the spacing factor seems to be its key air void characteristic to allow sufficient resistance to salt scaling (19). It should be noted that air entrainment only slows the freeze/thaw process instead of preventing it (10).

The use of supplementary cementitious materials, particularly fly ash, has been widely reported to have detrimental effects on the scaling resistance of properly air-entrained concrete, as it tends to refine porosity and increase the non-evaporable water content (20). One study suggested that the key was to allow sufficient time for high-volume fly ash concrete to develop strength before subjecting it to salt scaling (21). In contrast, the use of some cementitious material may improve the resistance of mortars and concretes to the combined action of frost and deicer, as in the case of a magnesium phosphate

cement-based binder prepared by mixing MgO with mono-ammonium phosphate, borax and fly ash (22).

### ***3.2.2. Reactions Between Deicers and Cement Paste—A Cation-Oriented Chemical Process***

Chemical mechanisms of attack by deicers can lead to damage of PCC in the common forms of map cracking, paste disintegration, internal microcracking, strength loss, mass gain, and expansion. The following strategies were recommended to mitigate the deleterious effects of deicers: 1) use less deicing chemicals; 2) use NaCl brines wherever possible, 3) use concrete sealants (e.g., siloxanes and silanes) and concrete mixtures including supplementary cementitious materials (e.g., ground granulated blast furnace slag and coal fly ash)(2).

#### *Sodium Chloride (NaCl)*

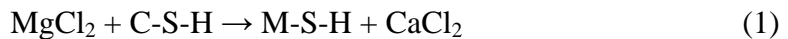
Sodium chloride (NaCl) remains the principal road deicer in use despite its well-known corrosive effects on metals. It has a eutectic point of  $-23^{\circ}\text{C}$ , good ice-melting rates at low temperatures and, above all, is relatively inexpensive. Generally, salt scaling appears to be limited to the concrete surface when NaCl is used. Unless reactive aggregates are included in thick concrete structures such as bridge decks, NaCl, when used as a deicer, does not cause serious deterioration in concrete except for the surface distress caused by the physical mechanism of scaling. Long-term use of NaCl does not result in strength loss in the cement paste matrix via chemical mechanisms except for the slow process of accelerating alkali-silica reaction.

While NaCl itself may be innocent, deicers originating from mines (rock salt, as opposed to solar salt) may contain significant traces of calcium sulfate. Research by Pitt et al.

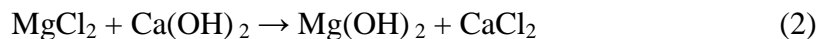
(1987) showed that even low levels of  $\text{CaSO}_4$  can damage mortar, especially in combination with freezing and thawing cycles, due to pore filling by possibly Friedel's salt and ettringite (23). To minimize such damage, changes in mix design or treating joints and cracks with silane sealers can be effective, while establishing restrictions on  $\text{CaSO}_4$  limits in rock salt used for deicing may be difficult.

### *Magnesium Chloride ( $\text{MgCl}_2$ )*

Numerous research studies have shown that  $\text{MgCl}_2$ , when used as a deicer, causes much more severe deterioration to concrete than  $\text{NaCl}$  or  $\text{CaCl}_2$ . This is due to the reaction between  $\text{Mg}^{2+}$  and the hydrated products in cement paste (2,24-27). As shown in Equation 1,  $\text{MgCl}_2$  can react with the cementitious calcium silicate hydrate (C-S-H) present in the cement paste and produce non-cementitious magnesium silicate hydrate (M-S-H) and calcium chloride ( $\text{CaCl}_2$ ):



$\text{MgCl}_2$  can also react with calcium hydroxide ( $\text{Ca(OH)}_2$ ), another hydrated product present in the cement paste in addition to C-S-H. As shown in Equation 2, this chemical reaction produces another non-cementitious material, magnesium hydroxide ( $\text{Mg(OH)}_2$ ), commonly known as brucite.



Since M-S-H and brucite are thermodynamically more stable than C-S-H and  $\text{Ca(OH)}_2$ , the two reactions are highly likely to occur when  $\text{MgCl}_2$  is applied as a deicer onto concrete. M-S-H and brucite have lower binding capacity than C-S-H and  $\text{Ca(OH)}_2$ , and

their formation in concrete thus significantly degrades concrete strength while increasing porosity.

In addition, great expansive forces usually accompany the formation of brucite, which further accelerates the concrete deterioration process. As a result, concrete degradation due to the reaction of  $Mg^{2+}$  with cement paste has been recognized as one of the major mechanisms through which  $MgCl_2$  deicer affects the durability of concrete structures (24-25,27-28).

The aforementioned  $MgCl_2$  impacts on concrete are substantiated further by research based on field data (25). In Iowa, core samples taken from existing concrete structures aged from eight to forty years all contained dolomitic limestone aggregates. The study revealed that  $MgCl_2$  deteriorated concrete by promoting expansion of the concrete through the formation of brucite and growth of other detrimental minerals. It was also reported that NaCl showed less detrimental effect than  $MgCl_2$  (25,29-30).

Detailed information regarding the mechanism of  $MgCl_2$  deteriorating concrete material can be found in many research studies. The consensus is that  $Mg(OH)_2$  and M-S-H are the most predominant reaction products, formation of which eventually leads to the degradation of concrete when  $MgCl_2$  is applied as a deicer (31-34), although different mechanisms were proposed for the formation and behavior of  $Mg(OH)_2$ .

A recent laboratory study reported the formation of another potentially detrimental phase, calcium oxychloride ( $3CaO \cdot CaCl_2 \cdot 15H_2O$ ), formed in cement mortars exposed to 15%  $MgCl_2$  solutions for 84 days, as confirmed by optical microscopy, SEM and microanalysis (35). The proposed mechanism was based on Eqn. 2 and Eqn. 3:



The petrographic evidence indicated that platy calcium oxychloride crystals and associated carbonate-substituted phase precipitated in air voids and cracks by consuming portlandite ( $\text{Ca}(\text{OH})_2$ ). In addition, Friedel's salt ( $3\text{CaO}\bullet\text{Al}_2\text{O}_3\bullet\text{CaCl}_2\bullet 10\text{H}_2\text{O}$ ) was detected in the specimens analyzed (35). In another laboratory study by the same group, the structures of brucite were also observed in the outer layers of the PCC specimens exposed to concentrated  $\text{MgCl}_2$  (2).

The difficulty of constructing durable concrete dams in salt mines led to research efforts in Poland investigating the long-term behavior of cement pastes exposed to a strong chloride solution, predominantly composed of  $\text{NaCl}$ ,  $\text{MgCl}_2$ , and  $\text{KCl}$  (36). Kurdowski found two cements: high-alumina cement and alkali activated slag, performed particularly well for over seven years because a stable skin-like layer of low permeability formed and protected the concrete core (36). Even after fifteen years the high-alumina cement had high strength and showed no deterioration. Portland and slag cements, however, were found to be particularly vulnerable to deterioration or unstable layers of chemical products. The difference is attributed to the higher porosity of portland and slag cements (36).

#### *Calcium Chloride ( $\text{CaCl}_2$ )*

$\text{CaCl}_2$  has been found to have a detrimental effect falling between that caused by  $\text{NaCl}$  and  $\text{MgCl}_2$ . It has also been found that concrete specimens exposed to  $\text{CaCl}_2$  deteriorated in a similar pattern to those exposed to  $\text{MgCl}_2$ , although at a slower pace and to a less severe degree. As shown in Equation 3,  $\text{CaCl}_2$  can also react with  $\text{Ca}(\text{OH})_2$  and form a hydrated calcium oxychloride (2,37).

At temperatures ranging from 40 to 50°F, hydrated calcium oxychloride can be generated in a relatively short period of time once  $\text{CaCl}_2$  is available. This reaction adds additional



stress to the concrete matrix. A recent study provided further evidence for this mechanism of  $\text{CaCl}_2$  attack in concrete (38).

The damaging impact of  $\text{CaCl}_2$  on concrete was examined in a comprehensive study conducted at Iowa State University (16). The study included five deicing chemicals— $\text{NaCl}$ ,  $\text{CaCl}_2$  with and without a corrosion inhibitor, potassium acetate, and an agricultural product as well as, freezing/thawing and wetting/drying exposure conditions. Comprehensive damaging criteria were set up and examined for the paste and concrete subjected to these deicing chemicals, including mass loss, scaling, compressive strength, chemical penetration, and microstructure of the paste and concrete. The deicing chemicals tested were found to penetrate into a given paste and concrete at different rates, leading to different degrees of damage. The two  $\text{CaCl}_2$  solutions caused the most severe damage compared to the others. The addition of the corrosion inhibitor in the  $\text{CaCl}_2$  solutions delayed the onset of damage, but failed to reduce the ultimate damage. Leaching of  $\text{Ca}(\text{OH})_2$  accompanied by some chemical alterations in concrete was also observed for specimens exposed to chlorides.

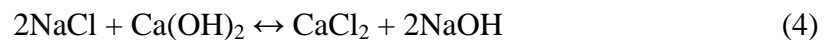
### ***3.2.3. Deicer Aggravating Aggregate-Cement Reactions***

#### *Chloride-Based Deicers Affecting ASR—An Anion-Oriented Chemical Process*

Alkali silica reaction (ASR) is a deleterious process caused by the chemical reaction between available alkalis from the cement paste and reactive silica in the aggregate of PCC. In ASR, the chemical reaction between hydroxyl ( $\text{OH}^-$ ) associated with sodium ( $\text{Na}^+$ ) and potassium ( $\text{K}^+$ ) and reactive forms of silica produces a gel that expands when sufficient moisture is available. The expansion of the gel can produce internal stress great enough to cause cracks in both cement paste and aggregates. Typical ASR distress is manifested by cracking, popouts and expansion.

ASR was first discovered as a stress to concrete structures in the United States by Stanton in 1940 (39). Failure of concrete structures later ascribed to ASR can be dated back to the late 1920s. Reactive aggregates, available alkalis and sufficient water are three prerequisites for ASR to occur. ASR has been conventionally controlled by limiting alkali content in cement and selecting aggregates of good quality.

Extensive research suggests that NaCl can initiate and/or accelerate ASR by supplying additional alkalis to concrete (40-46). An increase in pH of the concrete pore solution has been frequently observed and commonly proposed as the principal cause for the exacerbation of ASR in PCC exposed to NaCl (42,44,47). Nevertheless, this process was found to be quite slow and might be masked by other short-term effects. Equation 4 presents the mechanism of the pH increase in concrete pore solution resulting from the dissolution of Ca(OH)<sub>2</sub> in the presence of sodium chloride.



The Cl<sup>-</sup> ions from NaCl might also accelerate ASR when the OH<sup>-</sup> concentration remains above a certain limit (45,48). It was reported that high-alkali concrete exposed to NaCl solution expanded even more than high-alkali concrete exposed to NaOH. This was attributed to the combined effects of ASR and the formation of expansive chloroaluminates (49). In contrast, low-alkali concrete was sufficiently protected against ASR when exposed to NaCl (49).

For high-alkali concrete that is already affected by ASR, map cracking can occur at the surface due to a decrease in pH in the near-surface layer of concrete. This has been observed in field specimens indicating that chloride ions traveled less than 100 mm inside the ASR-affected concrete. Measurements of core samples from concrete structures exposed to NaCl deicer indicated that most chlorides existed in the water-soluble form. Scanning electron microscopy (SEM) observations and microprobe analyses on mortar

bars immersed in NaCl solution also suggested that binding of  $\text{Cl}^-$  ions in chloroaluminates or cement hydrates was a long-term process, which could be promoted at higher initial alkali concentrations (50).

A SEM/ Energy-dispersive X-ray (EDX) investigation of cracking deterioration observed in a 3-year-old pavement in central Iowa revealed that ettringite  $((\text{CaO})_6(\text{Al}_2\text{O}_3)(\text{SO}_3)_3 \bullet 32\text{H}_2\text{O})$ -filled air voids were centers of pressure causing the cracks, instead of ASR that might have been incorrectly identified (51).

It should be noted that the accelerating effect of NaCl on ASR is a slow process, and stress to the concrete surface may be more likely caused by physical mechanisms such as salt scaling rather than chemical mechanisms (25). Such a conclusion was made based on a laboratory observation where the 0.75 M NaCl solution caused more extensive deterioration to the concrete surface than the 3.0 M one (25).

As reported in literature,  $\text{CaCl}_2$  and  $\text{MgCl}_2$  do not have as obvious an effect on ASR as NaCl. A possible reason is that both  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  cations can react with the free hydroxyl ions ( $\text{OH}^-$ ) in the concrete pore solution and form products that are less soluble in water than NaOH or KOH. Therefore, exposure of concrete to  $\text{CaCl}_2$  or  $\text{MgCl}_2$  tends to decrease the pH value in the pore solution. As a consequence, the accelerating effect of  $\text{Cl}^-$  on ASR, if any, might be masked by the more dominant effect of the reaction between  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  cations with  $\text{OH}^-$  in the cement paste.

Prezzi et al., (1998) stress the need for laboratory tests that simulate actual field conditions to truly determine how  $\text{CaCl}_2$  and  $\text{MgCl}_2$  deicers affect ASR (52). In their study,  $\text{CaCl}_2$  and  $\text{MgCl}_2$  seemed to actually help reduce ASR-related expansions when added to concrete during mixing operations. When NaOH, KOH, LiOH, NaCl, KCl,  $\text{CaCl}_2$ ,  $\text{MgCl}_2$ , and  $\text{AlCl}_3$  were introduced to new concrete samples as admixtures and then tested according to ASTM C 1260, it was found that samples corresponding to

chlorides with monovalent cations had greater ASR expansion than reference concrete specimens, while the divalent and trivalent cations generally had reduced expansions (52). While this is in contrast to findings from a previous study in which  $\text{CaCl}_2$  accelerated ASR (49), the test temperature and salt concentrations were different in these two studies and thus making it difficult to directly compare the research findings. Yet another study tested ASR gel soaked in a solution consisting of 0.7M NaOH and 0.1M  $\text{CaCl}_2$ , where a non-expansive reaction product formed and the ASR gel did not repolymerize (53).

#### *CaCl<sub>2</sub> and MgCl<sub>2</sub> Affecting ACR—A Cation-Oriented Chemical Process*

Another deleterious process is commonly observed in concretes with a short service life. The principal reaction has the nature of an alkali-dolomite reaction between coarse aggregates containing reactive dolomite (calcium magnesium carbonate—i.e.,  $\text{CaMg}(\text{CO}_3)_2$ ) and cement paste, recognized as Alkali-Carbonate Reaction (ACR).

In ACR, dolomite from the aggregate reacts with  $\text{OH}^-$  in the cement paste to free magnesium cations ( $\text{Mg}^{2+}$ ) and carbonate anions ( $\text{CO}_3^{2-}$ ).  $\text{Mg}^{2+}$  then precipitates as brucite, while  $\text{CO}_3^{2-}$  reacts with portlandite from the cement to form calcite ( $\text{CaCO}_3$ ) and  $\text{OH}^-$ . The formation of brucite and calcite leads to crystal growth and thus increased pressure in concrete. This, together with the hydration state changes due to magnesium chloride hydrates, eventually leads to expansion and rapid deterioration of the concrete.

Both  $\text{MgCl}_2$  and  $\text{CaCl}_2$  deicers are known to deteriorate concretes containing reactive dolomite aggregates by accelerating ACR.  $\text{MgCl}_2$  contributes  $\text{Mg}^{2+}$  cations that can directly participate in the formation of brucite, whereas  $\text{CaCl}_2$  was found to accelerate ACR by enhancing the de-dolomitisation reactions, releasing magnesium to form brucite and M-S-H (26-27). No literature was found to report potential effects of NaCl on ACR.

*Acetate/Formate-Based Deicers Affecting ASR—An Anion-Oriented Chemical Process*

The last decade has seen an increase in the premature deterioration of PCC pavements, which coincided with the introduction of alternative deicers (potassium acetate, sodium acetate, and sodium formate) for winter maintenance. Such deicers have been used more extensively and for more years in European countries for winter maintenance than in the United States (1). The degree of distress in the PCC of European facilities ranges from mild to severe, in terms of surface cracking and repair and rehabilitation efforts.

Recent research conducted at Clemson University found that the acetate/formate-based deicers could induce increased levels of expansion in concrete with aggregates susceptible to ASR, and could trigger ASR in concrete that previously did not show susceptibility to ASR (54-56). The laboratory results from a modified ASTM C 1260 mortar bar test and a modified ASTM C 1293 concrete prism test indicated that both KAc- and NaAc-based deicer solutions showed significant potential to promote ASR in specimens containing reactive aggregates. Such solutions were also found to cause more rapid and higher levels of expansion within 14 days of testing and to lead to lower dynamic moduli of elasticity, compared with 1N NaOH solution (56). Increasing temperature or deicer concentration was found to accelerate the deleterious effects of deicers on the ASR in concrete.

Limited existing laboratory studies indicated that acetate-based deicers could cause or accelerate ASR distress in the surface of PCC pavement by increasing the pH of concrete pore solution. PCC pavements that were otherwise resistant to ASR might show rapid deterioration when exposed to these high-alkali solutions. The nature of the reactions associated with increased expansions in mortar bar tests remains unclear to date due to limited research conducted on this topic. It was proposed that such deicers react with one of the major hydrated products—portlandite—resulting in higher pH of the concrete pore solution. The high pH resulting from these interactions is likely to have an accelerating

effect on the expansions due to ASR. This mechanism was substantiated by SEM/EDX investigation of mortar bars after deicer immersion, which was unable to detect portlandite in the cement paste (57). Furthermore, the concrete specimens exposed to KAc deicer showed presence of certain secondary reaction products, the effect of which on the PCC durability merits further investigation (58).

Efforts have been made to mitigate ASR by adding various admixture materials. Research sponsored by the Federal Highway Administration (FHWA) used lithium compounds to successfully reduce ASR induced by the deicers (59). The effectiveness of other supplementary cementing materials (e.g., selected fly ash and slag) was also evaluated in reducing the ASR potential in presence of potassium acetate deicer. The effectiveness of fly ash in mitigating ASR in presence of potassium acetate was found dependent on the lime content, as well as the dosage level of the fly ash and the aggregate reactivity. Fly ash with lower lime content was generally more effective in reducing the expansions (55), whereas high-lime fly ash was found ineffective due to its possible negative interactions with the deicer (58). At the 40% cement replacement level, slag appeared to be effective in mitigating expansions in both KAc deicer solution and 1N NaOH solution (57). The addition of lithium nitrate to either KAc deicer solution or mortars alone was found to effectively reduce the mortar expansion (57).

### **3.3. Deicer Effects on Asphalt Concrete**

Of the two major types of pavements—PCC pavement and asphalt pavement—the latter is generally believed to be less affected by deicers. This is attributable to the comparatively higher chemical stability asphalt binder demonstrates to the chloride-based deicers which represent the majority of chemicals applied on highway pavements. Thus far, there are no specific guidelines established in the United States for application of deicers on asphalt pavements and little fundamental research carried out in investigating the asphalt/bitumen-deicer reaction, although more severe loss of skid resistance on

asphalt surface has been observed by state and federal highway agencies with the application of various road salts (60). Current research studying deicers effects on asphalt pavement is focused on improving surface skid resistance of the pavements of different mix types.

### ***3.3.1. Deicer Impacts on Skid Resistance***

During the 1976–1977 winter season, FHWA sponsored studies in the states of Maine, Michigan, Utah, and Vermont to determine if more sodium chloride was needed to clear *open-graded asphalt friction courses* during winter storms than was needed to clear conventional asphalt pavements (61). It was found that the clearing rates and appearance of open-graded and dense-graded pavements were different. Dense-graded pavement showed occasional faster clearing than open-graded pavements. The open-graded pavement, however, seemed to provide a superior skid-resistant surface during most storms without more salt used to maintain the surface (61).

Open-graded asphalt mixes commonly used in asphalt pavements fall into three categories: open graded friction course (OGFC), stone matrix asphalt (SMA), and open graded based material (OGBM), of which only OGFC and SMA are used as surface course. Accordingly, previous research related to deicer effects on the skid resistance of pavement surfaces focused mainly on these two types of mixes. OGFC and SMA are generically referred to as open-graded mixes (OGMs) or open-graded pavements (OGPs) in deicer studies. OGMs, especially the OGFC, are known to offer lower noise and higher friction between tires and road surface. However, in terms of the skid resistance when deicers are applied, the limited research efforts thus far have yielded quite contradictory conclusions regarding their performance under winter conditions. While some reports indicated that these mixes were problematic when subjected to wet-freeze conditions (62-63), others reported enhanced performance (64). Such problematic potentials, if proven to

be true, need to be accounted for, considering the increased wet-freeze frequencies on pavement surfaces when deicers are applied.

The Virginia Department of Transportation sponsored a study to examine its winter maintenance techniques of applying sodium chloride in granular, pre-wetted, and liquid forms. The snow removal and ice control operations followed the recommendation by the FHWA Project T and E 28. There were no significant differences in the performance of the different surface mixes, including OGFC and dense-graded mixes (65). A more recent study by the Oregon Department of Transportation was conducted on the effects of liquid magnesium chloride on OGP. Skid tests were performed on four sections of two different highways in Oregon under three conditions: 1) no deicer application; 2) after a deicer application rate of 15 gallons/lane mile; and 3) after a deicer application rate of 30 gallons/lane mile. The results of the skid tests showed that the application of deicer appeared to have little if any effect on the Friction Number (FN), which were all well above the FHWA-recommended minimum FN values (66).

Due to harsher winter weather that produces more snow and ice, Nordic countries and Canada use more deicers on highways and airport runways than the United States, leading to more extensive research conducted in these areas. Fundamental research has been conducted in these countries to investigate the potential reactions between asphalt materials and various deicers.

### ***3.3.2. Deicers Affecting Pavement Structure***

Thermal cracking, differential heaving, and loss of bearing capacity during spring thaw are often identified as the main mechanisms involved in the pavement deterioration in cold climates. Frost action within the pavement granular layers can be aggravated by an ice enrichment process and differential freezing conditions associated with the contamination of the base material by deicing salt (67).



A comprehensive laboratory study evaluated the relative destructive effects of various deicers on asphalt pavement, considering the effect of freeze/thaw cycles (68-69). This study involved actual aggregates and asphalt specimens cored from the field, as well as four types of deicers used on both highway and airport pavements, namely, urea, NaCl, sodium formate (NaFm), and potassium acetate (KAc).

Various degrees of material disintegration as a combined result of frost action and deicers were observed, revealing that the effect from freeze/thaw cycling was significant whereas the effects of different deicers on both the aggregates and the asphalt concrete mixes varied. The extent of damage due to freeze/thaw cycling in distilled water was less than that caused by any deicer used. A critical range of deicer concentration was found to exist between 1% and 2% by weight of solid deicer to deicer solution, in which the maximum damaging effect of deicers to the aggregate was observed. The limestone aggregates showed a higher resistance to disintegration than the quartzite aggregates when subjected to freeze/thaw cycles in the presence of the deicers. The urea was found to have the highest damaging effect among all the deicers on both the aggregates and asphalt concrete samples, while the least damaging deicer for limestone was NaCl and for quartzite was KAc.

The indirect tensile strengths (ITS) of the samples exposed to deicers were mostly higher than those exposed to distilled water, while all of them were found to be significantly lower than those of the intact samples. However, there was no significant deterioration identified for the mechanical properties of the samples exposed to potassium acetate, sodium formate, or sodium chloride, relative to distilled water. Conditioning asphalt samples using freeze/thaw cycles in the presence of a deicer solution also caused a decrease in the modulus of elasticity. The lowest average elastic modulus was associated with the samples in urea, and visual inspection indicated significant damage by urea (69). Based on weight measurements and density calculations, asphalt mix sample immersed in NaFm experienced the most disintegration after 25 cycles, whereas urea (followed by

KAc) was the most detrimental deicer after 50 cycles (70). Exposure to freeze/thaw cycles and deicers was found to affect the viscosity of the recovered asphalt binder and the gradation of recovered aggregates. The freeze/thaw cycles seemed to result in soft asphalt binder, while the deicers caused asphalt hardening. However, the authors noted that these findings were inconclusive due to the difficulties involved in testing and the inaccuracies in measuring viscosity of the recovered asphalt. Overall, this laboratory investigation found urea to be the most detrimental deicer, while the other deicers “induced relatively small damage, comparable to that caused by distilled water” (68). It should be noted that chemical reactions might have been slowed by the low temperatures involved in this study and that damage in the field could occur as a result of reactions between deicer residues and asphalt during hot summer temperatures (68).

A follow-up study was conducted at higher temperatures on asphalt pavement samples taken from the Dorval International Airport (Montreal, Canada) to clarify the role played by the deicers in asphalt deterioration, and to determine whether the damage was attributable to the physical freeze/thaw action. Only 15 freeze/thaw cycles were performed before subjecting some samples to 40 wet/dry cycles at 40°C. This research confirmed the previous finding that softening occurs during freeze/thaw and exposure to deicers causes hardening. After the freeze/thaw and wet/dry cycles, the asphalt samples in NaAc showed the greatest loss of strength and elasticity, followed by those in NaFm. Interestingly, all samples showed increased strength after the warm wet/dry cycles and all except NaFm and NaAc showed increased elasticity after the warm wet/dry cycles. However, the dry samples not exposed to freeze/thaw or wet/dry cycles had the greatest elasticity and nearly the highest strength. Overall, the Canadian studies did not indicate significant damaging effects of KAc and NaFm on asphalt pavement (68,71). It should be cautioned, however, that these results were based on laboratory experiments with only two samples of asphalt pavement and the mix design for each pavement was undeterminable from the reports.

### ***3.3.3. Acetate/Formate-Based Deicer Affecting Airfield Asphalt Pavements***

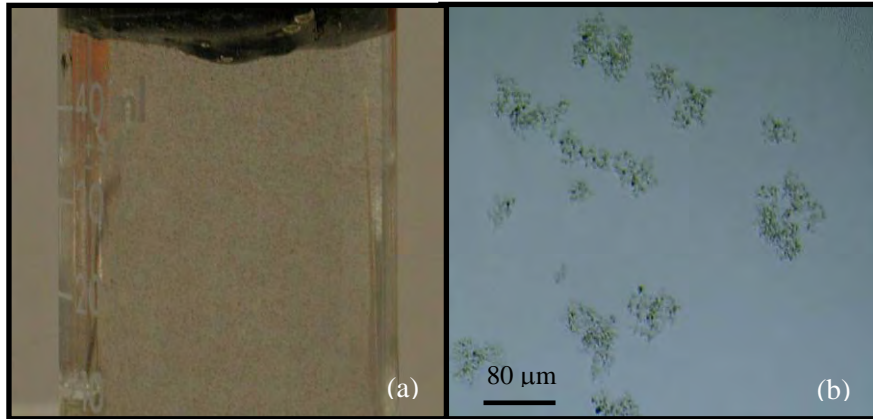
Concurrent to the use of acetate/formate-based deicers in the 1990s, asphalt pavement in Europe saw an increase in pavement durability problems. At some Nordic airports, these problems emerged as degradation and disintegration of asphalt pavement, softening of asphalt binders, and stripping of asphalt mixes occurring together with loose aggregates on the runways (72-73). Such problems were not identified prior to the airports changing from urea to KAc- and KFM-based deicers.

In 2001, serious asphalt durability problems were identified at airports in Nordic countries that used acetate/formate-based deicers (72). Heavy binder bleeding and serious stripping problems were observed occurring together with loss of asphalt stability. Soft, sticky, and staining binder came to the surface, often leaving strong stains on electrical devices and on the airplanes. The binder of the asphalt base layer was “washed off,” and the aggregates experienced a severe loss of strength. In the laboratory, tests indicated chemical changes in the binder after exposure to the deicer in the form of emulsification, distillation, and an increased amount of polycyclic aromatic hydrocarbons (PAHs). A field investigation was conducted subsequently that confirmed the deleterious effects of acetate-based deicer on the asphalt pavement. The bitumen and the mastic squeezed to the surface of the core, and the concentration of the deicer had a clear influence on its solubility. Some bitumen was dissolved into the pore liquid, and pure stone particles were found inside the core. The limestone filler was found fully dissolved by the deicer liquid and the rest of the mastic became brittle and grey-colored. A large increase in the porosity of asphalt was also noticed (72-73).

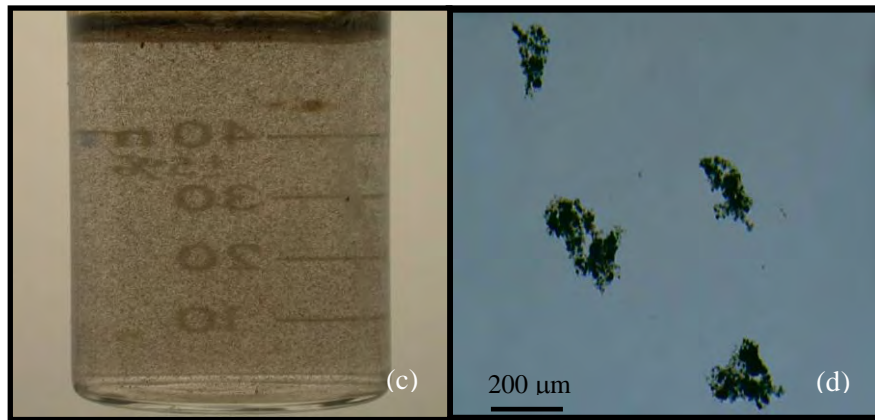
To address the observed problems, a joint research program—the JÄPÄ Finnish De-icing Project—was established to conduct extensive laboratory and field investigations on this subject. The goal of JÄPÄ was to provide answers to three fundamental concerns—i.e., how the damage is generated, how to determine the compatibility between asphalt and

deicing materials, and whether it is possible to prevent damage by mix design. The research showed that formate/acetate-based deicers significantly damaged asphalt pavements. The damaging mechanism seemed to be a combination of chemical reactions, emulsification and distillation, as well as generation of additional stress inside the asphalt mix. Asphalt binders soaked in the deicer solution were found to have lower softening points and tended to dissolve at temperatures as low as 20°C (68°F). Asphalt mixes soaked in the deicer solution were found to have lower surface tensile strength and lower adhesion (72-73). It seemed clear that deicer (formate or acetate), water or moisture, and heat were necessary for the damage to occur. In the field, such damage mainly occurred during the repaving process or on hot summer days with residual deicers from the winter season, as dynamic loading and unloading reduced the time it took for damage to occur.

A recent study at the WTI Corrosion and Sustainable Infrastructure Laboratory was able to reproduce acetate-induced emulsification of asphalt similar to the field observations at Nordic airports (74). Aqueous solution tests of asphalt binder in water and four NaAc solutions of different concentrations (5% to 40%) showed a bilinear trend of weight loss increasing with the NaAc concentration. Both visual inspection and optical microscopy (as shown in Figure 4) indicated that a significant amount of asphalt emulsification occurred in NaAc, but not in water or aqueous solutions of NaCl or sodium hydroxide (NaOH) with a pH of 9 (equivalent to the measured pH of 40% NaAc solution). For the two tested asphalt binders, PG 58-22 exhibited slightly higher emulsification than PG 67-22. In the calcium-magnesium-acetate aqueous solution, asphalt emulsification occurred similarly to that in NaAc. These results confirmed that asphalt emulsification should be attributed to the acetate anion,  $\text{CH}_3\text{COO}^-$ , and excluded the possibility that high alkalinity was responsible for the asphalt emulsification in NaAc. Asphalt emulsification also occurred in a NaFm aqueous solution.



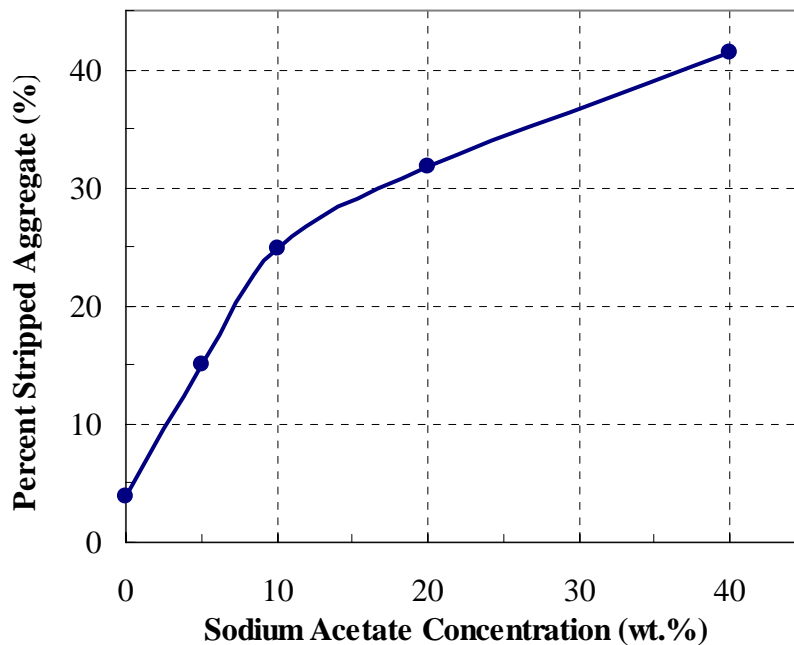
(a), (b) The 24-hour Reservation of the 60°C (140°F) Aqueous Solution Test with the 20% Acetate Concentration



(c), (d) The 24-hour Reservation of the 60°C (140°F) Aqueous Solution Test with the 40% Acetate Concentration

**Figure 4 Digital photos (left) and optical microscopic images (right) showing the suspension solution of asphalt subsequent to the 60°C (140°F) aqueous solution test (74).**

The effects of NaAc on asphalt mixes were examined by conducting a modified ASTM D 3625-96 Boiling Water Test, which was originally designed to test the susceptibility of asphalt mixes to moisture damage by accelerating the effect of water on bituminous-coated aggregate with boiling water. Stripping occurred for both crushed gravel and limestone aggregate particles included in the asphalt mix exposed to NaAc, suggesting that aggregate properties play at most a secondary role in asphalt emulsification (74). As indicated in Figure 5, a significant amount of aggregate was stripped after exposure to the NaAc solutions and the aggregate stripping followed a bilinear trend with weight loss increasing with the NaAc concentration.



**Figure 5 Percent stripped aggregates at different concentrations of sodium acetate after the modified boiling water test (74).**

Phase I of the Airfield Asphalt Pavement Technology Program Project 05-03: *Effect of Deicing Chemicals on HMA Airfield Pavements* includes a literature review, interviews with managers at 36 airports that use deicers and have asphalt pavement, as well as laboratory testing. Seven airports indicated that pavement deterioration had occurred, but the cause was unknown except in one case most likely attributable to the type and source

of asphalt binder and aggregate. Preliminary laboratory testing of asphalt pavement samples composed of either a chert gravel or diabase with two binders (PG 64-22 and PG 58-28) exposed to KAc and NaFm was conducted. The presence of polycyclic aromatic hydrocarbons (PAHs) was inconclusive after vacuum-induced saturated samples were stored for four days at 60°C (140°F). However, significant generation of carboxylate salts had developed after the asphalt mixes were exposed to the deicers, although this may not be related directly to deicer-induced damage. Indirect tensile strength tests showed PG 64-22 to be “somewhat more resistant” (75), and that chert gravel had significantly less strength when exposed to deicers compared to water. A long-term durability test developed by Advanced Asphalt Technologies also showed chert to be very susceptible to moisture damage, particularly when exposed to KAc or NaFm. Soundness tests of both types of aggregate in magnesium sulfate, KAc, and NaFm were acceptable and also showed that direct attack on the aggregate by the deicers was not occurring (75).

The JÄPÄ—Finnish De-icing Project studied the ingredient materials in asphalt pavement individually and the roles they played in the damaging mechanism were ranked accordingly (76). The key test results of each ingredient material are as follows.

Effects of Formate/Acetate-Based Deicers on Aggregates: The main reason for pavement damage was not due to poor quality of aggregates. Mineral aggregate might be a reason secondary to asphalt binders in pavement damage. The decomposition level of acidic aggregates was higher than for caustic aggregates, but was still acceptable. However attention should be paid to the weathering resistance of aggregates used in airfields to extend the lifespan of asphalt pavements.

Physical Effects of Formate/Acetate-Based Deicers on Bitumen/Asphalt: 1) High density of deicer solution such as 1.34 kg/dm<sup>3</sup> for the 50 wt.% solution enabled the deicer solution to penetrate into bitumen by gravity. 2) Very low surface tension between deicer chemicals and asphalt facilitated stripping and emulsification of

asphalt mixes. 3) Formate/acetate-based deicers had pH values usually between 9 and 11, and the higher the pH the more aggressive the deicer would be. 4) Formate/acetate-based deicers were very hygroscopic, which kept the road surface constantly wet and retained water inside the asphalt to overfill the air voids.

Chemical Effects of Formate/Acetate-Based Deicers on Bitumen/Asphalt: When exposed to deicers, composition changes of bitumen/asphalt occurred in the hydrocarbon classification C10-C40. When exposed to deicers, large organic molecules such as the PAHs grew in bitumen. Deicers in asphalt were found in both the liquid and gas phases. PAHs in the asphalt samples could migrate and become dissolved in the deicer.

Failure Process of Asphalt Pavements: Deicers migrate into the asphalt after application onto pavements and saturate asphalt mixes during the winter. The deicer solution intrudes into asphalt due to gravity and for other unknown reasons, especially when asphalt temperature rises significantly (a result of a hot asphalt layer laid or summer weather). Due to the low surface tension between deicers and bitumen, the deicers are absorbed in the bitumen, which, in turn, starts to emulsify. It is possible that the chemical composition of the bitumen changes during emulsification. Due to emulsification the bitumen comes loose and the aggregate particles get cleaned, followed by bleeding and stripping.

The preliminary research by Advanced Asphalt Technologies suggested the damaging mechanism is mainly a disruption of the asphalt–aggregate bond due to ASR. Expansive pressures typical of ASR-damaged concrete are not perceived to be the problem, but rather the bond disruption and increased susceptibility to moisture damage. Advanced Asphalt Technologies is currently working on Phase II, which includes more significant laboratory testing and field investigations (75).



However, the research by Pan et al. at our research group (2008) shows that: 1) asphalt emulsification occurs in asphalt mixes with both reactive and non-reactive aggregates, and 2) asphalt emulsification does not occur in NaOH solutions of the same pH values as the NaAc solution, which indicates that asphalt emulsification may be a more critical mechanism of asphalt mix deterioration than ASR unless very reactive aggregates are used in the asphalt mix (77). We proposed a detailed and specific mechanism of acetate-induced asphalt emulsification based on contact between acetate anions ( $\text{CH}_3\text{COOH}^-$ ) and asphalt, which can be greatly increased at high summer and/or re-paving temperatures due to the tendency of asphalt to swell. For NaAc, aqueous solution tests of asphalt binder were performed at several concentrations and temperatures and the resulting suspended substance was examined using Fourier Transform Infrared Spectroscopy. No significant amounts of new chemicals were identified, and intermolecular binding between the acetate anion  $\text{CH}_3\text{COOH}^-$  and the alkane component of asphalt was inferred. Van der Waals forces anchor the lipophilic organic chain ( $\text{CH}_3-$ ) of the acetate anion to the molecular chain of asphalt ( $\text{CH}_3-\text{CH}_2-$ ). At the same time, the hydrophilic polar end of the acetate anion ( $\text{COO}^-$ ) forms hydrogen bonds with water molecules and pulls on the asphalt, overcoming the intermolecular forces within the asphalt. Asphalt emulsion is maintained by Brownian motion and repulsive forces on the flocs. The emulsification of asphalt reduces the asphalt–aggregate bond and can lead to adhesion failure in the pavement. There is also the potential that the aggregate preferentially bonds with the acetate anion, which has a higher polarity than the asphalt molecules (74).

To prevent or mitigate the effects of deicers on asphalt pavement, the first and most important countermeasure is to follow best possible practices in asphalt mix design and paving. Responses to the ACRP survey point towards adoption of some of these preventive measures: one European airport reduced asphalt pavement air void to 3.0%; another European airport indicated polymer-modified binder is used; and one U.S. airport changed the asphalt binder to PG 76-32 citing current Federal Aviation Administration specifications (1). Nonetheless, the JÄPÄ Project research showed that the resistance of asphalt pavement to deicers can be improved only partially by mix design. According to

the laboratory results, binders with high viscosity or polymer-modified binders were recommended when formate/acetate-based deicers were to be used. High-quality (sound) aggregates could also improve the durability of asphalt pavements in presence of such deicers, and so could aggregates with a higher pH. The void contents of the asphalt mixes were recommended to be kept low enough to limit deicer solution in pores. Other suggestions to prevent asphalt damage are summarized below (78):

1. Prefer harder bitumen (penetration max 70/100) or modified bitumen.
2. Use alkaline aggregates and avoid limestone filler.
3. Test the compatibility of the materials in advance.
4. The most secure way is not to use acetates and formates on asphalt structures.
5. When repaving, the wearing course containing residual deicers must be milled away, and recycled asphalt pavement (RAP) should not be used if it is heavily contaminated (17).

### **3.4. Conclusions**

Based on the literature review, deicers may pose detrimental effects on portland cement concrete (PCC) infrastructure and thus reduce concrete strength and integrity (as indicated by expansion, mass change and loss in the dynamic modulus of elasticity). Such risks of deicers on the durability of PCC structures and pavements exist through three main pathways: 1) physical deterioration of the concrete through such effects as salt scaling; 2) chemical reactions between deicers and cement paste (a cation-oriented process, esp. in the presence of  $Mg^{2+}$  and  $Ca^{2+}$ ); and 3) deicers aggravating aggregate-cement reactions (including an anion-oriented process in the case of chlorides and acetates/formates affecting ASR; and a cation-oriented process in the case of  $CaCl_2$  and  $MgCl_2$  affecting ACR). The proper use of air entrainment, high-quality cementitious materials and aggregates, and mineral admixtures is promising in mitigating the deicer impact on PCC.

Based on the literature review, deicers may pose detrimental effects on asphalt pavement. While their impact on skid resistance is still inconclusive, deicers are known to affect pavement structure and cause loss of the strength and elasticity of asphalt concrete. Exposure to freeze/thaw cycles and deicers was found to affect the viscosity of the recovered asphalt binder and the gradation of recovered aggregates. Formate/ acetate-based deicers were found to significantly damage asphalt pavements, through the combination of chemical reactions, emulsifications and distillations, as well as generation of additional stress inside the asphalt concrete. In order to manage deicer effects on asphalt concrete, it is recommended to: 1) follow best possible practices in asphalt mix design and paving (e.g., low void contents); 2) use binders with high viscosity or polymer-modified binders; 3) use alkaline aggregates or high-quality (sound) aggregates (avoid limestone filler or heavily contaminated RAP when acetates/formats are used as deicers); and 4) test the compatibility of the materials in advance.

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## **CHAPTER 4. CORROSION OF DEICERS TO METALS IN TRANSPORTATION INFRASTRUCTURE**

### **4.1. Introduction**

In the last two decades, the growing use of deicers has raised concerns about their effects on motor vehicles, transportation infrastructure, and the environment (1-4,). One study estimates that road salt imposes infrastructure corrosion costs of at least \$615 per ton, vehicular corrosion costs of at least \$113 per ton, and aesthetic costs of \$75 per ton if applied near environmentally sensitive areas, plus uncertain human health costs (5). Each year the United States and Canada use approximately 15 million and 4–5 million tons of deicing salts, respectively (6). Motorists and trucking associations have become wary of the effects of deicers on their vehicles, as the problem of vehicular corrosion (though generally cosmetic) has been documented. On average, the cost of deicer corrosion on vehicles was estimated to be \$32 per year (7). In addition, chemicals may cause corrosion damage to transportation infrastructure such as reinforced or pre-stressed concrete structures and steel bridges (8). The deleterious effect of deicing salts on reinforcing steel bar (rebar) in concrete structures is well known (9-11). A recent study conducted for the U.S. National Cooperative Highway Research Program (NCHRP) identified corrosion on steel rebar as the primary concern surrounding deicer use, followed by detrimental effects to vehicles, concrete in general, structural steel, and roadside structures (12). The cost of installing corrosion protection measures in new bridges and repairing old bridges in the Snowbelt states is estimated to be between \$250 million and \$650 million annually (13). Parking garages, pavements, roadside hardware, and non-highway objects near winter maintenance activities are also exposed to the corrosive effects of road salts. It should be noted that any repairs to the infrastructure translate to costs to the user in terms of construction costs, traffic delays and lost productivity. Such indirect costs are estimated to be greater than ten times the cost of corrosion maintenance, repair and rehabilitation (14).

This chapter presents a synthesis of information regarding the corrosion effects of common deicers to metals in transportation infrastructure, with a focus on steel rebar in concrete structures. The following section documents the corrosion impacts that NaCl, CaCl<sub>2</sub> and MgCl<sub>2</sub> have on metals compared with those of alternative deicers, and is followed by discussions of methods to quantify and manage deicer impacts to metals.

## **4.2. Deicer Impacts on Metals**

### ***4.2.1 Chloride-Based Deicer Impacts on Steel Rebar***

Chloride ingress, either from marine environments or from chloride-based deicers, is one of the primary forms of environmental attack for reinforced concrete structures (15), which can lead to rebar corrosion and a subsequent reduction in the strength, serviceability, and aesthetics of the structure. The chloride permeability of concrete is thus considered a critical intrinsic property of the concrete (16). The remediation of concrete bridges in the United States, undertaken as a direct result of chloride-induced rebar corrosion, would cost U.S. highway departments \$5 billion per year (17). Premature deterioration of bridge decks, as well as the contamination of parking garages due to the application of deicing salts, has been reported (13).

In addition to chloride-induced rebar corrosion, chloride-based deicers can exacerbate the scaling problem and freeze/thaw damage of concrete. The use of properly cured, air-entrained portland cement concrete, however, can prevent such physical deterioration of concrete. Otherwise, in cold-climate regions, the synergy of freeze/thaw cycles and rebar corrosion may lead to problems in reinforced concrete structures, with serious economic and safety implications.

#### ***4.2.2. Mechanism for Chloride-Induced Corrosion of Steel Rebar***

Concrete normally provides both chemical and physical protection for the embedded steel reinforcement. Cement hydration leads to the high alkalinity ( $\text{pH} \approx 13\text{--}14$ ) of the concrete pore solution, which promotes the formation of an approximately 10-nm-thick oxide/hydroxide film at the steel surface (18). This protective passive film effectively insulates the steel and electrolytes so that the corrosion rate of the steel is negligible. The concrete cover also prevents or at least retards the ingress of aggressive substances toward the rebar surface.

Localized corrosion of rebar may occur when water and oxygen are available at the steel surface and the passive film is jeopardized by a decrease in the pH of the concrete pore solution and/or by the presence of enough water-soluble (free) chloride ions (11). Chloride-induced corrosion of steel rebar generally follows these steps:

*A. Ingress of chloride into the concrete to a point where a threshold chloride concentration is reached at the embedded reinforcement depth.*

Corrosive agents (e.g., deicer solution) may penetrate through the concrete via capillary absorption, hydrostatic pressure, or diffusion. The ingress of gases, water or ions dissolved in aqueous solutions into concrete takes place through pore spaces in the cement paste, at the cement paste–aggregate interfaces or through micro-cracks. It is believed that the most important factor in the durability of concrete is permeability (19), which is related to its micro-structural properties such as the size, distribution, and interconnection of pores and micro-cracks (20).

It is generally believed that only free chlorides can promote pitting corrosion, while the bound chlorides such as those adsorbed on C-S-H (calcium silicate hydrate) or

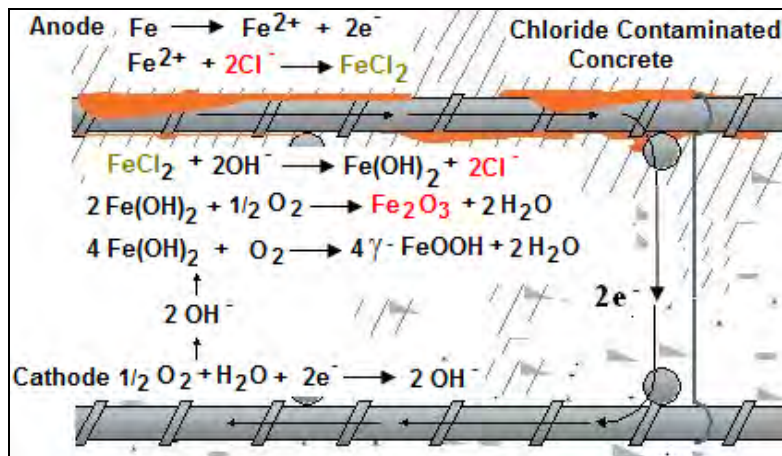
chemically bound with concrete  $C_3A$  (tricalcium aluminate) or  $C_4AF$  phases (e.g., Friedel's salt,  $3CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 10H_2O$ ) do not. However, a recent study suggests that bound chlorides also play a role in corrosion initiation, as a large part of them are released as soon as the pH drops to values below 12 (21). The concentration ratio of free chloride to total chloride in concrete may range from 0.35 to 0.90, depending on the constituents and history of the concrete (22).

The chloride threshold to initiate active corrosion of steel in concrete has been expressed as the free chloride concentration, total chloride concentration, or chloride-to-hydroxyl concentration ( $[Cl^-]/[OH^-]$ ) ratio. Chloride concentrations as low as  $0.6 \text{ kg/m}^3$  in concrete have been projected to compromise steel passivity (18). Another study reported a threshold total chloride concentration of 0.20 wt% by weight of cement to initiate rebar corrosion in bridge decks (23). The  $[Cl^-]/[OH^-]$  ratio is a more reliable indicator than the chloride concentration, considering that the competition between aggressive  $Cl^-$  and inhibitive  $OH^-$  governs the pitting/repassivation of steel. The gradual ingress of atmospheric carbon dioxide into the concrete, a process known as carbonation, may jeopardize the passive film by reducing the pH of the concrete pore solution. However, the corrosion due to carbonation progresses at a much slower rate than that which is due to chloride ingress (24).

Research in aqueous solutions has indicated that for chloride-contaminated concrete the pitting corrosion occurs only above a critical  $[Cl^-]/[OH^-]$  ratio (25). Through a probability simulation model, the threshold  $[Cl^-]/[OH^-]$  for corrosion of bare steel rods in high pH solutions was once predicted to be 0.66 in the presence of oxygen bubbles attached to the steel and 1.4 in the case of air. Such a result agreed favorably with experimental data. In the same model, it was concluded that the threshold ratio should be about 1.4 for typical reinforced concrete and in excess of 3 for high quality concrete with minimal air voids (26). The chloride threshold generally increases with increasing concrete quality.

*B. Local disruption of the passive film and onset of active corrosion in the form of corrosion cells (18, 26).*

The local disruption of the passive film initiates corrosion cells between the active corrosion zones (anode) and the surrounding areas that are still passive (cathode), as shown in Figure 6. In this step, the pit growth can only be sustained above a critical  $[Cl^-]/[OH^-]$  ratio, or the rebar surface will be re-passivated by forming an iron oxide/hydroxide layer (27).



**Figure 6 A typical corrosion cell in a salt-contaminated reinforced concrete.**

As implied in the cathodic and anodic reactions above, aside from pH, temperature and oxygen content play important roles in rebar corrosion. Corrosion of reinforcing steel was found to vary with oxygen contents and temperatures of the corrosion-inhibitor-added deicing salt and salt substitute solutions (28). Oxygen contents in solutions under the control condition decreased as the amount of deicers increased. The reinforcing steels under the freeze/thaw cycle condition showed the least corrosion, whereas those under the dry/wet cycle condition showed the most severe corrosion (28).



*C. Accumulation of solid corrosion products (oxides/hydroxides) in the concrete pore space near the rebar surface and buildup of tensile hoop stresses around the rebar (29).*

*D. Cracking or spalling of the concrete covering the reinforcement.*

As a result of this step, moisture, oxygen, and chlorides can gain more direct access to the embedded steel, leaving it more vulnerable to environmental conditions. Therefore, the corrosion rate may be further accelerated (30).

#### ***4.2.3. Comparing Chloride-Based Deicers in Terms of Metallic Corrosion***

For practical purposes, all chloride-based deicers were ranked equally high in causing corrosion of the reinforcing steel in a recent NCHRP study, even though hygroscopic chlorides of magnesium and calcium can be more aggressive to the exposed metals than NaCl because of the longer time of wetness (12). One laboratory study evaluated the corrosivity of various 3% deicer solutions by intermittently spraying them on carbon steel coupons at room temperature and found that the relative order of deicer corrosivity was as follows from the highest to the lowest: CaCl<sub>2</sub>, MgCl<sub>2</sub>, NaCl, NaCl with a corrosion inhibitor, MgCl<sub>2</sub> with another corrosion inhibitor, CMA, and H<sub>2</sub>O (31).

A study using simulated concrete pore solutions indicated that the corrosion behavior of galvanized steel in the presence of chlorides was controlled by the pH value of the electrolyte, which varies with the cation associated with the chloride anion (32). MgCl<sub>2</sub>-based deicers applied onto concrete could reduce the pore solution pH (from 12.6 to 9.0 for saturated solutions) by replacing Ca(OH)<sub>2</sub> with Mg(OH)<sub>2</sub>, which could result in the loss of the iron oxide layer at the rebar surface even in absence of chloride ions (33).

Therefore,  $\text{MgCl}_2$  promotes rebar corrosion by decreasing the threshold chloride level for initiating corrosion (34).

The cation ( $\text{Na}^+$ ,  $\text{Ca}^{2+}$ , or  $\text{Mg}^{2+}$ ) associated with  $\text{Cl}^-$  also affects the chloride diffusion coefficient (35), and the ranking of diffusion coefficients seems to be independent of the salt concentrations used (12). In one laboratory study (35), the chloride diffusion coefficient in ordinary portland cement (OPC) mortar with  $w/c$  of 0.5 was measured at 9.1, 22.9, and  $29.0 \times 10^{-12} \text{ m}^2/\text{s}$ , respectively, for  $\text{NaCl}$ ,  $\text{CaCl}_2$  and  $\text{MgCl}_2$  at saturated concentrations. In another laboratory study of much more dilute salt solutions (36), the chloride diffusion coefficient in OPC paste was measured at 6.6, 9.9, and  $20.8 \times 10^{-12} \text{ m}^2/\text{s}$ , respectively, for  $\text{NaCl}$ ,  $\text{CaCl}_2$  and  $\text{MgCl}_2$  at 0.5 M concentration. The chloride diffusion coefficients for  $\text{MgCl}_2$  are typically two to three times greater than  $\text{NaCl}$  (34-36), which may significantly reduce the time to corrosion initiation for the rebar in concrete. The effective diffusion coefficient of  $\text{CaCl}_2$  was found to fall between that of  $\text{NaCl}$  and  $\text{MgCl}_2$  (35-36). It should be noted that temperature variations have a significant impact on diffusion coefficients and the related transport process as well.

#### ***4.2.4. Acetate/Formate-Based Deicer Impacts on Metals***

A survey of U.S. airports in 2006 indicated that  $\text{KAc}$  and sand were most widely used for snow and ice control of airfield pavements, followed by airside urea,  $\text{NaAc}$ , sodium formate, propylene glycol-based fluids, ethylene glycol-based fluids, etc. (37). Acetate-based deicers ( $\text{KAc}$ ,  $\text{NaAc}$ , and  $\text{CMA}$ ) have also been used on some winter roadways as non-corrosive alternatives to chlorides.

Acetate/formate-based deicers are widely used on airport pavements because they were considered non-corrosive deicer alternatives to chlorides, despite their possible role in accelerating corrosion via some increase in the electrolyte conductivity (12). It was found that changing from  $\text{NaCl}$  to an acetate deicer decreased the corrosion rate of steel rebar in

a simulated concrete pore solution by more than a factor of ten (38). Recently, however, potassium formate was reported to cause serious corrosion to landing gear and associated wiring of some Boeing airplane models and the corrosion risk of acetate/formate-based deicers to cadmium-plated steel has raised concerns by aircraft manufacturers and airlines (37). A recent study in our laboratory revealed that while NaAc- or KAc-based deicers were non-corrosive to mild steel, they were comparably as corrosive as chloride-based deicers to galvanized steel (39).

CMA is generally considered non-corrosive to metals (13), even though this consensus is mostly based on existing laboratory studies involving the direct exposure of rebar or steel coupons to CMA solutions, which may not represent the case where the rebar is embedded in concrete (12). Electrochemical and weight loss tests of 14- to 17-month duration indicated that bridge structural metals, including steel, cast iron, aluminum, and galvanized steel corroded considerably less in CMA solutions than in NaCl solutions (40). Full and half immersion, vapor space, sprays, and dip testing of ASTM A-36, A-325, and A-588 steel, gray cast iron, and aluminum indicated that CMA solutions were less corrosive to all the metals tested than NaCl solutions (41). However, similar to NaCl, CMA caused a substantial shift of the corrosion potential of steel in mortar, simulated pore solutions, and concrete slabs, indicating the increased risk for steel corrosion (41). This may be attributed to the fact that CMA reduced the pH of simulated pore solutions by precipitating OH<sup>-</sup> ions as Ca(OH)<sub>2</sub> and Mg(OH)<sub>2</sub> (41). It is noteworthy that in another study, the steel embedded in concrete ponded with CMA solutions did not show any significant potential shifts or corrosion whereas the steel embedded in concrete ponded with NaCl solution did (42). In CMA solutions of 2 wt.% and higher, reverse polarization scans indicated an unusual electrochemical behavior occurred with three current reversals. It is proposed that carbon dioxide is formed as a consequence of an electrochemical reaction involving the acetate ion. The carbon dioxide then dissolved in the solution, leading to the precipitation of insoluble carbonates at cathodic sites on the steel surface (43).

Currently there are conflicting data as to whether CMA can be used as an effective corrosion inhibitor for chloride-induced corrosion of reinforcing steel. The ASTM G 109 ponding test results suggested that CMA as an additive to NaCl (in a ratio of 1 to 2) did not inhibit the rebar corrosion in concrete (44). One study confirmed that sodium acetate, urea and CMA were only marginally effective as corrosion inhibitors for rebar in concrete, by examining the electrochemical behavior of iron in cured cement pastes (45). In contrast, another study indicated that adding CMA to a steel-and-concrete system undergoing active chloride-induced corrosion slowed corrosion after 30 days and stopped corrosion after 60 days (46). Compared with salt solution made with pure NaCl, a solution made with a 20/80 NaCl/CMA mixture (w/w) was 45% less corrosive to steel (47). The impedance and voltammetric measurements confirmed that adding CMA to a simulated pore solution diminished the corrosion rate and increased the protectiveness of surface films (48).

### **4.3. Quantification of Deicer Impacts on Metals**

#### ***4.3.1. Common Test Methods for Deicer Corrosivity***

The following sections describe common methods for testing deicer corrosivity. Other test methods such as ASTM B117 are not included since they are rarely used for the evaluation or quality assurance of deicer products.

#### ***4.3.2. PNS/NACE Test Method***

This test method is based on the National Association of Corrosion Engineers (NACE) Standard TM0169-95 as modified by the Pacific Northwest Snowfighters (PNS). The test procedure uses 30 ml of a 3% chemical deicer solution per square inch of coupon surface area for the corrosion test (49). The PNS/NACE test involves a gravimetric method that

entails cyclic immersion (10 minutes in the solution followed by 50 minutes exposed to air) of multiple parallel coupons for 72 hours on a custom-designed machine. The gravimetric method gives the average corrosion rate over a period of time. The weight loss result in MPY (milli-inch per year) is translated into a percentage, or percent corrosion rate (PCR), in terms of the solution corrosivity relative to a eutectic salt brine.

#### ***4.3.3. SAE J2334 Test Method***

This test method developed by the Society of Automotive Engineers (SAE) places metal specimens in an enclosed chamber and exposes them to changing climates over time. The test procedure is cyclic in nature, consisting of humid stage, salt application stage, and dry stage, and the number of cycles and test duration can be varied (50). It has been found that 80 cycles of such an accelerated laboratory test corresponded well with five years of outdoor, on-vehicle testing for steel (51). One challenge in implementing the SAE laboratory test method lies in the need to precisely control the relative humidity of the test environment.

#### ***4.3.4. SHRP H-205.7 Test Method***

This Strategic Highway Research Program (SHRP) test method covers evaluation of the corrosive effects of deicers on metal substrates through continuous immersion, and is used to evaluate the corrosivity of other aqueous, near neutral pH solutions (52). The test requires a longer exposure time (a few weeks) before weight loss data are collected. This test method is also intended to evaluate the effectiveness of corrosion-inhibiting additives to deicing chemicals. One drawback in the SHRP laboratory test method lies in the lack of wet/dry cycles that simulate the field exposure of metals to deicers.

#### ***4.3.5. A Proposed Test Method***

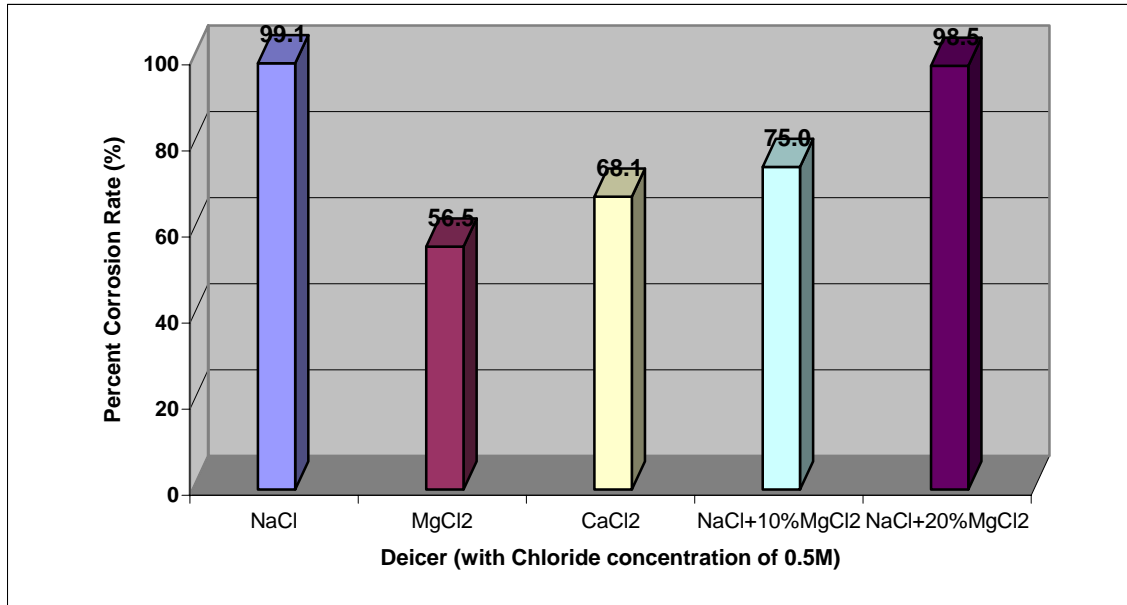
We consider electrochemical techniques an attractive alternative to the gravimetric methods described above, as they allow rapid determination of the corrosion rate of metals and reveal information pertinent to the corrosion mechanism and kinetics. In many practical applications, the use of linear polarization resistance (LPR) is preferred due to its simplicity, and LPR testing is referenced in ASTM G 3 (Standard Practice for Conventions Applicable to Electrochemical Measurements in Corrosion Testing); ASTM G 96 (Standard Guide for On-Line Monitoring of Corrosion in Plant Equipment [Electrical and Electrochemical Methods]); ASTM G 102 (Standard Practice for Calculation of Corrosion Rates and Related Information from Electrochemical Measurements); and ASTM B 117 (Standard Method of Salt-Spray [Fog] Apparatus). However, there are concerns over its validity and reliability when LPR is used to quantify the corrosion rate, as it is prone to measuring errors of the test instrument and other variations. For Tafel polarization, the limitation is that the applied perturbation of large amplitude may lead to a significant change in the surface state of electrodes, in the solution composition, or in the controlling corrosion mechanism and kinetics. Shi and Song found that the corrosion potential ( $E_{\text{corr}}$ ) and corrosion current density ( $i_{\text{corr}}$ ) derived from weak polarization curves were useful to predict the PCR (percent corrosion rate) value at reasonable accuracies (53). The electrochemical technique was able to rapidly evaluate the corrosivity of deicer products in the presence and absence of corrosion inhibitors. The authors also suggest the use of a multi-electrode array (also known as wire beam electrodes) in place of the one-piece working electrode in order to enhance the reliability of the electrochemical test and to allow possible investigation of non-uniform corrosion (54).

To bring to fruition an electrochemical-polarization-based standard test protocol for deicer corrosivity, wet/dry cycles and control of the test environment (temperature, relative humidity, etc.) should be incorporated into the test procedure and weak polarization curves of metal coupons should be periodically measured for deicer products

typically used by maintenance agencies at various concentrations. We envision that there would be a strong correlation between the electrochemical data and the PNS/NACE test results.

#### ***4.3.6. Comparing Test Methods***

The relative corrosivity of deicers is dependent on many details related to the metal/deicer system. Therefore, no general conclusions should be made when ranking corrosion risks of different deicer products. Instead, it is important to note the test protocol employed, the metal coupons tested, the deicer concentrations, the test environment, etc. For instance, in a recent study in our laboratory, the PNS/NACE corrosion test using ASTM C4130 carbon steel coupons suggested that plain  $\text{MgCl}_2$  was the least corrosive among five common deicers with the same  $[\text{Cl}^-]$  concentration of 0.5M— $\text{NaCl}$ ,  $\text{MgCl}_2$ ,  $\text{CaCl}_2$ ,  $\text{NaCl}+10\text{wt.}\% \text{MgCl}_2$ , and  $\text{NaCl}+20\text{wt.}\% \text{MgCl}_2$ —as shown in Figure 7 (53). Xi and Xie performed metal coupon testing following the ASTM B117 and the PNS/NACE test methods and also found  $\text{MgCl}_2$  to be less corrosive than  $\text{NaCl}$  to the bare metals tested (stainless steel 410 and 304L, aluminum 2024 and 5086, copper wires, and mild steels) (55). Nonetheless, the SAE J2334 test results led to the opposite conclusion. The inconsistencies in the test results were attributed to the different moisture conditions and to the different properties of the two salts in a high humidity environment.  $\text{MgCl}_2$  was found to be more corrosive than  $\text{NaCl}$  in humid environments (due to its hydrophilic nature and the higher viscosity of its solution), and  $\text{NaCl}$  was found to be more corrosive under immersion and in arid environments (55).



**Figure 7 Corrosivity of the five chloride-based deicers (PNS/NACE test)**

It is also extremely difficult to relate laboratory test results of corrosion resistance to the actual field performance of metals. For instance, corrosion-inhibited deicer product must prove to be at least 70% less corrosive than NaCl, i.e., with a PCR value of 70 or less, to be qualified for sale in the PNS states. However, not all qualified deicer products reached this goal in the field, as revealed by an evaluation project in the State of Washington. The research project compared the corrosion of steel and aluminum exposed to different roadway or roadside environments where NaCl, corrosion-inhibited MgCl<sub>2</sub>, or corrosion-inhibited CaCl<sub>2</sub> were applied for winter maintenance (56). Exposure of steel coupons mounted underneath motor vehicles to corrosion-inhibited chemicals consistently resulted in less corrosion than exposure to NaCl. These figures ranged as high as 70% less corrosive than NaCl, and averaged 43% less corrosive. For steel coupons mounted on guardrail posts, more corrosion was found from the exposure to corrosion-inhibited chemicals than from exposure to NaCl, which may be attributed to the difference in longevity and migration behavior of chlorides and corrosion inhibitors in the field, or to the possible effects of stray currents or galvanic corrosion in the field. Corrosion results



for sheet aluminum and cast aluminum were less consistent, likely due to the small weight losses susceptible to experimental errors and interferences. The corrosion patterns were consistent between the two years of evaluation (56).

#### **4.4. Countermeasures to Manage Metallic Corrosion due to Deicers**

Given the importance of the issue, the authors hereby present a wide range of countermeasures that are currently available to manage metallic corrosion due to deicers. They can be used individually or in combination to mitigate the corrosive effects of deicers.

First, there is consensus that effectively addressing concrete durability begins at the design and materials selection stage by using high-quality concrete and adequate concrete cover. Increasing the thickness of the concrete cover over the steel rebar can be beneficial (33), with the thicker concrete layer acting as a barrier to prevent various aggressive species from migrating towards the rebar surface, and therefore increasing the time required for rebar corrosion to initiate. However, the cover thickness cannot exceed certain limits for mechanical and practical reasons (24). One laboratory study of rebar-concrete prism specimens exposed to 600-day seawater spray cycles identified the water-to-cement ratio as the dominant factor that controls rebar corrosion, while the  $\text{Cl}^-$  concentration relative to  $\text{OH}^-$  of the pore fluid was of secondary importance (10). Another study of steel-reinforced concrete cylinders subjected to various laboratory conditions indicated that the rebar in high performance concrete (HPC) specimens ( $w/c=0.33$ , concrete thickness:75 mm) performed much better than those in OPC specimens ( $w/c=0.6$ , concrete thickness:75 mm) in resisting chloride-induced corrosion (57).

In addition to an appropriate concrete mix design, permeability-reducing admixtures (e.g., mineral and polymer admixtures) are expected to reduce the risk of rebar corrosion

and enhance concrete durability (58-63). For instance, the chloride diffusion coefficient for NaCl, CaCl<sub>2</sub> and MgCl<sub>2</sub> at saturated concentrations was significantly reduced to 1.4, 1.5, and  $1.8 \times 10^{-12}$  m<sup>2</sup>/s, respectively, in slag-blended cement mortar, confirming the beneficial effects of mineral admixtures (35). There are two types of concrete porosity that can affect chloride diffusion: macroporosity due to entrapped or entrained air and capillary porosity due to the presence of free water. Silica fume and other pozzolans can reduce macroporosity since they make concrete more compact, while decreasing the *w/c* ratio can reduce capillary porosity. As such, concrete with silica fume or other pozzolans can have diffusion coefficients lower than  $10^{-12}$  m<sup>2</sup>/s, especially when the water-to-cementitious-materials ratio is lower than 0.4.

Other best practices at this stage include the addition of corrosion-inhibiting admixtures to fresh concrete (59-60, 64-68), the surface treatment of steel rebar (69-76); or the use of alternative reinforcement materials (77-78). For instance, the use of steel fiber reinforcement in concrete limits the deterioration of concrete, while improving its resistance to damage under severe conditions (79).

Secondly, the corrosive effects on rebar from concrete deicers can be mitigated by controlling the ingress and accumulation of deleterious species. Existing research generally agrees that a hydrophobic surface treatment with good quality products (e.g., silanes and siloxanes) helps delay/reduce the ingress of chlorides and moisture into the concrete and thus improves the durability of reinforced concrete structures (80-88). However, there are conflicting data regarding whether such treatment would benefit existing concrete decks with a relatively high level of chloride contamination in the concrete.

Previous research has indicated that once chloride-induced corrosion of the reinforcing steel is initiated in the concrete structure, the only effective means to stop corrosion is electrochemical methods such as cathodic protection (CP) and electrochemical chloride

extraction (ECE) (89). CP can stop further corrosion of the reinforcing steel regardless of the chloride content in the concrete by directly shifting the steel potential from its natural state (corrosion potential) to a value below the equilibrium potential of steel, thus stopping the anodic dissolution (90). While measured chloride profiles indicated that little chloride migration occurred at low CP current densities of  $0.01 \text{ A/m}^2$ , migration away from the rebar and general chloride depletion in its vicinity were observed at current densities of  $0.05 \text{ A/m}^2$  or higher (91-92). CP was demonstrated to induce microstructure alterations and some micro-cracking, while effectively retarding corrosion-induced crack initiation and propagation (93). While both techniques proved to extend the service life of the treated structure, ECE offers more advantages over the use of CP such as the elimination of regular maintenance, as it is a one-time treatment electrically removing  $\text{Cl}^-$  from contaminated concrete while generating beneficial hydroxyl ions ( $\text{OH}^-$ ) at the rebar (94-97). While ECE gradually gains acceptance by practitioners as a viable rehabilitation measure, numerous research efforts have been devoted to examine its efficiency, influential factors, and limitations (98-101). ECE can also alter the chemistry and morphology of the cement paste especially near the steel-concrete interface, leading to Na-rich, Ca-Al-rich, Fe-rich, or Ca-rich crystals, an alkali-silica rich gel at the interface (98-99) and a higher number of pores with a smaller pore size (101) in concrete.

Thirdly, the corrosive effects on rebar from concrete deicers can be mitigated by injecting beneficial species into concrete. Alkanolamines and amines and their salts with organic and inorganic acids have been patented as corrosion inhibitors for surface treatment of chloride-contaminated concrete, often as active ingredients of migrating corrosion inhibitors (MCIs). Such organic inhibitors have been said to penetrate rapidly into concrete due to their high vapor pressure under atmospheric conditions, but existing research related to their penetration behavior into concrete has been inconclusive so far, likely due to the diversity in porosity and chemistry of concretes investigated and test methods used (102-104). Treatment of corroding reinforced concrete with one MCI product was able to decrease the rate of rebar corrosion induced by concrete carbonation, both for laboratory conditions and site structures (104). Another MCI product was able to reduce the corrosion rate only when the initial chloride content was below 0.16 wt.% by

weight of cement ( $w/c=0.4$  and  $0.6$ ), whereas there was no beneficial effect when the initial chloride content was greater than  $0.43$  wt.% (105).

Electrical injection of corrosion inhibitors (EICI) is a relatively new technique that uses a setup similar to ECE to drive inhibitor ions into concrete while at the same time removing  $Cl^-$  ions out of concrete. The feasibility of this technique was first demonstrated in the late 1980s (94), when quaternary ammonium and phosphonium corrosion inhibitors were developed specifically for electrical injection into concrete concrete ( $w/c=0.5$ ). The study showed that such inhibitor injection could provide adequate corrosion protection to rebar embedded in chloride-contaminated concrete. Limited studies have been published since the SHRP study, likely due to the high cost of the aforementioned corrosion inhibitors. A recent study investigated the electromigration of two organic base corrosion inhibitors, ethanolamine ( $pK_a$  9.5) and guanidine ( $pK_a$  13.6) (103). In this EICI process, an electric field was applied between steel embedded in concrete and an external anode, with the cathodic current density galvanostatically controlled in the range of  $1\sim5$   $A/m^2$  for 3–14 days. Experiments under the same conditions but without an electric field were also conducted by applying the corrosion inhibitors to similar saturated concrete surfaces from external electrolytes. The inhibitor concentration profiles indicated that the two inhibitors were effectively injected into the carbonated reinforced concretes investigated, and their electrical injection in non-carbonated concrete was far less effective. In carbonated concrete, the inhibitors became concentrated near the embedded steel. In non-carbonated concrete ( $w/c=0.65$ ,  $pH>13$ ), guanidine penetration was accelerated to a modest extent by the applied field but a two-week,  $5A/m^2$  treatment did not cause sufficient amounts of the inhibitor to reach the rebar at a cover depth of 35mm. Ethanolamine penetration in non-carbonated concrete was not significantly enhanced by the electric field. These findings were explained in terms of the influence of the pH of the concrete pore solution on the degree of ionization of the organic bases and hence on their tendencies to migrate and neutralize cathodically generated hydroxyl ions (106). In a recent study in our laboratory, we assessed the potential applicability of EICI as a routine electrochemical treatment (107). Eight organic chemicals were selected for preliminary evaluation in terms of their corrosion inhibition effectiveness for ASTM A588 steel in

chloride-containing simulated pore solutions. The best performers (tetrabutylammonium bromide and tetraethylammonium bromide) were then further evaluated for their diffusion coefficient in concrete ( $w/c = 0.5$ ) via a customized electro-migration test. The study identified the selection of corrosion inhibitors as a critical component to the successful implementation of EICI practice as a rehabilitative measure for salt-contaminated concrete. The modeling results indicated that when an appropriate corrosion inhibitor was utilized, it was feasible to electrically inject a sufficient amount of inhibitor into salt-contaminated concrete within a reasonable time frame (107).

Furthermore, the use of an applied electric field has been demonstrated to be effective in realkalizing carbonated concrete (108), to drive  $\text{Li}^+$  into concrete and mitigate ASR (109), and to inject cations (e.g,  $\text{Zn}^{2+}$ ) to rehabilitate concrete cracks (110).

Finally, in order to minimize the corrosive effects of deicers to metals in transportation infrastructure, it is important for maintenance agencies to continuously seek non-corrosive deicer alternatives (39) and optimize the application rates of deicers using advanced technologies such as snowplows equipped with sensors (111). It should be cautioned that deicer products that are non-corrosive to one metal might be corrosive to other metals (39) and additives used to inhibit certain metallic corrosion may have little to no inhibition effect on other metals (12).

#### **4.5. Conclusions**

In cold-climate regions such as the northern United States and Canada, snow and ice control operations are crucial tools in maintaining highways subject to cold and snowy weather. The growing use of deicers has raised concerns about their effects on motor vehicles, transportation infrastructure, and the environment.

Chloride ingress, either from marine environments or from chloride-based deicers, is one of the primary forms of environmental attack for reinforced concrete structures. Localized corrosion of rebar may occur when water and oxygen are available at the steel surface and the passive film is jeopardized by a decrease in the pH of concrete pore solution and/or by the presence of enough water-soluble chloride ions. Chloride-based deicers can exacerbate the scaling problem and freeze/thaw damage of concrete. Deicers may also pose a detriment to concrete infrastructure through their reactions with the cement paste and thus reduce concrete integrity and strength, which in turn may foster the ingress of moisture, oxygen and other aggressive agents onto the rebar surface and promote rebar corrosion.

For practical purposes, all chloride-based deicers were ranked equally high in causing corrosion of the reinforcing steel in a recent NCHRP study, even though hygroscopic chlorides of magnesium and calcium can be more aggressive to the exposed metals than NaCl because of the longer time of wetness. The cation ( $\text{Na}^+$ ,  $\text{Ca}^{2+}$ , or  $\text{Mg}^{2+}$ ) associated with  $\text{Cl}^-$  also affects the pH value of the electrolyte and the chloride diffusion coefficient in concrete and thus poses different levels of corrosion risk to the rebar in concrete.

Acetate/formate-based deicers are widely used on airport pavements because they were considered non-corrosive deicer alternatives to chlorides. A recent study in our laboratory revealed that while NaAc- or KAc-based deicers were non-corrosive to mild steel, they were comparably corrosive as chloride-based deicers to galvanized steel.

We consider electrochemical techniques an attractive alternative to the gravimetric methods commonly used to evaluate deicer corrosivity (PNS/NACE, SAE, and SHRP methods), as they allow rapid determination of the corrosion rate of metals and reveal information pertinent to the corrosion mechanism and kinetics.

The relative corrosivity of deicers is dependent on many details related to the metal/deicer system. Therefore, no general conclusions should be made when ranking corrosion risks of different deicer products. Instead, it is important to note the test protocol employed, the metal coupons tested, the deicer concentrations, the test environment, etc. It is also extremely difficult to relate laboratory test results of corrosion resistance to the actual field performance of metals.

There are many ways to manage the corrosive effects of deicers, such as: selection of high-quality concrete, adequate concrete cover and alternative reinforcement, control of the ingress and accumulation of deleterious species, injection of beneficial species into concrete, and use of non-corrosive deicer alternatives and optimal application rates.

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## CHAPTER 5. ENVIRONMENTAL IMPACTS OF DEICERS

### 5.1. Introduction

In cold-climate regions such as the northern United States and Canada, winter maintenance is often the activity of highest priority for transportation agencies. Large amounts of solid and liquid chemicals (known as deicers) as well as abrasives are applied onto winter roadways to keep them clear of ice and snow. The deicers used by highway agencies are mainly chloride-based salts. Acetate-based deicers (potassium acetate, sodium acetate, and calcium magnesium acetate—CMA) have also been used on some winter roadways. Airports use mainly acetates and glycols as deicers for their pavements and aircrafts, respectively. In addition, formates (sodium formate and potassium formate) and bio-based products have emerged as potential alternative deicers.

The past decade has seen growing use of deicers due to customer expectation of a higher level of service, while at the same time there has been a paradigm shift from reactive to proactive winter maintenance strategies, and the concerns over detrimental environmental impacts of abrasives has become apparent (1,2). Each year the United States and Canada use approximately 15 million and 4–5 million tons of deicing salts, respectively (3).

Through repeated applications and plowings, large amounts of deicers and abrasives are deposited alongside roadways. They then migrate to the environment adjacent to the roadway, including adjacent water bodies. Highway runoff, originating from salting, sanding, and other maintenance activities, poses threats to water resources (4-7), but the damaging impacts depend on site-specific conditions and concentrations of pollutants in the receiving environments. One case study found decreases in the diversity and productivity of aquatic ecosystems at some sites with inflow of highway runoff containing sediment (8). In another case study physical, chemical, and biological

parameters indicated that deicing activities using IceBan (a magnesium chloride-based deicer) and traction sand had no measurable negative impact on an adjacent creek (9). A study from the Michigan Department of Transportation (DOT) suggested that endangered and threatened species and the habitat on which they depend for survival could be adversely affected by the use of certain deicers. In addition, groundwater and vulnerable aquifers can be affected by any material applied or spilled on the land, including deicers and sand. However, none of the studied deicers posed widespread adverse environmental threats (10). Yet, a survey conducted for the NCHRP 577 Report found water quality to be of greatest concern to its respondents, with air quality, vegetation, endangered species, and subsurface well contamination also mentioned as highly relevant (11).

Hidden costs due to environmental impacts should be weighed against benefits and direct costs when selecting snow and ice control materials in order to conduct winter maintenance activities in an environmentally friendly and fiscally responsible manner. It has been shown that repeated applications of deicers and abrasives may adversely affect the surrounding vegetation, water bodies, aquatic biota, and wildlife (8,12). In extremely sensitive environments, small applications of deicers may be detrimental to the ecosystem. While most highway segments do not fall into this category, improvements are still necessary to minimize future risks.

The variety of active ingredients and additives that deicers are composed of allow for unique blends to be made to accommodate a wide range of conditions, which can in turn lead to environmental problems associated with each blend. Environmental parameters that vary for each deicer include: eutectic point and effective temperature range, biological oxygen demand (BOD), chemical oxygen demand (COD), pH, water solubility, and nitrogen, phosphorus, cyanide, and heavy metal content. Below is a description of each of these parameters. The environmental impacts of deicers are summarized in Table 5.

### ***5.1.1. Temperature***

The eutectic point is the temperature at which the liquid phase borders directly on the solid phase, representing the minimum melting temperature of the aqueous deicer solution. The eutectic point of a deicer solution is usually reported on the MSDS. This, however, does not provide practical guidance on the temperature range in which the deicer will work effectively. Therefore, it is desirable to test and report the effective temperature range of deicers.

### ***5.1.2. Biological Oxygen Demand (BOD)***

The biological oxygen demand is the measure of 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.

### ***5.1.3. Chemical Oxygen Demand (COD)***

The chemical oxygen demand is the amount of oxygen consumed by the chemical breakdown of organic and inorganic matter, and is considered another good way, in addition to BOD, to measure water quality. COD is generally reported as a quantity in mg/L.

### ***5.1.4. pH***

The pH of deicers is an important parameter to consider. The pH is the negative log of the hydrogen ion concentration in solution and represents the intensity of the acidic (low pH)

or basic (high pH) character of a solution. Frequently the pH is close to neutral (pH=7), and therefore has little effect on the surrounding environment. Deicers with acidic pH (lower than 7) can acidify soil and water, while deicers with basic pH (higher than 7) can make soil and water basic. Altering the pH of an ecosystem can have many adverse effects.

#### ***5.1.5. Water Solubility***

The water solubility and decomposition rate of deicers are important in defining the fate and potential transport behavior of the deicer as well as potential reactions that may occur.

#### ***5.1.6. Nitrogen, Phosphorus, Cyanide, and Heavy Metals***

Forms of nitrogen present in snow and ice control products include:

- Nitrite ( $\text{NO}_2^-$ )
- Nitrate ( $\text{NO}_3^-$ )
- Ammonia ( $\text{NH}_3$ )
- Organic Nitrogen (TON)
- Total Kjeldahl Nitrogen (TKN)
- Total Nitrogen (TN)

Total Kjeldahl nitrogen is determined by combining ammonia and organic nitrogen and was investigated in Chapter 8. The evaluation of ammonia is necessary because of potential toxicity to aquatic life at high concentrations (11). TKN is reported as mg/L.

Phosphorus is present in many forms with orthophosphate ( $\text{PO}_4^{-3}$ ), which is readily soluble, and total phosphorus (TP), which includes bound and combined phosphorus (11). Phosphorus is reported as mg/L. The PNS total concentration limit set for phosphorus is 2500ppm or mg/L (14). Due to phosphorus restrictions for many Colorado basins, CDOT requires total phosphorus concentrations of 25mg/L or less, much lower than PNS recommends.

The presence of nitrogen (N) and phosphorus (P) in deicers in substantial quantities can cause limiting of nutrients in aquatic systems. Additions of these nutrients can promote excessive growth of some aquatic organisms.

Ferric ferrocyanide (Prussian Blue) and sodium ferrocyanide (Yellow Prussiate of Soda) compounds are commonly added to solid NaCl as anti-caking agents. Evidence suggests these materials have limited bioavailability under natural field conditions (11), but total cyanide concentration should be considered for potential environmental impacts. Heavy metal concentrations in deicer should be considered because heavy metals can persist in the environment and have toxicological effects on flora and fauna. Table 4 provides a list of the heavy metals for which the PNS Association requires testing and the total concentration limits allowed in deicers (14).

**Table 4 Colorado DOT and PNS-defined heavy metals of interest and their total allowable limits in deicer products (13-14).**

Element	Total concentration limits (mg/L)	
	Colorado DOT	PNS
Ammonia	5	-
Arsenic	5	5
Barium	10	100
Cadmium	0.15	0.2
Chromium	0.1	1
Copper	0.2	1
Lead	1	1
Mercury	0.05	0.05
Molybdenum	15	-
Zinc	10	10
Selenium	0.3	5
Cyanide	0.125	0.2

Toxicity of deicers to flora and fauna should also be considered. Standard testing protocol recommended by the Strategic Highway Research Program (SHRP) includes seed germination (Environmental Protection Agency EPA/560/5-75/008) and Fathead Minnows (EPA/600/4-85/013) toxicity testing (15). Toxicity tests can be reported as the lethal concentration for 50% of the population (LC<sub>50</sub>) at an acute dose or a chronic dose, as well as the lowest observed effect level (LOEL) or no observed effect concentration (NOEC) (reported as mg/kg body weight).

#### ***5.1.6. Rate of Application***

In addition to the chemical properties unique to each deicer, the quantity of deicer applied is of equal importance in its effectiveness and environmental impacts. Deicers may have detrimental effects on soil, vegetation, and water bodies once the concentration reaches elevated levels (10,16-17). For instance, while NaCl is relatively harmless at low

concentrations, if excessive quantities are applied for winter maintenance or unnecessary leaching from stockpiles occurs, the environment adjacent to the road can be severely impacted including increased chloride concentrations in adjacent waterways. Application rates reported by CDOT personnel are listed in Chapter 6 Table 9.

This chapter presents a synthesis of the environmental impacts of common deicers (as well as abrasives). Of the common deicers, NaCl (liquid and solid) with or without sand and MgCl<sub>2</sub> are the most commonly used in Colorado. The following section documents the impacts NaCl, CaCl<sub>2</sub> and MgCl<sub>2</sub> have on adjacent environments, compared with those of the selected alternative deicers, potassium acetate and sodium acetate/formate. Environmental impacts of other common deicers are also briefly discussed.

## **5.2. Environmental Factors**

The potential impacts of deicers are dependent on a variety of factors unique to each site (16), primarily: temperature, light, humidity, wind, soil water concentration, soil texture and drainage, and the amount of precipitation.

Ambient air temperature and pavement temperature will dictate the type of deicer to be used, the application rate and, in turn, the melting rate of snow (16). Topography can create isolated pockets of roadway that maintain much warmer or colder temperatures than the majority of the roadway and should be considered. Light exposure can cause volatilization of deicer compounds creating varying roadway conditions. Increased humidity may cause MgCl<sub>2</sub> and CaCl<sub>2</sub> to become slick and sticky, actually decreasing road traction to worse-than-icy conditions. Humidity has also been shown to play an important role in the deterioration of PCC pavements and the corrosion of reinforcing steel in concrete structures. Humidity should be considered especially for anti-icing practices. Wind speed and direction at the time of deicer application and post application can pick up and carry the compounds off the roadways to adjacent soil, foliage and

waterways. The Connecticut DOT found that airborne salt traveled up to 300ft from roadways under heavy traffic conditions on primary or interstate highways, with salt spray transported up to 500ft downwind under high wind conditions (16). Deicer migration into soils adjacent to roadways can cause soil swelling and compaction, change soil electrical conductivity, and lead to loss of soil stability via dry/wet cycles, osmotic stress, and mobilization of nutrients (18). The quantity of precipitation as rain and snowfall will affect the dilution factor of the applied deicer as well as the flushing rate of the system (16). There is some evidence suggesting that elevated deicer concentrations in some water systems are compensated for by the elevated water flows associated with the storm for which the application was necessary (16), but this is highly variable and site-specific and cannot be considered a rule-of-thumb.

### **5.3. Environments to Consider**

#### ***5.3.1. Surface, Ground, and Drinking Water***

The level of surface water contamination from deicers is a function of the amount of time the deicer takes to reach the water body, the dilution factor, the residence time of the water body, and the frequency and rate of deicer application (19). Groundwater contamination from deicers is dependent on the frequency of the precipitation, the texture and drainage characteristics of the roadside soil, the distance the groundwater is from the surface and from the roadway, the permeability of the aquifer material, the direction and rate of groundwater flow, and the deicer application rate (19). For example, shallow and localized aquifers are at greater risk of contamination than deep and regional water sources. For groundwater sources to return to the pre-contaminated condition, dilution and flushing usually can take days to years. A study of Mirror Lake in New Hampshire has shown that applied deicing salt has not broken down in the aquatic environment; instead it is accumulating and may have led to contamination of public and private wells (20-21).



### **5.3.2. Soils**

Factors that affect the concentrations of deicer in the soil are the soil type and texture, as well as its cation exchange capacity, permeability, and infiltration capacity (19). Amrhein et al. (1992) studied the effect of deicers on metal and organic matter mobilization in roadside soils (22). Soils adjacent to roadways were sampled from areas that receive heavy traffic and treatment with deicing salts. The sampled soils were used to simulate runoff of salty water from the roadway due to snowmelt or rainwater by leaching the columns with solutions of NaCl, CMA, or de-ionized water. Concentrations of Cr, Pb, Ni, Fe, Cd, and Cu were found in the salt solution leachates and, in general, concentrations increased with increasing salt concentration. These findings suggested that ligand complexation and competitive exchange affected mobilization of the metals. Soils leached initially with NaCl followed by de-ionized water, showed extensive mobilization of organic matter and elevated concentrations of Cr, Pb, Ni, Fe, and Cu. In this second treatment metal mobilization was caused by dispersion of organic matter under conditions of high exchangeable  $\text{Na}^+$  and low electrolyte concentration.

### **5.3.3. Flora**

Common deicer exposure mechanisms to plants include increased concentration in the soil and water, which can result in uptake by plant roots, and accumulation on foliage and branches due to splash and spray (16). The most common exposure route is splash or runoff from the roadways. On primary highways within 100ft of the road, highway agencies estimate that 5% to 10% of the plants in high use sections are affected by deicers, and report that shrubs and grasses can tolerate increased concentrations better than trees. Plants with broader leaves are generally affected more than plants with narrow leaves (16). Studies have shown that the slope of the roadside adjacent to the treated roadway is an important variable in the extent of plant injury from deicer treatment, with

vegetation showing effects up to 20ft away on flat surfaces, 40 to 55ft away for steep down slopes, and 10ft up slope (16).

Aerial drift of deicers due to vehicle splash, plowing, and wind has been observed to impact vegetation adjacent to roadways. Nicholson and Branson (1990) showed deicer particulates deposited on the road, could be removed and re-suspended by vehicular traffic (23). Wet conditions, increased vehicle speed, wind currents, and updrafts generated by vehicular traffic caused redistribution of deicers off the roadway into the adjacent environment (24). Deicing particles have been observed up to 330ft (100m) from the roadway (25) and ranging from 6 to 130ft (2-40m) (26-27). Kelsey and Hootman (1992) observed sodium deposition within 400ft (122m) of a toll way and sodium related plant damage within 1240ft (378m) of the toll way (24). Field tests have shown that 20 to 63% of the NaCl based deicing salts applied to highways in Sweden were carried through the air with 90% of this deposited within 65ft (20m) of the roadside (27). Deicing salt exposure due to spray within 33 to 65 ft (10 to 20m) of the road was demonstrated to cause a greater severity of foliar damage than soil uptake alone (28-30). Field and greenhouse studies have found direct application of  $MgCl_2$  to be more damaging to plant foliage than NaCl, causing decreased photosynthesis rates on exposed foliage adjacent to roadways (31). Many studies have indicated that needle necrosis, twig dieback, and bud kill are associated with areas of heavy deicing salt usage, with trees and foliage down wind and facing the roadside more heavily affected than trees further away (26,28,32-33).

Native plant succession or loss of native plant species due to deicer use has been observed in soils adjacent to roadways and in low flush-rate surface waters adjacent to roadways, as well as in wetland-type environments that receive water flow from treated roadways. In wetlands with elevated deicer concentrations a decrease in plant community richness, evenness, cover, and species abundances has been observed (34). In wetlands specifically, reducing and/or halting deicer treatment can allow for native plant recovery

after multiple water years, but this includes non-native species re-introduction as well (16,35).

#### ***5.3.4. Fauna***

Deicers are generally at most low to mild skin and eye irritants to humans as can be referenced in the MSDS. Issues arise when there is direct ingestion of product, generally in the case of wildlife. Salt may accumulate on the side of roadways during spring as snow melts and following application of deicers that attract deer and other wildlife to areas where there are few natural salt sources (36). The presence of wildlife on roadways to glean deicing salts has led to increased incidents of wildlife–vehicle collisions (37).

### **5.4. Environmental Assessment of Deicers by Group**

#### ***5.4.1. Abrasives***

The application of abrasives such as sand can decrease air quality by increasing the concentration of small particles in the atmosphere (38). Solid chemicals may also become particulates in the air. Particles smaller than 10 microns (0.01mm) in diameter, known as PM-10, are regulated by the EPA and may become suspended in the air and contribute to respiratory problems and cause eye and throat irritation. Inhaled particulate matter may increase breathing difficulties for sensitive populations, causing respiratory damage and possibly lung cancer. Airborne particles have led to decreased air quality especially in urban settings, which is one of the concerns addressed by the U.S. Clean Air Act (39).

Communities with excessive PM-10 particles in the air may surpass limits imposed by the Clean Air Act and be categorized as “non-attainment” areas. In such communities the use of abrasives is only allowed on a limited basis (e.g., Metro Denver and Utah’s

Wasatch Front). Following the “non-attainment” categorization Colorado reduced sanding applications and as of 2002 has not been out of compliance. Through these measures air quality in Colorado has improved, and since the switch, Colorado has not surpassed the air particulate limit (40).

Other environmental issues associated with the use of abrasives include increased water turbidity from suspended solids, clogging of streams and storm water drains, and reduced oxygenation within the stream and river beds. Particle sizes less than 2mm become especially problematic because they can block the movement of oxygen into streambed gravel. Increased quantities of particles less than 6mm in size can smother macro-invertebrates and fish eggs, affecting both food chains and fish reproduction.

#### ***5.4.2. Chlorides***

Deicers that contain chlorides include sodium chloride, calcium chloride, magnesium chloride, and potassium chloride. Known issues associated with the use of chlorides as deicers are increased salinity in adjacent water ways and soils, degradation of the environment along the roadside, and infiltration of sodium, magnesium, calcium, and chloride into soils and drinking water (16).

##### *Chlorides in Water*

Colorado water quality standard Regulation No. 31 is a secondary drinking water limit that states water chloride concentrations above 250mg/L may affect the taste of the water, and the EPA has set the maximum chronic exposure levels for chloride content in water at 250mg/L (41-42). Chlorides are readily soluble in water and difficult to remove, and so concerns have been raised over the effects on water quality. For protection of aquatic life, the U.S. EPA specifies the one-hour average (acute) and four-day average (chronic)

concentrations of chloride should not exceed 860mg/L and 230mg/L more than once in three years, respectively. These levels were developed for chloride associated with sodium, whereas chloride associated with potassium, magnesium, and calcium would be more toxic to aquatic life, and thus should be managed at lower concentrations (43).

Chloride concentration in freshwater lakes and rivers generally ranges from 0 to 100mg/L, with most concentrations lower than 20mg/L. Winter concentrations following road salting have been recorded as high as 10,000mg/L and 18,000mg/L (16,18). Generally, the highest salt concentrations in surface waters are associated with winter or spring thaw flushing events. Elevated concentrations generally dilute quickly due to the flushing event. This was also observed in a comprehensive study in which water samples indicated the effects from deicing salt (NaCl) and dust inhibitor (MgCl<sub>2</sub>) applied to sections of the road elevated stream chloride concentrations, but these elevated concentrations were only present for a brief amount of time and the overall concentrations were relatively low (44).

Studies have found that chloride concentrations in highway runoff are typically low enough that chloride is quickly diluted in receiving waters. Therefore, the impact of chemical products on receiving waters may be negligible in many cases, depending on the type and designated use of the receiving water, and on the drainage system used to discharge the runoff (7). In a Washington DOT (WSDOT) field evaluation, however, chloride levels in roadside soils, surface water and underlying groundwater were found to be generally low and well below any applicable regulatory standards or guidelines (45). In Montana, water samples taken from three streams adjacent to highways in 2003 and 2004 indicated that chloride levels did rise in these streams during winter maintenance months, but only spiked to 36mg/L in one sample, still below EPA regulations. Most chloride levels in these streams during winter months, however, were less than 15mg/L (46).

In a similar evaluation of water quality in New York, elevated chloride concentrations were measured in streams, lakes and groundwater supplies due to winter maintenance. It was found that during runoff, chloride concentrations spiked to above 1,000mg/L. As a result, there has been an increase of mean chloride levels in Otsego Lake by 1.0mg/L each year. Groundwater samples from wells near the lake were also tested for chloride concentrations. Traditionally, the chloride concentration of these wells would have measured 1 to 2mg/L, but they tested at 40 to 60mg/L (47). These groundwater samples show increased chloride concentrations over time; yet, they remain below drinking water regulations set at 250mg/L by the U.S. Public Health Service (48). Accumulation of salts in private and public wells has been seen across the state of Massachusetts and has been attributed to winter maintenance practices (21).

Suggested application rates of NaCl are 100 to 300 pounds per lane mile (30 to 90 kg per lane km) of solid material, and 45 to 165 gallons per lane mile (105 to 388 liters per lane km) of 23% liquid salt brine (49). These rates are in the same range as reported by CDOT personnel but in general are more conservative (Chapter 6 Table 9). An application rate of 300 pounds per lane mile of NaCl applied to a layer of ice 0.2in (0.5cm) thick in Milwaukee resulted in an initial salt solution of 69,000 to 200,000mg/L during heavy snowmelt. Runoff to surrounding soil and water bodies from this type of application may be in the thousands of mg/L (5).

The effects of highway NaCl deicer application on groundwater quality were studied at a site in northwestern Indiana using a variety of geochemical indicators (50). Site characteristics such as high snowfall rates; large quantities of applied deicers; presence of a high-traffic highway; a homogeneous, permeable, and unconfined aquifer; a shallow water table; a known groundwater-flow direction; and minimal potential for other sources of chloride and sodium to complicate source interpretation were used to select a study area where groundwater was likely to be affected by deicer application. Chloride and sodium from highway deicers were found present in the aquifer throughout the year. The highest concentrations of chloride and sodium in groundwater were found in samples

collected during the spring and summer from wells open to the water table within about nine feet of the highway.

Chloride concentrations exceeded the U.S. EPA secondary maximum contaminant level of 250mg/L for drinking water at seven wells down gradient from the highway during late winter, spring, and summer samplings (50). The chloride standard was exceeded only in water from wells with total depths that are less than about 10 feet below land surface. Sodium concentrations in water periodically exceeded the EPA drinking-water equivalency level of 20mg/L in both the uppermost (deicer affected) and lower one-thirds of the aquifer. Some deicer may have been retained in the aquifer and unsaturated zone between annual salt-application periods.

Chlorides enter water systems via migration through soil into groundwater or from road runoff directly input into waterways. Sodium chloride migration through soils can cause soil swelling, can increase soil electrical conductivity, cause loss of soil stability from drying and wetting cycles, and cause osmotic stress and mobilization of nutrients and metals impacting the localized environment (18,51). Research has shown 10% to 60% of the sodium chloride applied to roads enters shallow subsurface waters and accumulates until steady-state concentrations are attained (18). Shallow wells, reservoirs, and low-flow surface waters adjacent to roadways or storage centers are most susceptible to deicer contamination (16). Improper sodium chloride storage has caused problems with well water and reservoir concentrations. Wells most likely to be affected are generally within 100ft down-gradient of the roadway in the direction of groundwater movement. Salt concentrations in drinking water supplies have been increasing over time due to road runoff from treated roads, natural brines and salt deposits in native rock material, industrial and agricultural chemicals, and water treatment and water softening processes (16).

Large sodium chloride loads to lakes and ponds have been shown to affect the available oxygen at depth, by causing density stratification, in effect reducing water circulation and aeration at depth, causing a loss of DO and mortality of organisms. Reduced oxygen can also cause increased nutrient loading and therefore cause increased algal growth, further depleting DO (16).

### *Chloride in Soils*

Sodium chloride has been shown to affect soil within 15ft of roadways, and sodium accumulation can cause increased soil density, reduced permeability, higher alkalinity, moisture retention, and loss of soil fertility, which can reduce plant growth and therefore influence erosion (16,52). Chloride moves faster through soil than sodium, which results in higher sodium retention in soil, while chloride has been shown to mobilize heavy metals from the soil into groundwater (16,53). Sodium can displace metals in soil as well; this is exacerbated in soils with high clay content and in soils with high exchangeable sodium ratio (ESR) (18). Sodium ions ( $\text{Na}^+$ ) from deicers are highly soluble in water and can break down soil structure. They can also decrease permeability (10). Magnesium and calcium ions have been found to increase soil stability and permeability (53).

### *Chloride Effects on Plants*

Chloride is thought to be more harmful than sodium to plants (16). Excessive chloride exposure presents itself as inhibited growth, browning, and premature aging of leaves and needles, tree limb death, and plant death induced by osmotic stress. Salt concentrations from 0.5 to 2% dry weight have been shown to cause discoloration to severe leaf burn, defoliation, and plant death, and salt deposits on leaf surfaces can cause localized dehydration. Plants with broader leaves are generally affected more. Shrubs and grasses in general can tolerate increased sodium chloride concentrations better than trees.



The accumulation of road salt could be detrimental to the surrounding vegetation. For instance, on a 3,700ft (~1.1km) stretch of highway in New Hampshire, nearly 14,000 trees died and had to be replaced (54). Environment Canada also reported that many woody plant species exposed to road salt had vanished from Canadian roadsides (55). The sodium ( $\text{Na}^+$ ) and chloride ( $\text{Cl}^-$ ) can be toxic to vegetation when excessive accumulation occurs in the soil. Tolerance to NaCl for some vegetation, specifically pine seedlings, is as low as 67.5ppm in soils. For seed germination and root growth to occur for grasses and wildflowers, the NaCl concentration in soil should be less than 100ppm. Some woody and herbaceous species, however, tolerate up to 200ppm of NaCl (56). In one study, chloride concentrations in soil near a Canadian highway were taken. It was found that soil in the median had a chloride concentration of 1,050ppm, and at 33ft (10m) from the highway, the concentration was 890ppm (57). Both values are well above the aforementioned thresholds of pine seedlings, grasses and wildflowers.

An indirect effect of sodium ions on vegetation is that they are highly soluble in water, and can bind to clay soil particles, break down soil structure, and decrease permeability (10). A study performed in Massachusetts evaluated the effects of NaCl on vegetation near roadways. Of the species tested, pines and sumacs had the most widespread, severe damage while grasses, ferns, maples and oaks were tolerant of high salt concentrations. It was found that sodium concentrations in damaged pine needles were about 75 times that of healthy pine needles (58). A study of the effect of sodium chloride on ponderosa pine and Greenleaf Manzanita performed in Lake Tahoe, California and Nevada, found little damage to trees 40ft from the Interstate (highway 80) (59). Due to tree mortality concerns in the Lake Tahoe basin, state highway agencies in California and Nevada studied a corridor of highway and found an estimated 10 to 15% or 20,000 trees, were affected to some degree by salt, of the trees affected by salt, approximately one-third showed signs of other types of injury or disease (60).

$\text{MgCl}_2$  and  $\text{CaCl}_2$  contain a higher concentration of chloride than NaCl by weight, and therefore may be more harmful when applied at the same rates (10), causing similar

effects to vegetation such as growth inhibition, scorched leaves, or even plant death (10,16-17,31).  $MgCl_2$  has the highest chloride concentration of 75%, followed by  $CaCl_2$  with 64%, and  $NaCl$  with 61% (17). Magnesium and calcium are both crucial for plant growth; however, an excess of either nutrient in the soil may result in other deficiencies. For example, excess magnesium may result in calcium deficiencies, and excess calcium may reduce the availability of magnesium and potassium (17,58). Another concern when using magnesium- and calcium-based products is that magnesium ions ( $Mg^{2+}$ ) and calcium ions ( $Ca^{2+}$ ) are soluble in water and can exchange with heavy metals in soil, potentially releasing them into the environment (10).

### *Chloride Effects on Animals*

Generally, sodium chloride impacts on fauna are minor because it is difficult to reach and sustain the necessary high concentrations (16). High and persistent chloride concentrations in streams adjacent to roadways can harm fish at concentrations from 400 to 12,000mg/L, cause growth changes in plankton at concentrations greater than 1,000mg/L, and affect amphibian skin through osmality processes (16,37). Mammalian and avian behavioral and toxicological effects have been associated with ingestions of road salts. Additionally road salts may reduce wildlife habitat by reducing plant cover or by causing shifts in plant communities—in effect, decreasing food sources and/or shelter (18). The No-Observed-Effect Concentration (NOEC) for a 33-day early life stage test for fathead minnows was 252mg/L chloride, while shifts in populations and changes in community structures occurred at much lower concentrations of 12 to 235mg/L (18).

Winter maintenance chemicals are relatively non-toxic to aquatic organisms with some concerns about  $NaCl$  and  $CaCl_2$  (17). A Colorado DOT study examined the impacts of  $MgCl_2$  on several aquatic organisms and concluded that during the study period of 1997 to 1998  $MgCl_2$  had a very limited potential to cause environmental damage more than 20 yards (~18m) from the roadway, given a dilution factor of 1:500 of deicers entering the

roadside environment after application on the roadway (61). Yet, in Michigan, the DOT concluded that winter maintenance deicers had the potential to be toxic to aquatic organisms in streams with low flows or in wetlands and ponds with long turnover times. It was determined that the most sensitive areas were those where deicer usage is high, and roadway runoff enters small water bodies directly (10).

### *Chloride Based Deicer Effects on People*

While winter maintenance materials increase public safety by improving the driving conditions on winter roadways, they may pose threats to sensitive individuals through their negative impacts on water and air quality. Salt treatment of roadways introduces sodium, calcium, magnesium and chloride to waterways and groundwater that may be used for drinking, therefore it is important to consider the effects of salts on human health. The most likely way for individuals to ingest chemical products used for winter maintenance is through drinking water. Increased deicer concentrations in public water systems or in private wells may present a health risk to humans if excessive levels of nutrients and minerals are present. Increased sodium in the daily diet can lead to hypertension, or high blood pressure (16). Although it has not been proven that hypertension is a result of salt intake, many doctors advise patients to follow a low-salt diet to reduce symptoms of high blood pressure. No federal regulations for sodium or sodium chloride have been established because generally salt concentrations are very low in drinking water. Dieticians suggest limiting sodium intake to 1,000mg/day and the American Heart Association recommends drinking distilled water if sodium concentrations are greater than 20mg/L in tap water. Research has determined that if drinking water exceeds the maximum sodium levels of 200mg/L or chloride levels of 250mg/L, the taste of salt is noticeable (62-63). The U.S. EPA has estimated that drinking water should comprise less than 10% of a person's daily intake of salt, while Health Canada has estimated it to be even lower (17,63). In addition, anti-caking agents used in road salts frequently contain cyanide, which could be detrimental if the water source was

used for the domestic water supply and may cause additional toxicity to aquatic organisms (52).

In a study conducted by Levelton Engineering Ltd. in British Columbia, it was noted that deicing products might be harmful to human health if they were ingested, inhaled or come in contact with skin, depending on duration, concentration, frequency, and individual sensitivities to the chemicals (64). Of the four products tested (NaCl, CMA, CaCl<sub>2</sub>, and MgCl<sub>2</sub>), CaCl<sub>2</sub> was the only product that was both irritating to the eyes and skin on contact, and toxic if inhaled. Salt and CMA were slight eye irritants, but only CMA was a skin irritant. MgCl<sub>2</sub> proved to be the least harmful, being only a slight eye irritant and non-toxic if inhaled (17). The aforementioned conditions, however, are primarily a concern for winter maintenance personnel.

In a synthesis of information prepared by the Utah DOT, other health risks related to deicer used in winter maintenance in the public water supplies were identified (65). Besides the risks of hypertension and increased salt intake, sodium might adversely affect women with toxemia associated with pregnancy. However, most water supplies do not test high enough on a regular basis to warrant concern (65). Health risks associated with water quality were also addressed in the Road Salt and Winter Maintenance for British Columbia Municipalities report; however, it was stated that “water would become unpalatable to most people before these conditions would arise” (66).

#### ***5.4.3. Acetates and Formates***

Deicers that include acetates are sodium acetate, sodium acetate/formate, calcium magnesium acetate (CMA), and potassium acetate. Acetates have been extensively studied as alternatives to chloride-based products for snow and ice control because of reduced environmental impacts. In addition to the higher cost, which makes acetates infeasible for many agencies (17,53,56,67-68), the decomposition of acetate may result in

anaerobic soil conditions as well as oxygen depletion in surface waters (10,53). Testing of soil, vegetation, and streams in the North Island of New Zealand where CMA is used for both anti-icing and deicing has shown no negative impacts; however, the cost of the product was listed as a principal disadvantage (69).

#### *Acetates and Formates in Water and Soil*

The most pronounced environmental issue associated with acetate-based deicers is the increase in the biological oxygen demand (BOD) which reduces the available oxygen for organisms in the soil and aquatic environments (53,70). 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 (71). Sodium acetate/formate has been found to cause increased turbidity, hardness, and alkalinity in water, while limited research has found KFm to cause no undesirable changes in the groundwater chemistry as it tended to biodegrade in topsoil (72). Acetate is readily biodegraded by organisms (16), while the decomposition of CMA has been shown to take ~3.5 times longer in water than adjacent soils (73). CMA has also been found to increase pH in soil through stimulation of microbial activity (74). From this same study microbial decomposition of CMA was shown to precipitate cadmium (Cd) but with no observed negative effects on the environment.

The impact of CMA on groundwater appears to be negligible (75), but this may not be an issue yet as acetates are not used as widely as chloride-based deicers. To determine the effects of CMA on phytoplankton, water samples from 10 California lakes were incubated with 0.1, 1.0, and 10mg/L of CMA. Eight of the 10 lakes showed no significant effects of the addition (75).

### *Acetate and Formate Effects on Plants*

Sodium acetate/formate has been demonstrated to have positive impacts on pine and sunflower growth, acting as a fertilizer at concentrations of ~0.5g/kg of soil. At higher concentrations of 4g/kg, detrimental effects have been observed including low germination rates, low biomass yield, lateral stem growth, suppressed apical meristem growth, browning of leaves/needles, and senescence (71). Potassium formate concentrations less than 4kg/m<sup>2</sup> were found to have detrimental effects on vegetation (72). CMA can enhance plant growth by improving soil permeability and providing needed calcium and magnesium, which may be a valuable characteristic in areas where heavy salt use has resulted in soil compaction (75).

Calcium, magnesium, and potassium are essential plant nutrients; however, all three ions may be problematic if concentrations are too high. Exchangeable calcium in soil is generally between 300 to 5,000ppm. For a neutral soil, exchangeable magnesium will be greater than 500ppm. Potassium is usually present in very high concentrations (20,000ppm) in soil; however, only 100ppm of this is available as a plant nutrient (76). Since acetate is an organic ion, it is also a nutrient for many organisms. Yet, the decomposition of acetate may result in anaerobic soil conditions as well as oxygen depletion in surface waters (10,53). In two days, acetate concentrations of 100ppm would completely deplete the dissolved oxygen in water, whereas an acetate concentration of 10ppm would temporarily reduce oxygen supplies (53).

### *Acetate and Formate Effects on Animals*

Sodium acetate/formate deicer (Ice Shear) was reported to cause apparent fish disorientation, concave abdomen and spinal curvature, observed gill distention, and death (71). In general, CMA has low aquatic toxicity while potassium acetate, sodium acetate, and CMA-potassium (K) have greater aquatic toxicity (53). Acetate and formate have

been shown to promote bacterial growth (71), while CMA was found to stimulate bacteria and algae growth (70).

#### *5.4.4. Glycol*

Deicers composed of glycols—propylene glycol and ethylene glycol—are generally used only as airplane and runway deicers. Environmental issues associated with glycol-based deicers are increased BOD and carcinogenic effects to stream fauna.

#### *Glycol in Water and Effects to Animals and Plants*

Ethylene and propylene glycol increase the BOD of receiving waters, with propylene glycol exerting a higher BOD (77). Ethylene and propylene glycol are known endocrine disrupters (78). Ethylene glycol is acutely toxic to mammals, and occasionally has led to the death of animals following large consumption. When ingested, ethylene glycol depresses the central nervous system and can be fatal to humans even in small quantities, while propylene glycol is essentially nontoxic. Glycols have been shown to inhibit plant growth, but only slightly more than salt (79).

#### *Glycol Additive Effects*

Glycol-based deicer additives, ethoxylates (nonionic surfactants), have been demonstrated to degrade into the known endocrine disrupters nonylphenol and octylphenol. It appears that one or more of the additives in propylene glycol-based aircraft deicer fluids inhibits the growth of anaerobic methanogenic microorganisms, while aerobic microorganisms did not appear to be inhibited by the additives in propylene or ethylene glycol (80). Glycol biodegrades at a consistent rate in receiving waters, while additives have been found to remain in the receiving waters long after all the glycol has

decomposed (79). The additives tolyltriazole (flame retardant) and surfactant and buffering agents also contribute to this toxicity (77). Additives, other than glycols, used in aircraft deicing fluids can be found in aquatic systems and may be of greater risk than previously believed (81). Glycol-based anti-icing fluids used at airports are far more toxic to aquatic organisms than glycol that is used as a roadway deicer (82); this may be due in part to the concentrations being used.

#### ***5.4.5. Bio-Based Deicers***

In recent years, bio-based deicers, often from the fermentation and processing of cane or beet sugar syrup as well as corn, barley and milk, have been added to the list of winter maintenance materials (17,47,83). Most bio-based deicers are only partially composed of byproducts or co-products from the dairy and/or agricultural industry, and also contain or are to be used to pre-wet deicers including chlorides, acetates and abrasives to increase ice-melting capabilities, and act as corrosion inhibitors.

Deicers that are partially bio-based include IceClear, made of potassium lactate and many other proprietary protected products. Due to limited field and lab testing, little information is available on these. One product thoroughly studied is IceBan, a mix of  $MgCl_2$  and agricultural byproduct. In a report evaluating deicers from 1975, it was determined that IceBan exceeds PNS specifications for copper, zinc, and sulfate, and has a pH less than 4.0, which could result in acidification of soils and cause leaching of metals into surrounding waters (53). This may no longer be the case because IceBan is currently used by the Colorado DOT and IceBan 200 is currently on the PNS approved product list, and therefore must meet the requirements shown in Table 4.

A primary concern when using bio-based products is oxygen depletion. The organic materials the byproducts are composed of can cause temporary anaerobic soil conditions and oxygen depletion in surface waters when broken down. Oxygen depletion may also



occur in waterways if too much phosphorus is present. Phosphorus is usually introduced into the environment in concentrations of 14 to 26ppm from winter maintenance deicers. Colorado DOT has set standards for phosphorus in  $MgCl_2$  based deicers at 25mg/L or less (Table 4). This had cause deicer suppliers to reformulate the deicer mix design to meet the lower specification. Water quality standards may set a limit lower than this. Michigan, for instance, has set a limit for phosphorus in water at 1ppm from point discharges (10). Phosphorus spurs the growth of algae, reducing oxygen for other aquatic biota (53). Algae growth may be spurred by critical levels of dissolved phosphorus as low as 20ppb (84). In addition, bio-based products often contain high concentrations of nitrates (53).

#### **5.4.6. Urea**

Urea products are still used as deicers on runways of airports, but are not the product of choice because of the elevated nitrogen (N) content of ammonia in urea, which is harmful to aquatic life and causes increased algal blooms (77). There also is concern over the toxicity of urea and its additives, particularly tolyltriazoles used as corrosion inhibitors and flame retardants (78). To eliminate the toxicity, somewhat complicated nitrification and denitrification treatments are required for wastewater containing urea. Urea pellets are an airfield deicer approved by the U.S. Air Force, but their use is discouraged (77). No urea products are PNS approved.

### **5.5. Public Perception and Other Things to Consider**

An extensive public perception survey conducted for the Michigan DOT revealed that while residents recognize the benefits of deicing winter roads, they were concerned about the variety of environmental problems and the effects of road salt, strongly supporting the idea of finding an alternative to salt use on roadways. However, respondents also expressed strong reservations about the costs of alternatives (19). There was an even split

between respondents who supported using the same amount of chloride-based deicers and those who would reduce the current rate of application. Respondents suggested they were willing to accept some increased deicing costs in exchange for less vehicle rust, better water quality, and reductions in other perceived detrimental effects (19).

**Table 5 Summary of the environmental effects of deicers.**

	<b>Abrasives</b>	<b>Chloride</b>	<b>Acetate &amp; Formate</b>	<b>Glycol</b>	<b>Urea &amp; Bio/Agr-based</b>
<b>Soil</b>	Will accumulate.	Chloride, calcium, and potassium can mobilize heavy metals. Sodium can accumulate in soil and reduce soil permeability leading to increased soil density. Calcium can increase soil permeability and aeration. Magnesium can increase soil stability and permeability. NaCl can decrease soil fertility, leading to reduced plant growth and increase erosion.	Calcium and magnesium can mobilize heavy metals, increase soil stability, and permeability. CMA degradation may increase soil pH.	Readily biodegrades. Propylene glycol degradation may reduce hydraulic conductivity in anaerobic soils.	Use of urea can lead to increased nitrate concentrations. Little data is available on bio/agr-based deicers.
<b>Flora</b>	Can accumulate on foliage and in adjacent soils that contact the roots, potentially causing stress.	Chloride contact with foliage can cause leaf singe, browning, and senescence. Chloride contact can lead to osmotic stress. Salt tolerant species are recommended for use as roadside vegetation where chloride based deicers are used.	Few effects have been observed. At low concentrations acts as a fertilizer, at elevated concentration reduces seed germination, causing low biomass yield, leaf browning, and senescence.	Glycol can inhibit plant growth.	Little data is available on bio/agr-based deicers.
<b>Surface &amp; Ground Water</b>	Can increase turbidity, decrease gravel, and rock pool space leading to limited oxygen supply.	Chloride, sodium, calcium, and potassium ions easily go into solution, migrate, and can harden the water. Can cause density stratification in small receiving waters potentially causing anoxic conditions at depth. Potassium and calcium can mobilize heavy metals in water. Potassium can cause eutrophication of water.	Can leach heavy metals from soil that can transport into water. Has a high BOD and can cause oxygen depletion. Can increase turbidity and hardness of water.	Can increase BOD to a greater extent than any other deicer. Degrades in water faster than additives which can be toxic. Readily biodegrades.	Use of urea can lead to increased nitrate concentrations. Urea additives can be toxic. Little data is available on bio/agr-based deicers.
<b>Fauna</b>	Can reduce oxygen in stream beds and cause increased turbidity.	Chlorides have little to no impact when ingested unless extremely elevated concentrations are reached. Direct ingestion of salts by mammals and birds has caused behavior changes and toxicity. Concentrations of 250 mg/L have been shown to cause changes in community structures. Use of chlorides on roadways may lead to increased wildlife-vehicle collisions.	Can exert a high BOD which may cause anoxic conditions in aquatic environments. KAc and NaAc appear to be more toxic than CMA. Can promote bacteria and algae growth.	Ingestion of concentrated fluid can lead to death. A known endocrine disrupter.	Little data is available on bio/agr-based deicers.
<b>Human</b>	Can cause increased PM10 and can lead to air quality non-attainment issues. Can reduce stream visibility, alter stream and roadside habitat, and decrease aesthetics.	Skin and eye irritant. Drinking water with sodium concentrations >20 mg/L can lead to hypertension. Can increase chloride, calcium, potassium, and sodium concentrations above recommendations. Anti-caking agents may contain cyanide a known carcinogen.	Skin and eye irritant. Calcium and magnesium can increase water hardness.	Ingestion of concentrated fluid can lead to death. A known endocrine disrupter.	Use of urea can increase nitrate levels in water. Little data is available on bio/agr-based deicers.

## **5.6. Mitigation and Current BMP Efforts**

In the United States, environmental issues related to water quality, air quality and wildlife are regulated with the guidance of the Clean Water Act, Clean Air Act, and Federal Endangered Species Act, respectively. These laws also detail the identification and management of environmentally sensitive areas, such as those on the list of impaired streams for water quality and the list of PM-10 non-attainment communities for air quality.

Structural and non-structural Best Management Practices (BMPs) have been developed and are constantly evolving with the intent that deicers and abrasives released into the environment are minimized. Abrasives mainly contribute to suspended solids in water runoff and reduced air quality, while deicers become dissolved in runoff. The removal of suspended solids is best accomplished through settling, which is very efficient at removing sand-sized particles but less effective for clay- to silt-sized particles usually absent in sand used for road traction. Few structural BMPs can effectively remove deicing products that have dissolved. Structural BMPs include detention and settling ponds, chambers, wetland type environments, infiltration trenches and basins, sand traps and filters, wet and dry swales and vegetation filter strips (14). These structural BMPs must consider the potential for contaminated water to recharge into aquifers.

Non-structural BMPs are preventative measures designed to reduce the amount of deicers and abrasives applied to roadways, which can reduce the need for or dependence on structural BMPs. They are procedures, protocols, and other management strategies including but not limited to: utilizing environmental staff in construction and maintenance practices; proper training of maintenance professionals; utilizing tools like MDSS and other computer- and simulator-based training systems; passive snow control through snow fences and living fences; designing proper snow storage facilities; utilizing street sweeping; and improving deicing and anti-icing practices via better road weather

forecasts and appropriate application rates (14). Field monitoring of deicer use has allowed for lessons to be learned and for the implementation of site-specific BMPs.

## 5.7. Conclusions

Deicers can have significant impacts on the environment, and the impacts are dependent on a wide range of factors unique to each formulation and the location of application. The environmental effects of deicers are summarized in Table 5. Further testing is necessary for many of the deicers, and for this information to be made available to the public. To minimize the environmental impacts of deicer, it is crucial to make informed decisions by utilizing available resources including existing test methods and the PNS-approved deicer list (85). By identifying sensitive areas and species and setting limits for air and water quality, a framework can be established that all deicing products must meet, so that a toolbox approach may be implemented. Despite the potential damaging effects, the use of chemicals for snow and ice control can reduce the need for applying abrasives, and pose less threat to the surrounding vegetation, water bodies, aquatic biota, air quality, and wildlife.

## 5.8. References

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## CHAPTER 6. USER PERSPECTIVES REGARDING DEICER PRODUCTS

### 6.1 Survey of Deicer Performance and Impacts

The purposes of this survey were to gain insight on the deicer—deicing and anti-icing—products currently available and used by road maintenance agencies, and to highlight successes and lessons learned from professionals in the snow and ice control community (Appendix A). A total of 24 winter maintenance professionals participated in the survey with one from Finland, one from New Zealand, and the rest from the United States representing agencies in 15 different states (Appendix B&C). In some cases, participants did not answer all of the questions, often due to the lack of available scientific data. As a result, the summaries of some questions will have information provided by fewer than 24 respondents.

#### *6.1.1. Deicers Used by Respondents*

The first question posed to survey participants sought feedback on the type of deicers that are currently used for winter road maintenance. Table 6 reports the number and percentage of respondents who listed each deicer. The data indicate that solid salt, NaCl(s), is most frequently used, followed by abrasives, then magnesium chloride (MgCl<sub>2</sub>), agriculturally-based (Agr-based) deicers, calcium chloride (CaCl<sub>2</sub>), and then other deicers. It is interesting to note that less than 25% of the survey respondents used alternative deicers such as potassium acetate, sodium acetate, calcium magnesium acetate (CMA), and potassium formate, whereas conventional deicers such as abrasives and chlorides are still most widely used (likely due to cost considerations).

**Table 6 Deicers listed by respondents as being used by their organization, and the frequency of use.**

Deicers Listed	Abreviation	Frequency (n)	Percent of Respondents (%)
Abrasives (sand)	sand	17	71
Sodium Chloride (solid)	NaCl (s)	20	83
Sodium Chloride (liquid brine)	NaCl (l)	4*	17
Sodium Chloride & Abrasives	NaCl & sand	3*	13
Magnesium Chloride	MgCl <sub>2</sub>	14	58
Calcium Chloride	CaCl <sub>2</sub>	11	46
Clearlane®	NaCl, MgCl <sub>2</sub>	3	13
IceSlicer®	NaCl, KCl, MgCl <sub>2</sub>	3	13
Calcium Magnesium Acetate	CMA	2	8
Potassium Acetate	Kac	6	25
Sodium Acetate	NaAc	2	8
Potassium Formate	KF	1	4
Agricultural Based	Agr-based	12 <sup>†</sup>	50

\* Only counted if specified use in survey.

† Agr-based deicers included: Ice B'Gone® (n=2), Magic by Caliber® (n=1), beet and/or corn based (n=3), unspecified Agr-based as inhibitor mixed with MgCl<sub>2</sub> (n=2), unspecified Agr-based as inhibitor mixed with CaCl<sub>2</sub> and NaCl(l) (n=1), or an unspecified small amount of Agr-based listed generally as inhibitor (n=3), and Geomelt® (n=1).

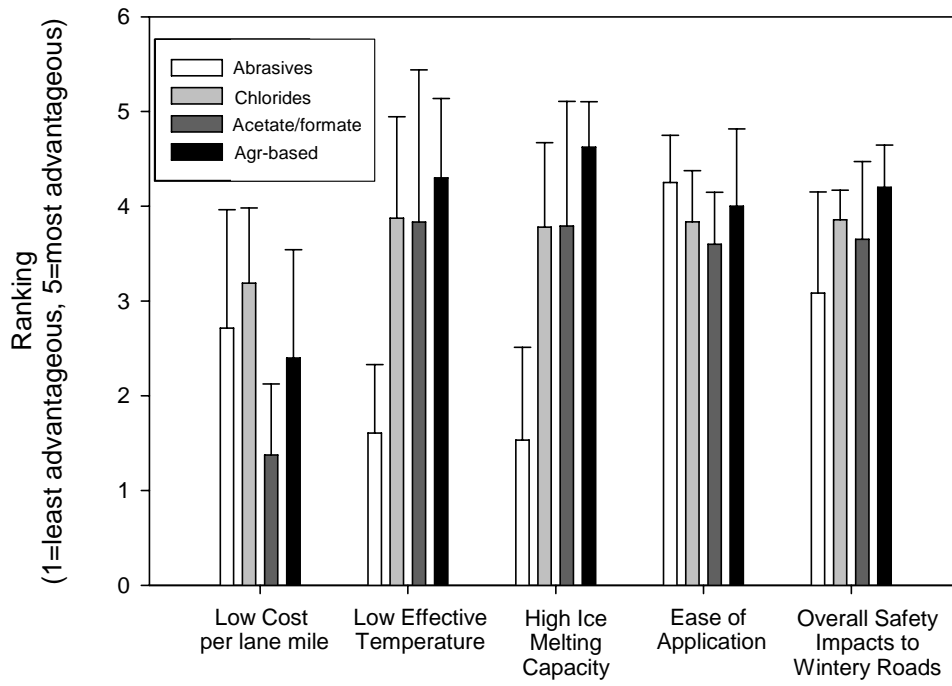
### **6.1.2. User-Perceived Ranking of Deicer Advantages**

Users were then asked to rank the advantages of specific deicers with respect to low cost per lane mile, low effective temperature, high ice melting capacity, ease of application, and overall safety benefits for winter roads based on field experience or research from the respondent's agency, and provide any further comments on the topic. The rankings were on a scale of 1 to 5, with 1 being the least advantageous and 5 being the most advantageous. The survey results are summarized in Table 7, where standard deviation is reported only if three or more people responded to that question, and n notes the number of people who responded.

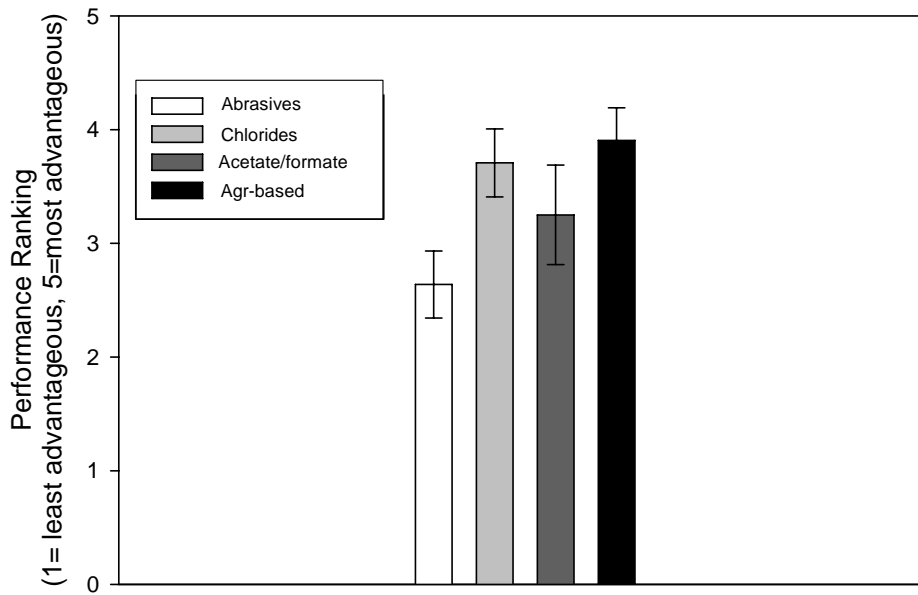
**Table 7 Deicers ranked by advantages, with 1 being the least advantageous and 5 being the most.**

Deicers Listed	Low cost per lane mile			Low effective temperature			High ice melting capacity			Ease of application			Overall safety impacts for winter roads		
	Avg.	St.Dev.	n	Avg.	St.Dev.	n	Avg.	St.Dev.	n	Avg.	St.Dev.	n	Avg.	St.Dev.	n
Abrasives (sand)	2.9 ± 1.7		7	2.4 ± 1.4		7	1.1 ± 0.8		8	4.0 ± 1.1		9	2.3 ± 1.4		9
Abrasives (volcanic)	3.0		1	1.0		1	1.0		1	4.0		1	4.0		1
Abrasives (non-volcanic)	4.0		1	1.0		1	1.0		1	4.0		1	2.0		1
Abrasives (pre-wet)	1.0		1	2.0		1	3.0		1	5.0		1	4.0		1
Sodium Chloride (solid)	4.2 ± 0.8		14	2.5 ± 1.0		15	3.3 ± 1.1		14	4.3 ± 0.9		16	4.3 ± 0.7		16
Sodium Chloride (liquid brine)	4.5 ± 0.6		4	3.0 ± 0.8		4	3.0 ± 0.8		4	4.3 ± 0.5		4	3.8 ± 0.5		4
Sodium Chloride & Abrasives	3.3 ± 0.6		3	2.3 ± 0.6		3	2.3 ± 0.6		3	3.3 ± 0.6		3	3.3 ± 0.6		3
Magnesium Chloride	2.6 ± 1.2		11	3.7 ± 0.8		11	3.4 ± 1.1		11	3.2 ± 0.7		12	3.8 ± 0.6		12
Magnesium Chloride (liquid)	2.0		1	5.0		1	4.0		1	4.0		1	4.0		1
Calcium Chloride	2.8 ± 1.0		9	4.3 ± 0.5		9	3.8 ± 1.2		9	3.1 ± 0.9		9	3.7 ± 0.5		9
Calcium Chloride (liquid)	3.0		1	5.0		1	5.0		1	4.0		1	4.0		1
Clearlane®	3.5		2	5.0		2	5.0		2	4.7 ± 0.6		3	3.7 ± 1.2		3
IceSlicer®	2.8 ± 1.3		4	4.0 ± 0.0		4	4.3 ± 0.5		4	3.8 ± 1.0		4	4.3 ± 0.5		4
Calcium Magnesium Acetate	1.0		1				5.0		1	4.0		1	5.0		1
Potassium Acetate	1.0 ± 0.0		3	5.0 ± 0.0		3	3.7 ± 1.5		3	3.0 ± 1.6		4	3.8 ± 0.5		4
Sodium Acetate	2.5		2	4.5		2	4.5		2	4.0		2	3.5		2
Potassium Formate	1.0		1	2.0		1	2.0		1	4.0		1	3.0		1
Sodium Acetate/Formate blended with Sodium Magnesium Acetate										3.0		1	3.0		1
Ice B'Gone®	4.0		1	5.0		1	5.0		1	5.0		1	5.0		1
Magic/Caliber®	3.0		1	4.0		1	4.0		1	4.0		1	4.0		1
unspecified	2.0		2	4.5		2	4.5		2	3.0		2	4.0		2
De-ice® (beet sugar)	2.0		2	5.0		1	5.0		1	4.0		1	4.0		1
Corn and Sugar beet	1.0		1	3.0		1	2.0		1	1.0		1	4.0		1
Geomelt®															





(A)



(B)

**Figure 8 User-perceived ranking of deicer performance as a function of (A) performance attributes and deicer type and (B) deicer type.**

### *Low Cost per Lane Mile*

As shown in Table 7, sodium chloride (liquid brine or solid), abrasives (non-volcanic), and Ice B’Gone were believed to have the lowest cost per lane mile, whereas pre-wet abrasives, CMA, potassium acetate, and potassium formate were considered to be more costly per lane mile. As shown in Figure 8A, among the various deicers, acetates and formates are generally considered to be the most costly per lane mile whereas chlorides were considered to be the least costly.

Several respondents commented that while abrasives might be low in cost initially, high application rates and requirement of cleanup due to repeated application significantly increase the cost per lane mile. It was also noted that abrasives can be costly to crush and use if it stays on the road for only a short duration and that pre-wetting can help them stay longer.

One respondent commented that sodium chloride (NaCl) remains the most economic product for winter operations. Another said that “there are a lot of chemicals out there, but until they can come a lot closer to the price of sodium chloride, rock salt will continue to be the primary snow and ice removal chemical.” Two respondents commented on liquid NaCl, stating that salt-brine systems are the most economical and after the initial equipment expenses, salt brine is very cost effective.

### *Low Effective Temperature*

As shown in Table 7, magnesium chloride (liquid), calcium chloride (liquid), Clearlane, potassium acetate, Ice B’Gone, De-ice, unspecified Agr-based, and sodium acetate were believed to be the best when it comes to low effective temperature, whereas abrasives, potassium formate and sodium chloride were considered to be the worst. As shown in

Figure 8A, there was no significant difference perceived in the effective temperature range when comparing acetates/formates against chlorides.

One respondent commented on potassium acetate, stating that it was used as an anti-icing agent and did not provide effective snow-melting capabilities but did a very good job at preventing ice from forming and depressing the freezing point. Another respondent commented that anti-icing with liquid NaCl and De-ice (beet sugar) had been very successful, with De-ice being very beneficial at colder temperatures. Yet another respondent said that by adding 5% to 10% of Agr-based or CaCl<sub>2</sub> deicer to liquid NaCl the freezing point was lowered and it remained on the pavement longer. A fourth respondent said that CMA had been a resounding success in their climate where temperatures stayed around zero each day, and they had managed to keep roads open longer or reopened more quickly than they had with their previous reliance on abrasives only. A fifth respondent said that Clearlane<sup>®</sup> had been very useful because it worked in very cold temperatures.

### *High Ice-Melting Capacity*

As shown in Table 7, calcium chloride (liquid), Clearlane, CMA, sodium acetate, Ice B'Gone, De-ice, unspecified Agr-based, and sodium acetate were believed to have the highest ice-melting capacity, whereas abrasives were considered to be the worst. It is also interesting to note that the ice-melting capacity of potassium formate and corn/sugar beet were ranked lower than chlorides, whereas that of other acetates/formates and Agr-based deicers was ranked superior to chlorides. Figure 8A shows no perceived difference in performance between chlorides and acetates/formates.

There were a few comments that may offer insight on this topic. One respondent said that sand is not an anti-icing or deicing agent as it does not melt any snow or ice but does provide temporary traction in cold conditions or times of heavy snowfall. One respondent

commented that potassium acetate did not provide effective snow-melting capabilities, but did a good job of preventing ice from forming. Another commented that the application of salt brine was highly effective at preventing ice from freezing on roads or preventing hard-pack from forming on roadways. A third said that anti-icing liquid products could be used to “burn through” packed ice and snow up to four inches thick.

### *Ease of Application*

As shown in Table 7, most deicers were considered relatively easy to apply with abrasives (pre-wet), Ice B’Gone, and Clearlane ranked as the easiest. As shown in Figure 8A, there was no significant difference in ease of application between alternative deicers and chlorides or abrasives. The only exception was with Agr-based corn and beet juice deicers, which one respondent ranked as very difficult to apply.

### *Overall Safety Benefits for Winter Roads*

As shown in Table 7, CMA, Ice B’Gone, sodium chloride (solid), and IceSlicer were believed to provide the highest overall safety benefits for winter roads, whereas abrasives (sand and non-volcanic) were considered to be the worst. As shown in Figure 8A, there was no significant difference perceived in the overall safety benefits for winter roads when comparing acetates and formates against chlorides.

Survey respondents’ comments on this topic with regard to abrasives include: abrasives used prior to icing of the roads creates its own hazard by causing reduced skid resistance; abrasives provide temporary traction in cold conditions or times of heavy snowfall; and abrasives do little for safety. Another respondent commented on this topic with regard to CMA, stating that, when applied too early for an event, skid resistance can be reduced due to its hygroscopic properties. Another respondent said that use of chloride-based

deicers may attract animals to roadways and perhaps increases the number of vehicle–animal collisions. One respondent commented that potassium acetate application on bridges reduces crashes on the bridges, and that though the crashes migrated down the road, they now appear to be less severe.

### *Summary of Respondents Ranking of Deicers Based on Positive Performance*

Figure 8B shows the user-perceived average ranking of all five categories by deicer, with the Agr-based products being the most advantageous and abrasives being the least, and no significant difference between chlorides and acetates/formates.

### ***6.1.3. User-Perceived Ranking of Deicers Disadvantages***

Users were asked to rank the disadvantages of specific deicers with respect to corrosion to metal, impacts on concrete and asphalt pavements, impacts on water quality, impacts on soil, vegetation, wildlife and human health, and overall effects on structures and the environment based on field experience or research from the respondent’s agency. A ranking of 1 to 5 represents the least to greatest impacts, respectively. The survey results are summarized in Table 8, where standard deviation is reported only if three or more people responded to that question, and *n* notes the number of people who responded.

#### *Corrosion to Metal*

As shown in Table 8, abrasives, acetates and formates, De-Ice, and corn and sugar beet were believed to be the least corrosive to metal, whereas chloride-based deicers were considered to be the most corrosive.

As shown in Figure 9A, among the various deicers, acetates and formates are generally considered to cause the least corrosion to metal, whereas chlorides were considered to cause the most. This is generally consistent with research findings from the literature review. A laboratory investigation using electrochemical and weight-loss tests of 14- to 17-month duration indicated that bridge structural metals, including steel, cast iron, aluminum, and galvanized steel corroded considerably less in CMA solutions than in NaCl solutions (1). A recent study in our laboratory revealed that while NaAc- or KAc-based deicers were non-corrosive to mild steel, they were comparably as corrosive as chloride-based deicers to galvanized steel (2).

Only one respondent commented on this topic, saying that corrosion to metals is too general to comment on and that the type of metal, temperature and humidity all play roles in the corrosivity of the deicer.

#### *Impacts on Concrete and Asphalt Pavements*

As shown in Table 8, abrasives, CMA, and potassium formate were believed to have the least impact on concrete and asphalt pavements, while all other deicers were ranked as having moderate impacts.

As shown in Figure 9A, acetates and formates are considered to have less impact on concrete and asphalt pavements than chlorides. This contradicts research findings from the literature review. While chloride-based deicing salts can exacerbate the scaling problem as concrete experiences freeze/thaw cycles, the use of properly cured, air-entrained PCC will prevent such physical damage. Long-term use of NaCl does not result in strength loss in the cement paste matrix via chemical mechanisms except for the slow process of accelerating alkali-silica reaction (ASR). NaCl can initiate and/or accelerate ASR by supplying additional alkalis to concrete. Numerous research studies have shown that  $MgCl_2$ , when used as a deicer, causes much more severe deterioration to concrete

than NaCl or CaCl<sub>2</sub>. This is due to the reaction between Mg<sup>2+</sup> and the hydrated products in cement paste. It has also been found that concrete exposed to CaCl<sub>2</sub> deteriorated in a similar pattern to those exposed to MgCl<sub>2</sub>, although at a slower and less severe pace. CaCl<sub>2</sub> and MgCl<sub>2</sub> do not have as obvious an effect on ASR as NaCl.

Both MgCl<sub>2</sub> and CaCl<sub>2</sub> deicers are known to deteriorate concretes containing reactive dolomite aggregates by accelerating the alkali-carbonate reaction (ACR). No literature was found to report potential effect of NaCl on ACR. Based on a modified ASTM 1260 mortar bar test, ongoing research by the Innovative Pavement Research Foundation (IPRF) found that the acetate/formate-based deicers could induce increased levels of expansion in concrete with ASR-susceptible aggregates, and could trigger ASR in concrete that previously did not show ASR susceptibility. Currently it is unclear how the deicer impact compares with the impact from other factors (traffic, freeze/thaw cycles, etc.) on the deterioration of concrete.

While chlorides have little negative impact on asphalt pavements, asphalt durability problems due to the use of acetate/formate-based deicers can be traced back to the 1990s, when degradation and disintegration of asphalt pavements, softening of asphalt binders, and stripping of asphalt concretes were found to occur together with loose aggregates on the runways at some Nordic airports. The mechanisms appear to be emulsifications and distillations, as well as the generation of additional stress inside the asphalt pavement. The degradation of concrete pavement from acetate-based deicers has also been observed at U.S. airports—in one case (Colorado Springs, Colorado, airport) causing damage at the site of airplane deicing that was estimated to cost between \$10 million and \$60 million to repair. A recent lab study by Pan et al. at the WTI Winter Maintenance and Effects Program (2008) revealed that potassium acetate might cause significant emulsification of asphalt and thus strength loss of asphalt concrete (3).

One respondent said that the “judge and jury are still out” on the long-term effects of different chlorides on concrete paste and reinforced concrete. Another respondent said that they do not use  $MgCl_2$  because of its effect on concrete pavement. Another commented that they have not noticed concrete degradation due to the use of potassium acetate, but also said that their inspections have not specifically looked for the types of damage recently reported.

### *Impacts on Water Quality*

As shown in Table 8, CMA and potassium formate were believed to have the least impacts to water quality, while abrasives (pre-wet), corn and sugar beet and Geomelt were considered the worst.

As shown in Figure 9A, acetates and formates were perceived to have less impact on water quality than chlorides, but there was not a significant difference. This is not consistent with the research findings from the literature review. Acetates and formates are known to exert a high biological oxygen demand (BOD) until they have degraded, which can lead to oxygen depletion in the water for up to a few days. The decomposition rate of acetates and formates varies with temperature. If acetates and formates are applied to soils prior to migration to water ways, they can decompose prior to reaching the water way. Such deicers are also known to increase turbidity and water hardness in both surface and ground waters. Magnesium and calcium chloride-based deicers increase water hardness in both surface and ground waters, while sodium chloride softens water. Chloride effects to surface water also include density stratification in small receiving waters which can cause anoxic conditions at depth.

A respondent commented that sand is the cause of PM-10 (particulate matter less than 10 microns) and TMDL (total maximum daily load) non-compliance concerns that affect both human health and water quality. Another respondent said that they only use



potassium formate for environmental reasons related to water quality. Another respondent commented that over-salting the roads will cause nutrient and BOD loading to aquatic environments and that amounts should be minimized. Comments from another respondent include: deicing products typically contain additives that can affect the potential for environmental impacts, some corrosion inhibitors are organics-based and may contribute to this problem, and it is desirable for deicers to contain fewer additives that contribute to elevated BOD and COD (chemical oxygen demand) and do not introduce phosphorus into the environment. The same respondent said that it is critical that deicers should not be over-applied, especially in areas near surface waters.

#### *Impacts on Soil, Vegetation, Wild life, and Human Health*

As shown in Table 8, CMA and sodium formate were believed to have the least impact on soil, vegetation, wildlife and human health, while abrasives (pre-wet) and Geomelt were perceived to have the greatest impacts.

As shown in Figure 9A, acetates and formates were perceived to have less impact than chlorides, but there was not a significant difference. This is consistent with the research findings from the literature review. Both acetates/formates and chlorides can affect soil through the potential mobilization of heavy metals into adjacent water and the increase in soil pH. The latter can reduce soil fertility, leading to reduced plant growth and increased erosion. Other effects include increased osmality and cation exchange capacity in the soil. Calcium and magnesium cations have been found to increase soil stability and permeability.

Acetate/formate effects to vegetation at high concentrations include reduced seed germination rates, lower biomass yield, leaf browning and senescence; while at low concentrations they can act as a fertilizer. Chloride-based deicer impacts on vegetation include leaf singing and browning. Elevated salt concentrations can cause osmotic stress

in vegetation. Salt-tolerant vegetation is available for most eco-regions to mitigate some of these effects.

Acetate/formate effects to aquatic organisms include the elevated BOD leading to potentially risky anoxic conditions in water as well as stimulated growth of bacteria and algae. Potassium acetate and sodium acetate are slightly more toxic than CMA when directly consumed. Chloride effects to aquatic organisms are minimal to none unless concentrations are extremely elevated, but concentrations of 250mg/l or greater can lead to change in community structures and food web dynamics. Direct ingestion by mammals and birds can cause behavior changes and mild toxicity, and salts can attract wildlife to roadways potentially increasing vehicle–animal collisions.

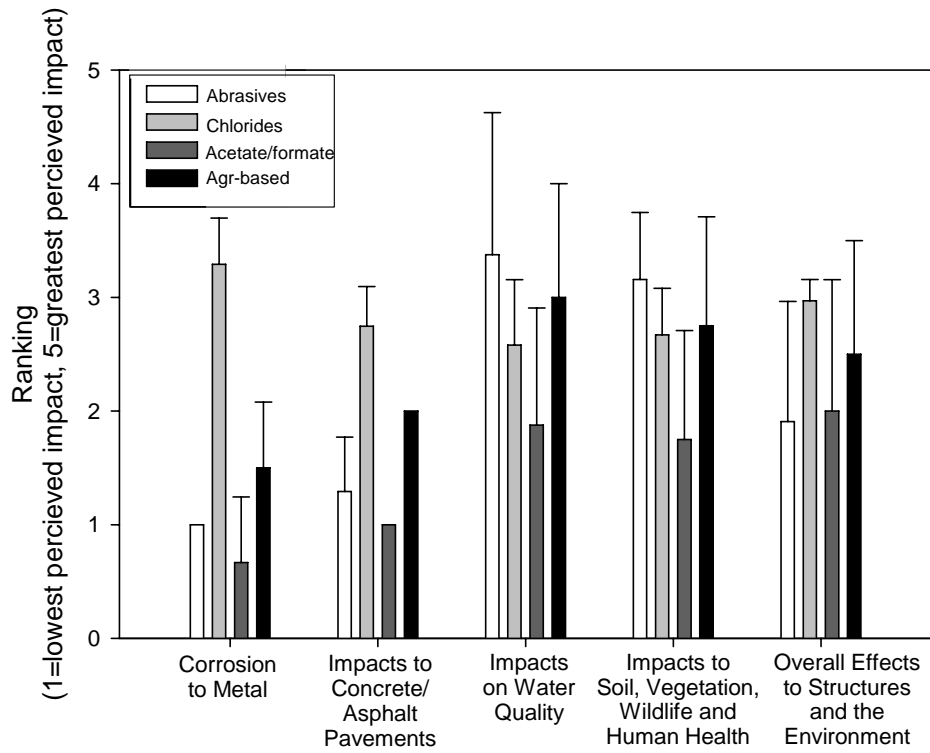
As mentioned above, one respondent commented that sand is the cause of PM-10 and TMDL non-compliance concerns that affect both human health and water quality. Another respondent commented on this topic and said some chemical elements such as sodium chloride or potassium chloride may be beneficial to some plants but may also attract mammals to roadsides, potentially increasing vehicle–animal collisions.

#### *Overall Effects to Structures and the Environment*

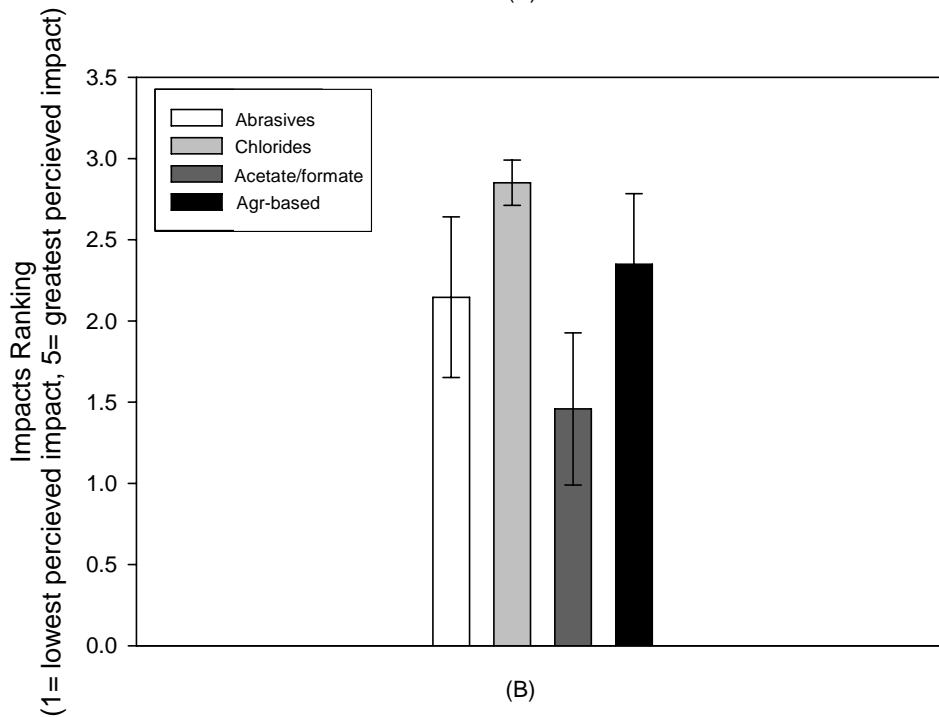
As shown in Table 8, abrasives (volcanic and non-volcanic), CMA, and potassium formate were believed to have the least overall effects on structures and the environment, while chlorides in general and Geomelt was perceived to have the greatest effect. As shown in Figure 9A, acetates and formates were perceived to have less impact than chlorides, but there was not a significant difference.

**Table 8 Deicers ranked by disadvantages, 1 having the least impact and 5 having the greatest impact.**

Deicers Listed	Abbreviation	Corrosion to metals			Impact on concrete and asphalt pavements			Impact on water quality			Impact on soil, vegetation, wildlife and human health			Overall effects on the environment	
		average	standard dev.	Percent	average	standard dev.	Percent	average	standard dev.	Percent	average	standard dev.	Percent	average	standard dev.
Abrasives (sand)	sand	1.0 ± 0.0		20	1.2 ± 0.4		23	3.5 ± 1.5		70	2.6 ± 1.3		53	2.6 ± 1.1	
Abrasives (volcanic)		1.0		20	1.0		20	2.0		40	3.0		60	1.0	
Abrasives (non-volcanic)		1.0		20	1.0		20	3.0		60	3.0		60	1.0	
Abrasives (pre-wet)		1.0		20	2.0		40	5.0		100	4.0		80	3.0	
Sodium Chloride (solid)	NaCl (s)	3.8 ± 1.0		76	3.0 ± 0.7		60	2.5 ± 1.1		49	2.7 ± 0.9		53	3.0 ± 1.0	
Sodium Chloride (liquid brine)	NaCl (l)	2.8 ± 1.5		55	2.7 ± 0.6		53	2.7 ± 1.2		53	3.3 ± 0.6		67	3.3 ± 0.6	
Sodium Chloride & Abrasives	NaCl & sand	3.3 ± 0.6		67	2.0 ± 1.0		40	3.7 ± 0.6		73	3.0 ± 0.0		60	3.0 ± 0.0	
Magnesium Chloride	MgCl <sub>2</sub>	3.3 ± 0.8		66	2.9 ± 1.4		58	2.1 ± 0.7		42	2.2 ± 0.8		44	2.9 ± 0.9	
Magnesium Chloride (liquid)	MgCl <sub>2</sub> (l)	4.0		80	3.0		60	2.0		40	3.0		60	3.0	
Calcium Chloride	CaCl <sub>2</sub>	3.4 ± 0.9		69	2.9 ± 1.2		58	2.8 ± 1.3		55	2.6 ± 1.0		51	2.9 ± 1.1	
Calcium Chloride (liquid)	CaCl <sub>2</sub> (l)	3.0		60											
Calcium Magnesium Acetate	CMA	1.0		20	1.0		20	1.0		20	1.0		20	1.0	
Potassium Acetate	K-acetate	1.0		20				2.5		50	3.0		60	3.0	
Sodium Acetate	Na-acetate														
Potassium Formate	K-formate	0.0			1.0		20	1.0		20	1.0		20	1.0	
Sodium Acetate/Formate blended with Sodium Magnesium Acetate	Na-acetate/formate, NaMg-acetate							3.0		60	2.0		40	3.0	
Agricultural Based	Agr-based														
Ice-B-Gone		2.0		40	2.0		40	2.0		40	2.0		40	2.0	
Magic/Caliber															
unspecified		2.0		40	2.0		40	3.0		60	3.0		60	2.0	
De-ice (beet sugar)		1.0		20	2.0		40	2.0		40	2.0		40	2.0	
Corn and Sugar beet		1.0		20	2.0		40	4.0		80					
Geomelt								4.0		80	4.0		80	4.0	
Other	Other														
Clear Lane		3.0		60	3.0		60	3.0 ± 1.0		60	2.3 ± 0.6		47	2.7 ± 0.9	
IceSlicer		3.0 ± 0.0		60	2.7 ± 0.6		53	2.0 ± 1.0		40	2.3 ± 1.5		47	3.0 ± 2.0	
Interstate melt 500		3.0		60	2.0		40	2.0		40	2.0		40	3.0	



(A)



(B)

**Figure 9 User-perceived ranking of deicer impacts as function of (A) impact category and deicer type and (B) deicer type.**

One respondent commented that while salt-brine systems are the most economical set-up, they are not as environmentally safe. Another respondent said that the Agr-based product De-ice is the most appealing as far as safety and environmental issues are concerned. A third commented that allowing snowpack to exist and merely treating the symptoms of slipperiness with abrasives is too costly in labor and equipment, and that this practice has environmental impacts because of the use of abrasives, doing little for safety and commerce.

#### *Summary of Respondents Ranking of Deicers Based on Negative Impacts*

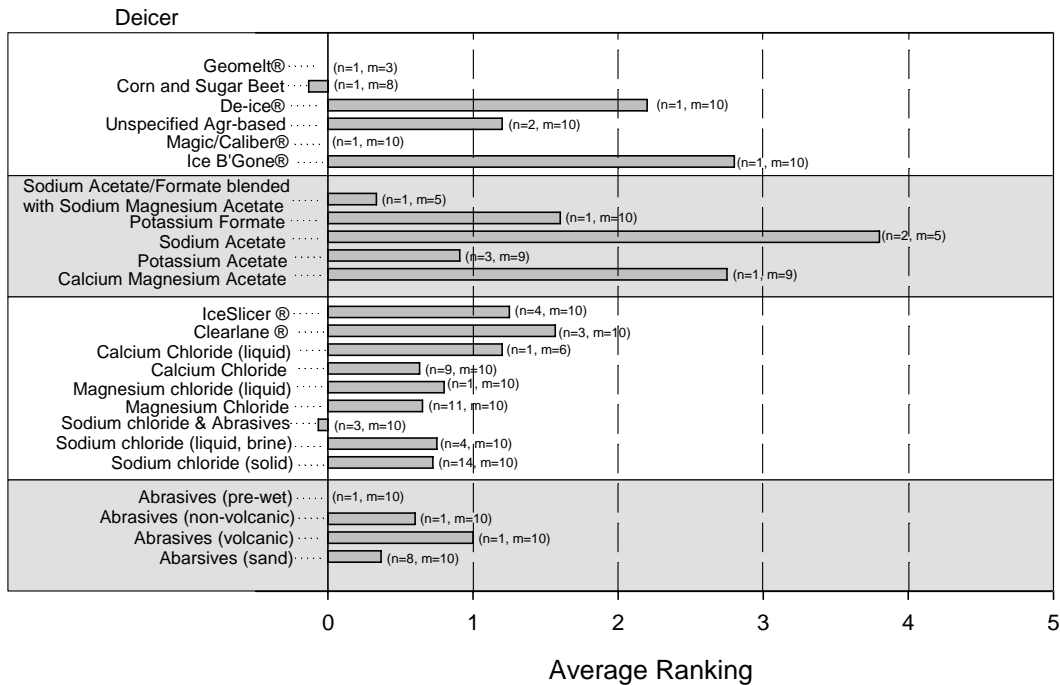
Figure 9B shows the user-perceived average ranking of all five categories by deicer, with acetates and formates in general perceived to have the least impacts and chlorides the most.

#### *Overall Ranking by Individual Deicer*

Figure 10 provides the overall ranking by individual deicer, determined by subtracting the average ranking of negative impacts from the average ranking of positive performance for each deicer. With this indicator, the best deicers (overall ranking >1) are listed as follows, in the decreasing order of preference:

- 1) Sodium acetate (n=2, m=5)
- 2) Ice B'Gone<sup>®</sup> (n=1, m=10)
- 3) CMA (n=1, m=9)
- 4) De-ice<sup>®</sup> (n=1, m=10)
- 5) Potassium formate (n=1, m=10)
- 6) Clearlane<sup>®</sup> (n=3, m=10)
- 7) IceSlicer<sup>®</sup> (n=3, m=10)

- 8) Unspecified Agr-based (n=2, m=10)
- 9) Calcium chloride liquid (n=1, m=6)



**Figure 10 Overall ranking by individual deicer, determined by subtracting the average ranking of negative impacts (Table 7) from the average ranking of positive performance (Table 8). Where *n* is equal to the number of respondents and *m* is equal to the number of criteria, out of ten, addressed by each respondent.**

Based on user perception, the worst deicers (overall ranking <0) are listed as follows:

- 1) Sodium chloride & abrasives (n=3, m=10)
- 2) Corn and sugar beet (n=1, m=8)

Based on the wide range in the number of people (*n*) that ranked the specific deicers, the survey results may be skewed by some survey respondents where *n* was 1. Similarly, the survey results may be skewed when the value of *m* was low. These low numbers are often

due to the lack of scientific data or field experience. For instance, many respondents provided ranking for chlorides and abrasives, as such products have been used by practitioners for many years. On the other hand, there were much fewer rankings provided for acetates, formates, or agr-based deicers, as such products are relatively new to practitioners and their long-term impacts are not as well-known.

#### ***6.1.4. General Comments on Anti-icing, Lessons Learned, and Future Deicer and Alternatives***

##### *Anti-icing*

Nine respondents made comments specifically related to the use of anti-icing practices. Respondents stated that anti-icing treatments with salt brine or  $MgCl_2$  would substantially reduce the amount of salt and sand placed on roadways; anti-icing can reduce total salt usage; anti-icing with salt brine and De-ice has been very successful, but  $MgCl_2$  and salt brine were preferred for anti-icing; and don't use  $CaCl_2$  for anti-icing. Other comments on anti-icing include: anti-icing reduces crashes and increases maintenance service levels; follow an anti-icing strategy and don't use sand;  $MgCl_2$  and anti-icing are not a "magic bullet" for all conditions; and proactive use of winter maintenance chemicals before the event works well.

##### *Lessons Learned*

Seven respondents made comments related to lessons learned on various aspects of winter road maintenance. Comments include:

- Don't panic if magnesium chloride gets slick. Just add water. Never apply magnesium chloride when road temperatures are above 32°F and rising. Don't apply magnesium chloride until you are sure that a storm is on its way.

- No matter how good the product is, the supplier is the key to your success. If they cannot provide accurate, consistent blends, this can create many problems for your agency.
- Equipment calibration should be done routinely (twice per year); otherwise you can be applying much higher rates of deicer than is needed.
- Proper training on application rates is important.
- Hotter mixes (2:1 or 3:1) instead of the standard 5:1 or 7:1 will reduce the amount of salt and sand applied to the roadway to maintain a bare road policy.
- Finding the value of corrosion inhibitors and identifying the realities of performance between chemicals will allow your DOT to become more strategic in your approach to buying, storing and applying the correct product at the correct time. Different geographic, demographic and climatic regions in our state require different approaches and eventually different products to maintain roads in the winter.
- The high cost of CMA and no alternative at present to match the environmental expectations, has driven us to introduce ice prediction technology to provide a “just-in-time, in-the-right-place” level of service. This also applies to abrasive use which will reduce the exposure to the hazards this can bring if applied on a “just-in-case” basis.
- Pre-wetting sand extends its life time on the road surface.



- Depending on the snow and ice event details (air temperature, wind, ground temperature, previous applications, future events forecasted, etc.) we will use a combination of anti-icing and/or deicing techniques. We will anti-ice with salt brine alone, or with a salt brine and De-ice<sup>®</sup> mixture. Mixing ratio depends on conditions. Every event is different in some way and we adjust accordingly.
- Only use calcium chloride in the liquid form (for deicing). (Note: the same respondent also had a comment: don't use CaCl<sub>2</sub> for anti-icing.).
- A ground temperature sensor installed for decision making during a storm is a must. I use a model 999J from Control Products, Inc.
- We do see a need for an enhanced salt product that can be delivered pre-mixed to our maintenance sites. This can eliminate our on-board pre-wet systems, which are difficult to maintain in the harsh winter environment on the back of a spreader.

#### *Future Deicers and Alternatives*

Three respondents commented that they do not see any promising alternative deicers becoming available in the near future. On the other hand four said they do see promising alternative deicers in the near future, adding that agricultural products are appealing. Two respondents commented that education of truck and plow drivers and providing the necessary support can lead to promising results.

### ***6.1.5. Conclusions Based on the Nationwide Survey***

A total of 24 deicer users participated in the survey with one from Finland, one from New Zealand, and the rest from the United States representing 15 different states and agencies.

Solid salt (NaCl(s)) is most frequently used, followed by abrasives, then magnesium chloride (MgCl<sub>2</sub>), agriculturally based (Agr-based), calcium chloride (CaCl<sub>2</sub>), and then other deicers. It is interesting to note that less than 25% of the survey respondents used alternative deicers such as potassium acetate, sodium acetate, calcium magnesium acetate (CMA), and potassium formate, whereas conventional deicers such as abrasives and chlorides are still most widely used.

Users were asked to rank the advantages of specific deicers with respect to low cost per lane mile, low effective temperature, high ice melting capacity, ease of application, and overall safety benefits for winter roads based on field experience or research from the respondent's agency. Figure 8B shows the user-perceived average ranking of all five categories by deicer, with the Agr-based products being the most advantageous and abrasives being the least and no significant difference between chlorides and acetates/formates.

Users were asked to rank the disadvantages of specific deicers with respect to corrosion to metal, impacts on concrete and asphalt pavements, impacts on water quality, impacts on soil, vegetation, wildlife and human health, and overall effects to structures and the environment based on field experience or research from the respondent's agency. Some findings from the survey were inconsistent with research findings from the literature review. Figure 9B shows the user-perceived average ranking of all five categories by deicer, with acetates and formates in general perceived to have the least impacts and chlorides the most.

Based on user perception, the best deicers (overall ranking >1) are listed as follows, in the decreasing order of preference: Sodium acetate, Ice B'Gone, CMA, De-ice, Potassium formate, Clearlane, IceSlicer, Unspecified Agr-based, and Calcium chloride liquid. The worst deicers (overall ranking <0) are Sodium chloride & abrasives and Corn and sugar beet. One caveat is that the surveys results may be skewed when a limited number of people provided the rankings or a limited number of criteria were ranked, which often occurred due to the lack of scientific data or field experience. For instance, many respondents provided ranking for chlorides and abrasives, as such products have been used by practitioners for many years. On the other hand, there were much fewer rankings provided for acetates, formates, or Agr-based deicers, as such products are relatively new to practitioners and their long-term impacts are not as well-known. Perceptions vary greatly with climates; a product that works well in one place may perform poorly in another, due to the discrepancies in road weather conditions (e.g., relative humidity).

Many survey respondents (38 percent) made some sort of comment on anti-icing practices, and about a third (30 percent) commented on the likelihood of future deicers or potential alternatives.

## **6.2 Survey of CDOT Winter Maintenance Practices**

The survey was conducted to provide insight on what procedures, equipment, and deicing products are being employed on the roadways of Colorado for snow and ice control. Fifteen questions were asked about the cost of deicers, the application rates, the methods of application, equipment used and storage, and any issues that might be encountered (Appendix D). We received input from all six DOT regions in Colorado. A total of thirteen people responded to the survey ranging from regional superintendants to maintenance supervisors. The most frequently skipped question referred to the modification of equipment to introduce other deicers.

### ***6.2.1. Deicers***

Eleven of thirteen respondents used NaCl and nine of 13 used MgCl<sub>2</sub> as primary deicers. Apex was listed as being used by five out of 13 respondents in the field. Table 9 shows the results from the survey, including what deicers each region used, the cost of each deicer with delivery to the region, and the application rates used.

### ***6.2.2. Cost***

Table 9 shows the cost of each deicer, both solid (s) and liquid (l) forms, and in which region they are used. NaCl (s) cost \$20.00 to \$42.00 per ton delivered to all regions in Colorado. MgCl<sub>2</sub> (l) was \$0.53 to \$0.84 per gallon delivered to all regions in Colorado. The two most used deicers NaCl (s) and MgCl<sub>2</sub> (l) were also consistently the cheapest deicers.

IceSlicer (s) cost \$92.00 per ton delivered to Region 2 in Colorado, while Apex (l) cost \$0.69 to \$0.86 per gallon in Regions 2–5. Caliber cold temperature modified (l) cost \$0.73 per gallon in Region 4. IceBan 300 (l) cost \$0.69 to \$0.72 per gallon delivered to Region 3. No prices were provided for NaCl (l), MgCl<sub>2</sub> (s), M1000 cold temperature modified (l), NaAc/NaFm, KAc (l), and Rapid Thaw (s).

### ***6.2.3. Equipment***

The equipment used in the field was standard for each site, with each applying solid deicers with Tandem and Midrange plow trucks with V-box sanders. The equipment used for liquid deicer application included 1000–6000 gallon semi spray tankers.

### ***6.2.4. Storage***

The solid deicers are usually stored in covered sheds. The liquid deicers are usually stored in 21,000 gallon tanks outside.

### ***6.2.5. Application Rates***

Table 9 shows the typical application rates for each deicer by region. Application rates for NaCl (s) ranged from 100 to 500 lb/l-m, with one respondent suggesting a higher range of 600 to 900 lbs/l-m. Application rates for MgCl<sub>2</sub> (l) ranged from 20 to 100 gallons/l-m.

**Table 9 Deicers listed by CDOT respondents according to their Region, the cost with delivery to the Region, and typical application rates.**

Deicer	Region	Cost	Application rate
NaCl (Solid)	1	\$42.00 per Ton Delivered	500 pounds per lane mile on average
	1		500 lbs per lane mile*
	2	\$30 to \$53 per ton	500 pounds per lane mile
	3	NA	300 to 500 lbs/ lane mile
	3	\$23.50 per ton	600lbs to 900 lbs per lane mile
	4	\$25.50 to \$32.00 per ton	200lbs per lane mile
	4	NA	100 to 500 lbs per lane mile
	4	\$29.50 to \$32.00 per ton	200 lbs. per lane mile
	5	NA	200-600 lbs per lane mile
	5	\$20-24 per ton	300-400 lbs per lane mile
MgCl <sub>2</sub> (Liquid)	6	NA	100-500 lbs per lane mile
	1	\$0.84 per gallon Delivered	25 to 45 gallons per lane mile
	1	\$0.70 per gallon	40-80 gallons per lane mile
	3	NA	40 to 80 gal/ lane mile
	3	\$0.55 per gallon	40 gallons per lane mile
	4	\$0.53 per gallon	40 gal per lane mile
	4	NA	20 to 100 gallons per lane mile
	4	\$0.57 per gallon	40 gallons per lane mile
	5	NA	30-80 gal per lane mile
	5	NA	40 to 80 gal per lane mile
MgCl <sub>2</sub> (Solid)	6	NA	20-100 gal per lane mile
	5	NA	300-400 lbs per lane mile
NaAcF (Liquid)	1	NA	500 lbs per lane mile
	3	NA	NA
IceBan 300 (Liquid)	4	NA	NA
	2	\$0.69 and \$0.72 per gallon	40 gallons per lane mile
Apex (Liquid)	4	NA	NA
	2	\$0.69 and \$0.72 per gallon	25 gallons per lane mile
	3	NA	40 to 80 gal/ lane mile
	3	\$0.76 per gallon	25-30 gallons a lane mile
	4	NA	NA
Rapid Thaw (Solid)	5	\$0.86 per gallon	30 to 60 gal per mile lane
	6	NA	80 to 100 lbs per lane mile
M1000 Cold Temp. Chloride (Liquid)	6	NA	60 to 80 gallons per lane mile
IceSlicer (Solid)	2	\$92 per ton	180 to 220 pounds per lane mile
	3	NA	100 to 300 lbs/ lane mile
	4	NA	100 to 350 lbs per lane mile
	6	NA	100-350 lbs per lane mile
Cold Temp. Modified Envirtech Caliber (Liquid)	4	\$0.73 per gallon	40 gal per lane mile
KAc (Liquid)	6	NA	20-100 gal per lane mile
	3	NA	NA

\*NaCl was specified as used as a liquid.

### ***6.2.6. Factors that Influence Application Rates***

Survey respondents were asked to provide input on how different environmental factors, such as wind speed and direction, temperature, humidity, and storm size, as well as traffic volume affect application rates. Application rates were reported as being greater for high-traffic roadways because the longer turnaround time required to apply the deicer to the roadway. Respondents suggested using  $\text{MgCl}_2$  (l) on roads with higher traffic because the traffic helps distribute the deicer on the road, while  $\text{NaCl}$  (s) salt-sand tends to blow off roads with higher traffic volumes. Respondents also added that solid deicers can be applied to curves, intersections, grades and critical areas, whereas liquids are applied to certain road segments.

As the intensity of the storm increases the application rate of the deicers may increase as well. Respondents commented that in a large storm, no solid deicers should be applied while it is snowing, whereas liquid deicers can be applied during and after the storm. Respondents also said that if the temperature is too low and intensity of the storm too great then deicers should not be applied. Respondents said that once the pavement temperature drops below  $-15^\circ\text{C}$  ( $5^\circ\text{F}$ ) liquid deicers should not be used and that only solid deicers should be applied. If the temperature reaches  $-8.9^\circ\text{C}$  ( $16^\circ\text{F}$ ) or below, then special cold-weather deicers should be applied.

Respondents stated that if the wind is blowing hard the use of chemical is usually stopped because the deicers are just blown off the roads. If the area is too windy there can be problems with using deicers because they can cause snow to build up on the roadway surfaces that otherwise would have blown off. One respondent noted that deicers do not usually work in high wind areas.

Respondents said that as humidity rises the need for sand increases and the use of liquid deicers should decrease. There should be no anti-icing during times of high humidity

because this could cause freezing problems. Humidity is a big factor, especially near rivers and lakes. One should not put too much deicer down because it may draw moisture to the road after the storm.

### **6.3 Survey of CDOT Deicer Priorities**

Even though the hidden costs of road salts to the infrastructure and surrounding environment can be substantial (4), such costs are often ignored in formulating highway winter-maintenance strategies. Some products for snow and ice control may cost less in regard to materials, labor and equipment, but cost more in the long run as a result of their corrosion and environmental impacts. Considerable amount of research is needed in order to fill the knowledge gap and establish a scientifically robust, defensible decision-making process for winter maintenance (4).

The survey was conducted to gain insight on how CDOT personnel prioritize various aspects of deicers including deicer performance, corrosion to metals, and impacts to pavements and the environment (Appendix E). We received input from all six DOT regions in Colorado. A total of six people responded to the survey ranging from bridge engineers to maintenance supervisors.

#### ***6.3.1. Survey Results***

Survey respondent rankings for deicer performance attributes varied greatly and this is most likely due to the difference in their job descriptions—for instance, headquarters personnel versus maintenance supervisor. The low cost for training and improved pavement friction were ranked as having the least relevance. The high ice melting capacity, low material cost per lane mile, ease of application, and low cost of application equipment were ranked as having the greatest relevance.



The corrosion effects of deicers on metals were consistently ranked as highly relevant, with low corrosion effect on rebar or dowel bars and slow penetration into concrete ranked as the highest. The low corrosion effect on aluminum was ranked as having the least relevance to deicer selection.

Deicer impacts on concrete and asphalt pavements were ranked by survey respondents as having great relevance, with an average overall decision weight of the category ranking of 8.5 out of 10. Deicer impacts on freeze/thaw resistance of concrete and impacts on aggregates (including ASR) of asphalt pavement received the lowest rankings in the corrosion to metal decision weight category.

Survey respondents also ranked some deicer impacts on the environment, including impact to water quality and air quality, as highly relevant, whereas deicer impacts on soil was not ranked as high.

### ***6.3.2. Multi-criteria Decision-making Framework for Deicer Selection***

We intend to lay the groundwork for a framework that allows an agency to assess the various deicer products on the market or to formulate its own deicer product based on laboratory testing and multi-criteria decision making (MCDM). The notions of alternatives, multiple attributes, conflict among criteria, decision weights and decision matrix from the deterministic, stochastic, or fuzzy MCDM methods (6) can be adopted for the selection or formulation of snow and ice control materials. The crux is to strike the right balance in meeting multiple goals of the highway agency, including safety, mobility, environmental stewardship, infrastructure preservation, and economics (4).

Rational decision-making guidelines can be developed to help winter maintenance managers in selecting the most suitable deicers for conditions in their agency or local jurisdiction, taking into account the array of factors involved, objectives and priorities, such as level of service requirements and local environmental or infrastructure concerns. A numerical evaluation of different alternatives within the given constraints can be conducted by placing different weights on the various aspects of deicer products, potentially related to cost per lane mile, ice melting capacity, ice penetration capability, ice undercutting capability, effective temperature, friction improvements, negative impacts on concrete and metals, etc.

The purpose of the following section is to describe a *deicer composite index* that would allow winter maintenance managers to numerically evaluate deicers based on their agency priorities or local needs and constraints. As an example, we apply the CDOT user priorities to the composite index, which would allow the most applicable deicer to be selected based on its relative ranking.

The survey responses provided by CDOT personnel show the variation in importance of each *deicer attribute* category, including: cost-effectiveness (per lane-mile), deicer performance, deicer corrosion to metals, deicer impacts to concrete and asphalt pavements, and deicer impacts on the environment. Each deicer attribute category or subcategory was assigned a *decision weight* based on the DOT user's input, as shown in Table 10.

**Table 10 Decision weights for various deicer attributes based on survey responses  
from personnel at all six CDOT regions.**

	<i>Decision Making Criteria</i>	<i>Average Decision Weight from CDOT Responses</i>	<i>Average Decision Weight for the Decision Category</i>	
<b>Cost</b>	Low materials cost per lane mile	7.17	7.00	
	Low cost for training	5.67		
	Low cost for application equipment	7.17		
	Other: ease of material handling	8.00		
<b>Safety/Deicer Performance</b>	Low effective temperature	7.50	7.08	
	Other: ability to use in higher temps at lower application rates	7.00		
	High ice melting capacity	7.83		
	Improved pavement friction	6.00		
<b>Corrosion to Metals</b>	Low corrosion effect on mild steel	7.83	7.93	
	Low corrosion effect on galvanized steel	7.67		
	Low corrosion effect on aluminum	6.67		
	Low corrosion effect on rebar or dowel bar	8.67		
	Slow penetration into concrete	8.83		
	Other: importance of maintenance to keep metals clean	10.00		
	Other: Importance of construction to protect metals	10.00		
<b>Impacts on Pavement</b>	<i>Overall low impact on concrete pavement</i>	8.00	8.56	
	Impact on freeze-thaw resistance of concrete pavement	8.00		
	Impact on silica reactivity (ASR) of concrete pavement	9.00		
	Impact on alkali-carbonate reactivity (ACR) of concrete pavement	8.50		
	Impact on scaling of concrete pavement	8.80		
	Impact on strength properties of concrete pavement	8.80		
	Impact on expansion of concrete pavement	8.80		
	Other: importance of a mix design to counter act the impacts	10.00		
	<i>Overall low impact on asphalt pavement</i>	8.00	7.76	
	Impact on aggregates (including ASR) of asphalt pavement	7.40		
	Impact on asphalt binder	7.60		
	Impact on degradation and disintegration of asphalt pavement	8.00		
	Impact on strength properties of asphalt pavement	7.80		
	Other: importance of mix design to counter act the impacts	10.00		
<b>Impacts on the Environment</b>	<i>Overall low impact on water quality</i>	8.25		8.38
	Total phosphate	9.00		
	Total nitrogen	8.50		
	Total organic carbon (TOC)	8.00		
	Total chloride	9.00		
	Biological oxygen demand (BOD)	7.50		
	Chemical oxygen demand (COD)	7.50		
	Aquatic toxicity	9.25		
	<i>Overall low impact on plants</i>	7.50	7.80	
	Browning/Singe	8.00		
	Senescence/Death	8.75		
	Root issues	7.50		
	Native species secession	7.25		
	<i>Overall low impact on soil</i>	6.80		7.89
	Conductivity	7.67		
	Heavy metal leaching	8.33		
	Microbes	8.33		
	Food web	8.33		
	<i>Overall low impact on wildlife</i>	7.75	8.06	
	Attraction to wildlife (wildlife-vehicle collisions)	8.25		
	Ingestion toxicity	8.25		
	Altered habitat and migratory paths	8.00		
	<i>Overall low impact on air quality</i>	8.25		7.92
	PM 10	8.50		
	Other: deicer aerosols	7.00		
	<b>Average Overall Ranking</b>			7.84

Note: The highlighted rows were not used to calculate the average decision weights in the last column since they are not directly related to deicer selection.

As shown in Table 11, the *deicer composite index* for each deicer product is calculated by multiplying the relevant *decision weights* with the *attribute values* indicating where the product's cost, performance or impacts fall in the specific category or subcategory. These attribute values can be estimated based on an overall examination of the existing literature and experimental data; or in some cases, calculated precisely based on the experimental data. Note that for performance attributes, the attribute values ranged from 1 to 10, with 1 being the worst and 10 being the best. For impact attributes, the attribute values ranged from 1 to 10, with 1 being the most deleterious and 10 being the least.

**Table 11 An example decision matrix illustrating the differences between three deicer products to be considered by the CDOT.**

	<i>Deicer Attributes for Decision-Making</i>	<i>Average Decision Weight (CDOT)</i>	<i>Attribute Value</i>			<i>Composite Indices</i>		
			Non-inhibited solid NaCl	Inhibited liquid MgCl <sub>2</sub>	K- or Na-acetate/formate	Non-inhibited solid NaCl	Inhibited liquid MgCl <sub>2</sub>	K- or Na-acetate/formate
<b>Cost-Effectiveness</b>	Low materials cost per lane mile, also including training, equipment and material handling	7.00	9	8	3	63.0	56.0	21.0
<b>Safety/Deicer Performance</b>	Low effective temperature, ability to use in higher temperatures at lower application rates, high ice melting capacity, and improved pavement friction	7.08	6	8	4	42.5	56.7	28.3
<b>Corrosion to Metals</b>	Low corrosion effect on mild steel, galvanized steel, aluminum, rebar or dowel bar, and slow penetration into concrete	7.93	3	8	9	23.8	63.5	71.4
<b>Impacts on Pavement</b>	Overall low impact on concrete pavement, including resistance to freeze-thaw, ASR, ACR, scaling, strength loss and expansion	8.56	4	8	5	34.2	68.5	42.8
	Overall low impact on asphalt pavement, including aggregates (ASR), binder, degradation & disintegration of asphalt pavement, and strength loss	7.76	7	7	3	54.3	54.3	23.3
<b>Impacts on the Environment</b>	Overall low impact on water quality, including total P/N/Cl, TOC, BOD, COD and aquatic toxicity.	8.38	7	7	3	58.6	58.6	25.1
	Overall low impact on plants, including browning/singe, senescence/death, root issues, and native species secession.	7.80	6	6	9	46.8	46.8	70.2
	Overall low impact on soil, including conductivity, heavy metal leaching, microbes, and food web.	7.89	6	6	8	47.4	47.4	63.1
	Overall low impact on wildlife, including attraction, toxicity from ingestion, habitat, and migratory paths.	8.06	3	6	8	24.2	48.4	64.5
	Overall low impact on air quality, including PM 10, deicer aerosols, etc.	7.92	9	9	7	71.3	71.3	55.4
<b>Overall deicer composite index</b>						<b>46.6</b>	<b>57.1</b>	<b>46.5</b>

In Table 11, the decision weights for cost-effectiveness (per lane mile) were based on data received from CDOT personnel in the survey discussed in this section (see Table 9) as well as overall evaluation of products on the market. The decision weights for deicer performance, corrosion to metals, and impacts on pavement were based on laboratory and field data collected for this project as well as the literature. The decision weights for impacts on the natural environment were derived from the Environmental Impacts Literature Review (Chapter 5).

As shown in Table 11, the *deicer composite index* was calculated to be 46.6, 57.1, and 46.5 for non-inhibited NaCl, inhibited liquid MgCl<sub>2</sub>, and K- or Na-acetate/formate deicers, respectively. This illustrates the challenges still faced by the highway maintenance agencies, given that none of the deicers evaluated is close to being perfect (which would have a deicer composite index of 100). With the CDOT user priorities identified in Table 10, the inhibited liquid MgCl<sub>2</sub> deicer products present a better alternative than either the non-inhibited NaCl or the K- or Na-acetate/formate deicers<sup>5</sup>. Nonetheless, it should be noted that such comparisons may no longer hold true when applied to a specific Colorado region where the user priorities deviate from what is shown in Table 10.

It should be cautioned that this is a preliminary attempt to illustrate how user priorities and experimental data can be integrated into a defensible decision-making process for selecting snow and ice control materials. There are many caveats in this framework, such as the use of laboratory data to predict field performance and impacts as well as the lack of an appropriate index to quantify environmental impacts given that environmental concerns are often site-specific. Additional research is needed before such a framework can be robust and reliable enough to be adopted by the CDOT managers to guide their operations.

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<sup>5</sup> While the non-inhibited NaCl and the K- or Na-acetate/formate deicers are tied in the overall deicer composite index, their values in each specific attribute differ as shown in Table 11.

## 6.4. References

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## **CHAPTER 7. DEICER PERFORMANCE: LABORATORY STUDIES**

### **7.1. Background**

According to a recent study by Levelton Consultants (2007), deicing products used in the field are selected based on two main criteria—cost and performance under various road weather conditions— while more factors need to be considered (1). Roadway maintenance agencies need unbiased information for snow and ice control operations, especially when it comes to the selection, pricing and quality assurance of deicer products. New deicing chemicals, additives or mixtures are continually introduced into the market by manufacturers for use in winter maintenance operations. Nonetheless, agencies currently do not have access to a robust set of performance testing procedures that would enable them to make informed decisions.

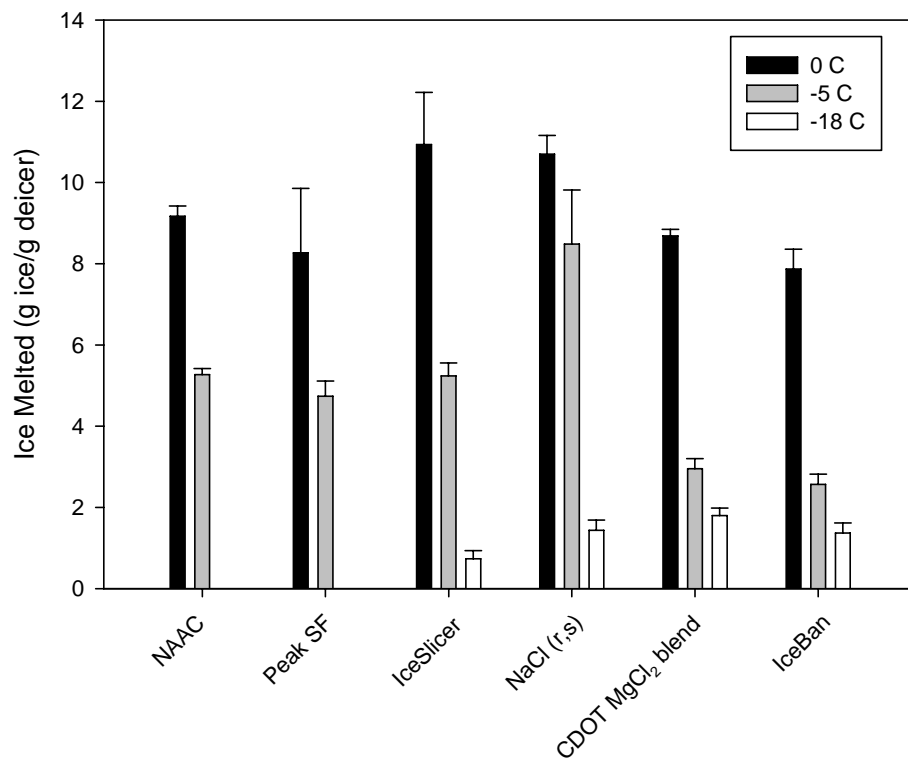
As part of the two-year study funded by the Colorado DOT, we conducted a series of laboratory tests to evaluate the performance of several alternative deicers compared with traditional chloride-based deicers. The research findings are presented as follows.

### **7.2. Results and Discussion**

#### ***7.2.1. Ice Melting Capacity of Deicers***

The ice melting capacity of the selected deicers varied as a function of product type and test temperature. The reagent-grade sodium chloride was tested as a control along with commercially available deicers that generally consisted of chlorides and additives. At 0°C (32°F), the differences in the 60-minute ice melting capacity were relatively small for all liquid and solid deicer products (Figure 11). At -5°C (23°F), the solid deicer products (IceSlicer, Peak SF, NAAC) performed better than the liquid deicer products (CDOT

MgCl<sub>2</sub> blend and IceBan). However, at -18°C (-0.4°F) liquid deicers outperformed the solid deicers, and the solid acetate and formate based deicers (NAAC or Peak SF) failed to melt any ice. Overall, the reagent-grade salt (NaCl (r,s)) outperformed all the commercially available liquid and solid deicers by performing well at all three temperatures. At approximately -18°C (0°F) Nixon et al. (2007) found MgCl<sub>2</sub> slightly outperformed NaCl, and at approximately -5°C (23°F) NaCl performed the best followed by MgCl<sub>2</sub> and then IceBan, which coincides with our results (Figure 11) (2).

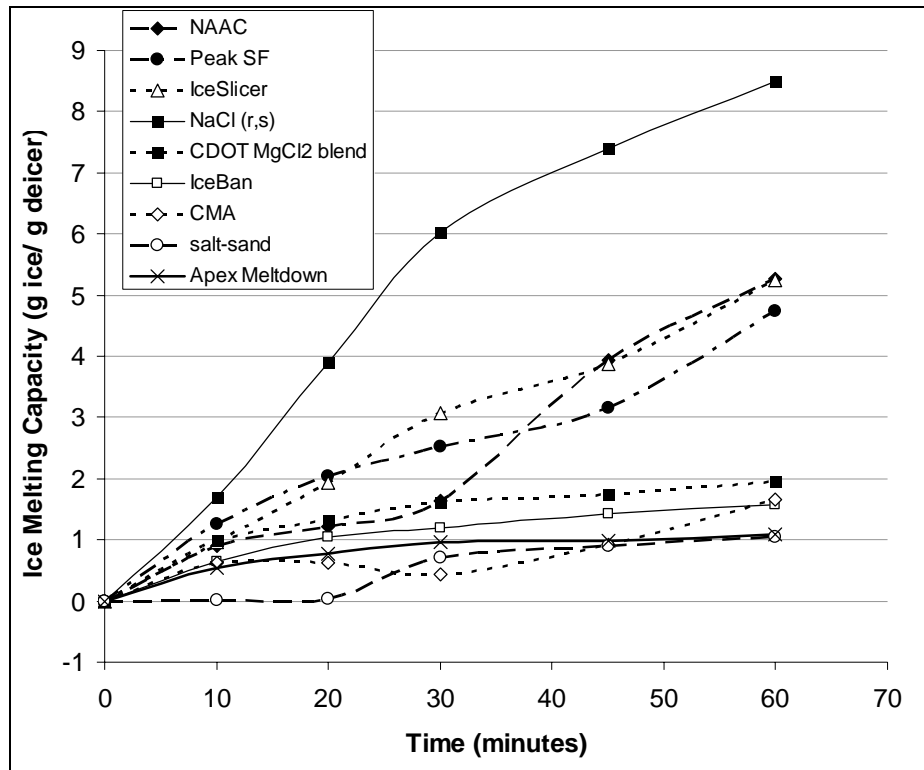


**Figure 11 Ice melting capacity as a function of deicer type and test temperature, with data from SHRP ice melting capacity test (60 minutes after application of deicer on the ice layer).**

Figure 12 shows the temporal evolution of the ice melting capacity of various deicers at air temperature of -5°C (23°F) and relative humidity of 26.6±6.6%. The reagent-grade salt, NaCl (r,s), outperformed all the commercially available liquid and solid deicers. The



evolution of ice melting capacity over time was somewhat different between reagent-grade chemicals and commercially available deicer products. The NaCl (r,s) melted more ice in the first 30 minutes, after which the rate of melting generally slowed down due to the dilution effect. In the case of the commercially available deicers most ice melting occurred in the first 20 minutes, after which the rate of melting leveled off. The exceptions to this were NAAC, with which more ice began melting after 30 minutes, and the salt-sand mixture, which leveled off after 30 minutes. The melting rate over time varied for each deicer in our study (Figure 12), whereas the melting rate measured by Nixon et al. (2007) was overall consistent for all deicers at all temperatures with the greatest amount of melting occurring in the first 10 minutes (2).



**Figure 12 Temporal evolution of ice melting capacity at  $-5^{\circ}\text{C}$  ( $23^{\circ}\text{F}$ ), with data from the SHRP ice melting capacity test.**

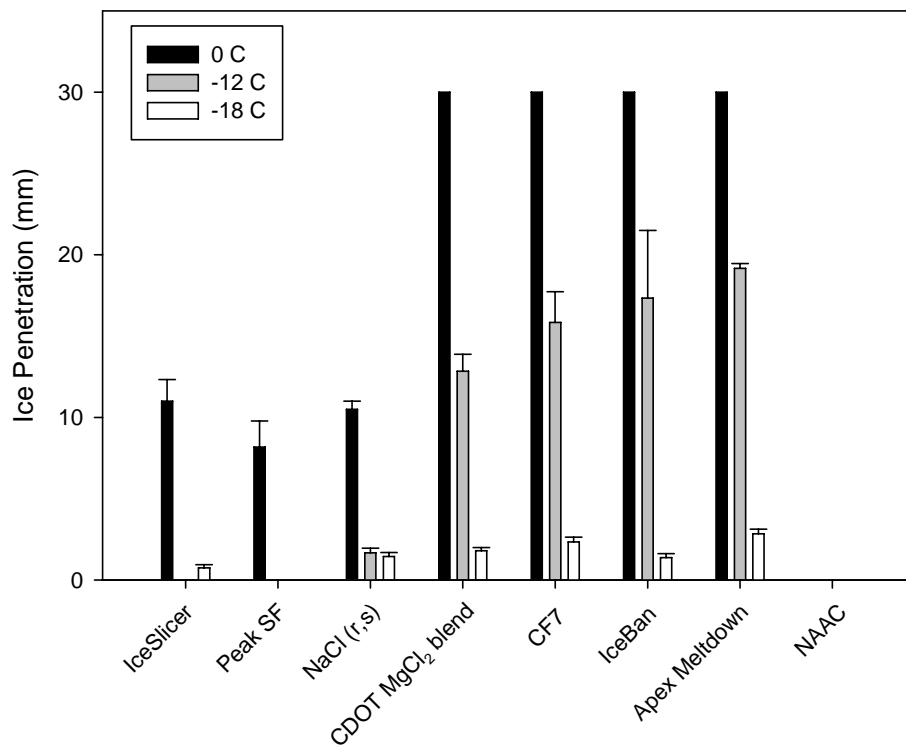
In general, there were two performance groups in the ice melting capacity study; the group with the higher ice melting capacity included IceSlicer, NAAC, and Peak SF, while the group with the lower ice melting capacity included CDOT MgCl<sub>2</sub> blend, Apex Meltdown, CMA, IceBan, and salt-sand. It is important to note that these results were collected at an air temperature of -5°C (23°F) and relative humidity of 26.6±6.6% in well-controlled laboratory conditions. The patterns may change when tested under different environmental conditions. In the field, the ice melting behavior of deicers may be further complicated by pavement type and microstructure, pavement temperature, available ultraviolet (UV) radiation, wind, traffic, residual chemicals and snow/slush on the icy pavement, etc.

While results from the SHRP ice melting capacity test method provide performance data that can be easily understood and used by field practitioners, reproducibility issues have been reported and the method has been modified in many studies to generate more consistent results (3-5). The rate of dissolution of solid deicers may have been a factor affecting reproducibility, which is dependent on the particle size and the amount of brine needed for reasonably accurate measurements. We reduced the surface area of the ice based on recommendations by Chappelow et al. (1993) to limit the errors resulting from absorption but this greatly limited the amount of brine generated, especially at colder temperatures (3).

### ***7.2.2. Ice Penetration of Deicers***

The ice penetration capability of the selected deicers also varied as a function of product type and test temperature. Overall, the liquid deicers outperformed the solids at all temperatures (Figure 13). At 0°C (32°F), the CDOT MgCl<sub>2</sub> blend, Apex Meltdown, CF7, and IceBan all penetrated to the bottom within 30 minutes of the 60-minute test. Penetration performance for all deicers gradually diminished as the temperature got colder.

As a group the solid deicers performed similarly well at 0°C (32°F) with the exception of the solid NAAC, which failed to penetrate into the ice at the three test temperatures. The solid Peak SF failed to penetrate into the ice once the temperature dropped to -12°C (10.4°F). IceSlicer showed penetration at 0°C, but not at -12°C (10.4°F). It is interesting to note that at -18°C (-0.4°F), the IceSlicer pellet became lodged in the ice column but the generated brine caused further penetration down the column.

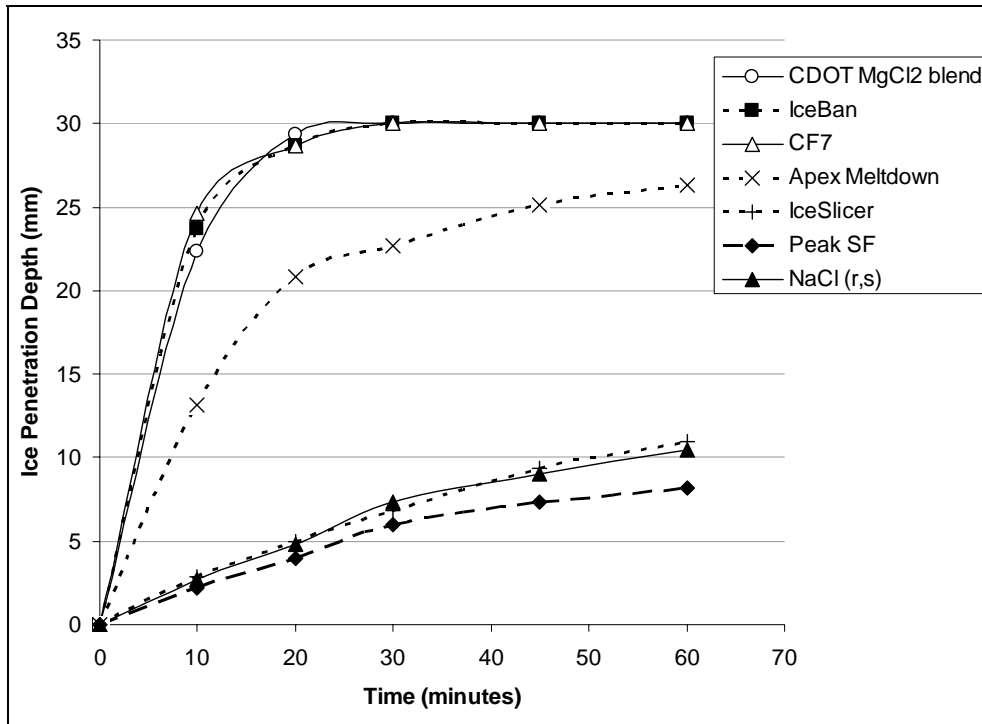


**Figure 13 Ice penetration depth as a function of deicer type and test temperature, with data from the SHRP ice penetration test (60 minutes following the application of deicer on the ice layer).**

The authors do not recommend this test method for evaluating solid deicers because the solid pellets often became lodged in the ice column and led to reproducibility issues. This

is consistent with a previous study by Nixon et al. (2007), which indicated that the ice penetration test was not a useful specification test (2).

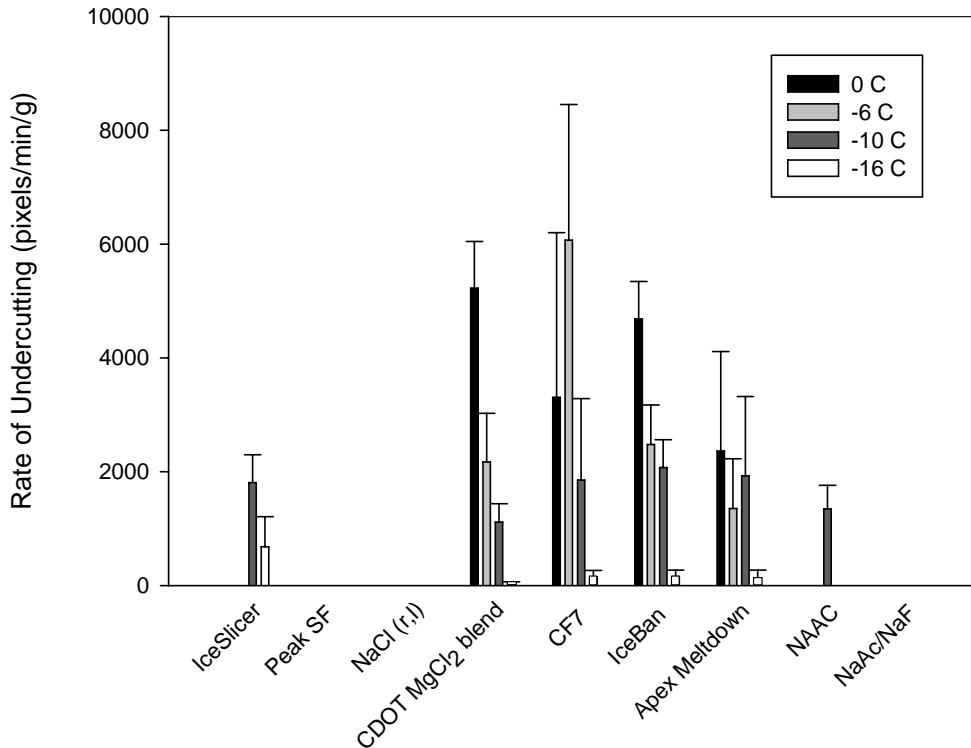
Figure 14 shows the ice penetration of various deicers over time at an air temperature of 0°C (32°F). The evolution of ice penetration over time was somewhat different for liquid and solid products. The liquid products CDOT MgCl<sub>2</sub>, IceBan, CF7, and Apex Meltdown penetrated more ice in the first 20 minutes, after which all the ice was melted or the rate of melting generally slowed due to dilution of the deicer. The solid products IceSlicer, Peak SF, and NaCl (r,s) penetrated the ice at a relatively consistent rate for the duration of the experiment (60 minutes). It is important to note that these results were collected at an air temperature of 0°C (32°F) in well-controlled laboratory conditions. The patterns may change when tested under different environmental conditions. In the field, the ice penetration behavior of deicers may be further complicated by pavement type and microstructure, pavement temperature, available UV radiation, wind, traffic, residual chemicals and snow/slush on the icy pavement, etc. Ice penetration testing conducted by Nixon et al. (2007) at approximately 0°C (30°F) found much lower ice penetration rates—less than 6mm for all deicers tested as compared to 30mm of ice penetration depth seen in Figure 14. Yet, the overall deicer performance is consistent with what Nixon et al. (2007) reported, where MgCl<sub>2</sub> and KAc showed good ice penetration and NaCl showed poor ice penetration (Figure 14) (2).



**Figure 14 Temporal evolution of ice penetration depth at 0°C (32°F), with data from SHRP ice penetration test.**

### *7.2.3. Ice Undercutting of Deicers*

The ice undercutting abilities of solid deicers were difficult to measure, as can be seen from the lack of data in Figure 15. At temperature ranges between -16°C (3.2°F) and -10°C (14°F) IceSlicer was the only deicer to reach the concrete substrate, all other solid deicers either demonstrated no notable effect on the ice surface or only partially melted down to the substrate, with some refreezing by 60 minutes. The NAAC deicer showed some undercutting at -10°C (14°F) but was ultimately refrozen by 60 minutes. At 0°C (32°F), all test deicers generally reached the substrate, however only some generated sufficient brine to begin the undercutting process.



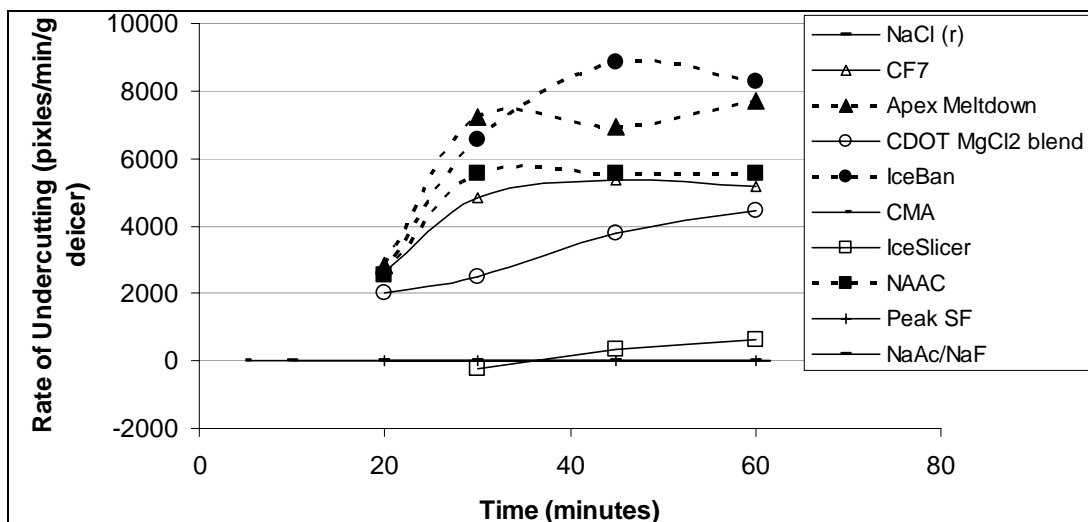
**Figure 15 Rate of ice undercutting as a function of deicer type and test temperature, with data from the SHRP ice undercutting test (60 minutes after application of deicer on the ice layer).**

Overall, the liquid deicer products worked better at undercutting and breaking the ice-concrete bond than solids, but no one liquid deicer significantly outperformed the others in the group. Generally the deicers performed better at warmer temperatures with the exception of NAAC, which showed its peak performance at -6°C. Salt brine (23% liquid, reagent-grade), Peak SF, and the sodium acetate/formate (NaAc/NaFm, 50% blend of NAAC and Peak SF) deicers were tested but showed no ice undercutting at the three test temperatures.

Figure 16 shows the ice undercutting of various deicers over time, at an air temperature of 0°C (32°F). Among the deicers tested for the ice undercutting ability, NaCl (r,l),

CMA, Peak SF, and NaAc/NaFm yielded no results at -10°C (14°F). In general undercutting did not initiate until 20 minutes into the test. The products Apex Meltdown, NAAC, and CF7 showed high rates of ice undercutting between 20 and 30 minutes, after which the undercutting rates leveled off. The product IceBan showed high rates of ice undercutting from 20 to 45 minutes after application, after which undercutting rates dropped off. The CDOT MgCl<sub>2</sub> blend product showed a consistent undercutting rate from 20 to 60 minutes after application. IceSlicer caused undercutting to occur initially but the generated brine refroze until 40 minutes into the test when undercutting was re-initiated. Overall, IceBan and Apex Meltdown had the greatest area of undercutting.

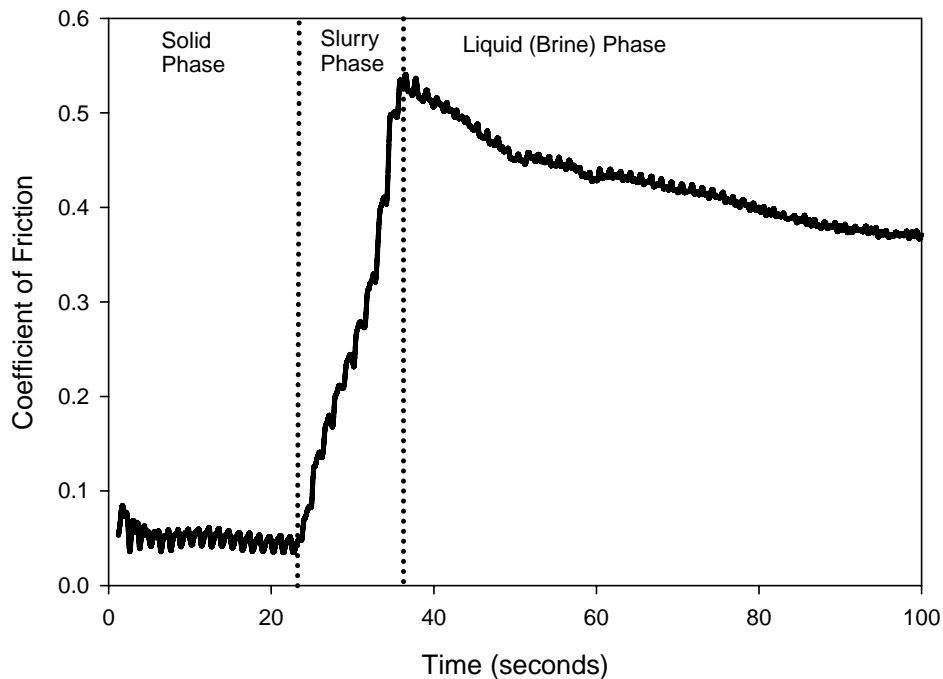
While results from this test method provide insight and performance data that can be used to guide field applications, the method itself is plagued by reproducibility issues that are difficult to address, especially for solid deicers. At this time we do not recommend using this test method to evaluate solid deicers. In addition, many deicers initially appeared to be undercutting and breaking the ice-concrete bond, but in fact the dye was moving across the surface of the ice and only giving the appearance of undercutting.



**Figure 16 Rate of ice undercutting over time at -10°C (14°F). The deicers CMA, Peak SF, NaAc/NaFm, and NaCl (r,l) were tested but yielded not results.**

#### 7.2.4. Friction Coefficient of Deiced Pavement

The coefficient of friction was measured for deicers applied to an ice surface over time. Figure 17 shows the three transition phases the samples experienced. The solid phase shows the coefficient of friction of the deicer on the ice surface following application of the deicer. The slurry phase represents the coefficient of friction of the deicer as it is melting through the ice surface, and the liquid (brine) phase represents the coefficient of friction of the diluted and liquefied deicer on the concrete surface.

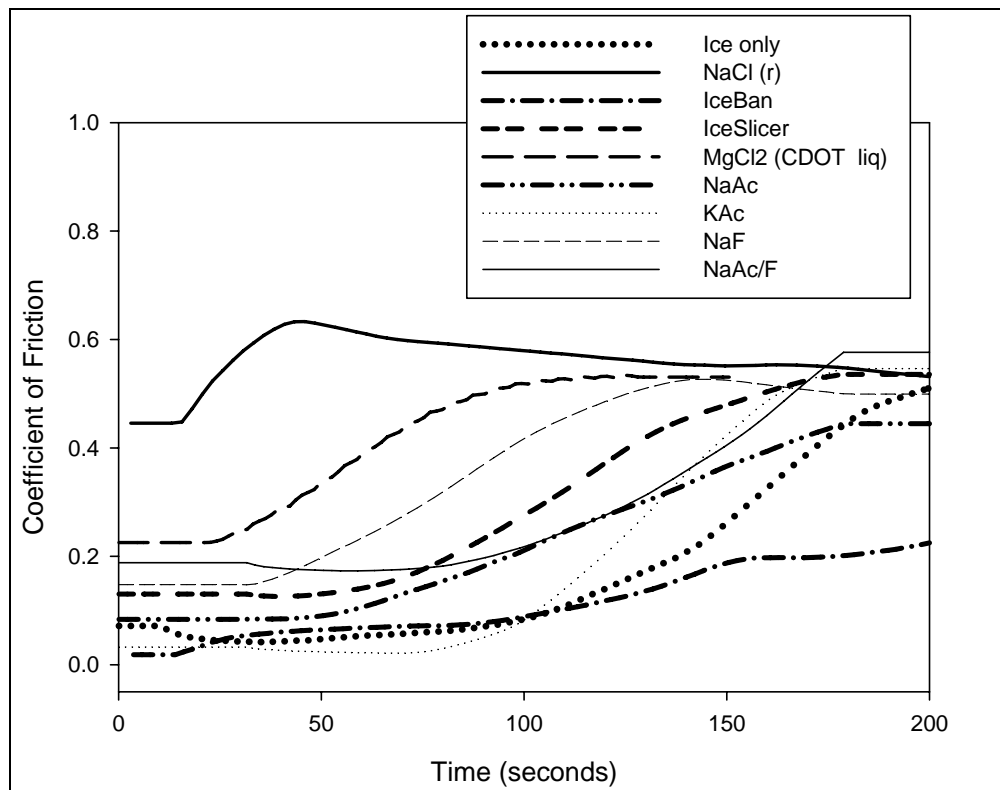


**Figure 17 Transition phases observed during tribometer testing.**

Figure 18 shows the coefficient of friction for each deicer tested over time. Each deicer tested went through all three transition phases with the amount of time of each phase varying.



The coefficient of friction on the ice was lower than the coefficient of friction on the wet concrete surface (Figure 9), showing that the ice is more slippery than wet concrete. Partly due to the immature nature of this test method, the friction test results had great variance and did not show any significant difference between liquid and solid deicers or between chloride-based deicers and the acetate- or formate-based deicers. Nonetheless, the tribometer test revealed that the IceBan led to the lowest friction coefficients on both the ice and the deiced concrete, meaning more slippery conditions, whereas IceSlicer had the greatest variance of friction coefficients on the ice. The latter may be attributed to the clay or aggregate material naturally embedded in IceSlicer.

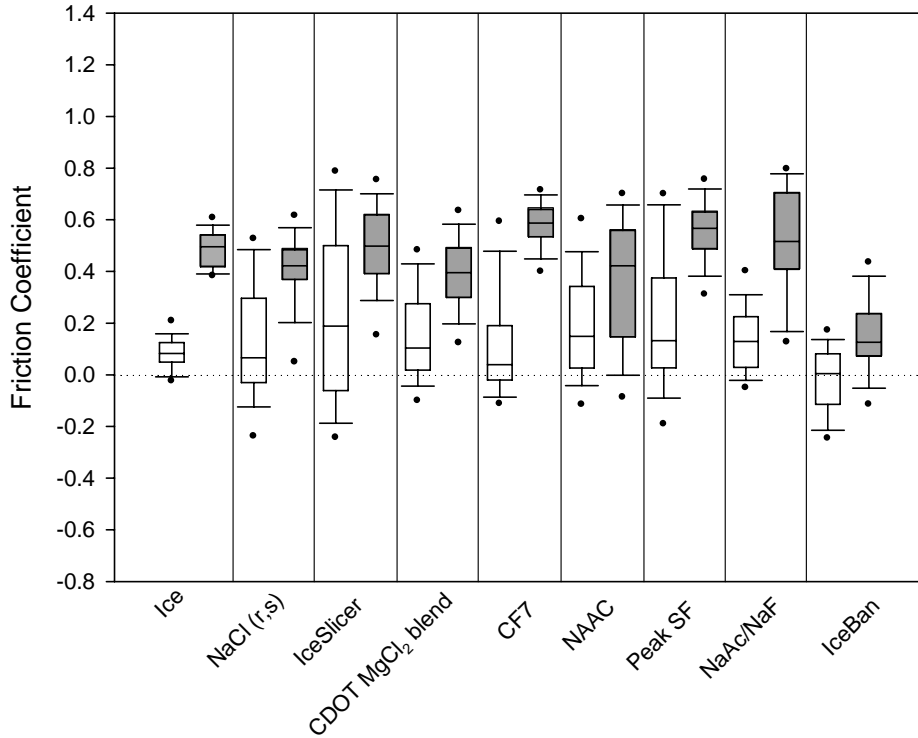


**Figure 18** The coefficient of friction data collected for each deicer tested over time.

The current practice for DOTs is to measure the friction coefficient of wet and icy roads with a friction wheel, which is attached to the back of a vehicle on a trailer and towed.

The NCHRP project 6-14 found that the use of friction measurements can improve winter maintenance operations and mobility, but using a device with an extra wheel may not be practical in the field (6). There have been recent advances in friction measurement devices, such that they can provide real-time data in order to facilitate the determination of deicer application rates based on road surface conditions.

The quantification of friction coefficients of deiced pavement is a new application of the tribometer. While the data in Figure 19 demonstrate the feasibility of this technology, the tribometer and the test procedures need to be modified in order to provide laboratory data that are reliable and representative of field experience. The tribometer holds promise as a potential standard test protocol to assess the safety implications of deicer products, if more research is conducted to establish its test results with field friction test data.



**Figure 19** Box plots of tribometer data with friction coefficient on the y-axis and deicer type of the x-axis. The white boxes show the friction coefficient of deicers on the ice (solid phase), while the gray boxes show the friction coefficient of the deiced concrete (liquid brine phase).

### 7.2.5. Thermal Properties of Deicers

Differential scanning calorimetry (DSC) was used to quantify the thermal properties of deicers. Figure 20A–D shows the heating-cycle thermogram for the tested deicers. The peak at the warmer temperature range for each thermogram defines the characteristic peak—the point at which ice crystals begin to form, which corresponds well with the effective temperature for the deicer. At temperatures colder than the characteristic peak ice crystal formation begins and can lead to slippery pavement in the field environment and reduced effectiveness of the deicer. It is interesting to note that the DSC thermograms were very reproducible for each deicer at a given dilution rate and heating

rate, and thus may serve as a “fingerprint” tool for quality assurance of deicers. For instance, IceSlicer and reagent-grade NaCl (r,s) were the only deicers consistently featuring two equally strong peaks in the warming cycle (Figure 20D).

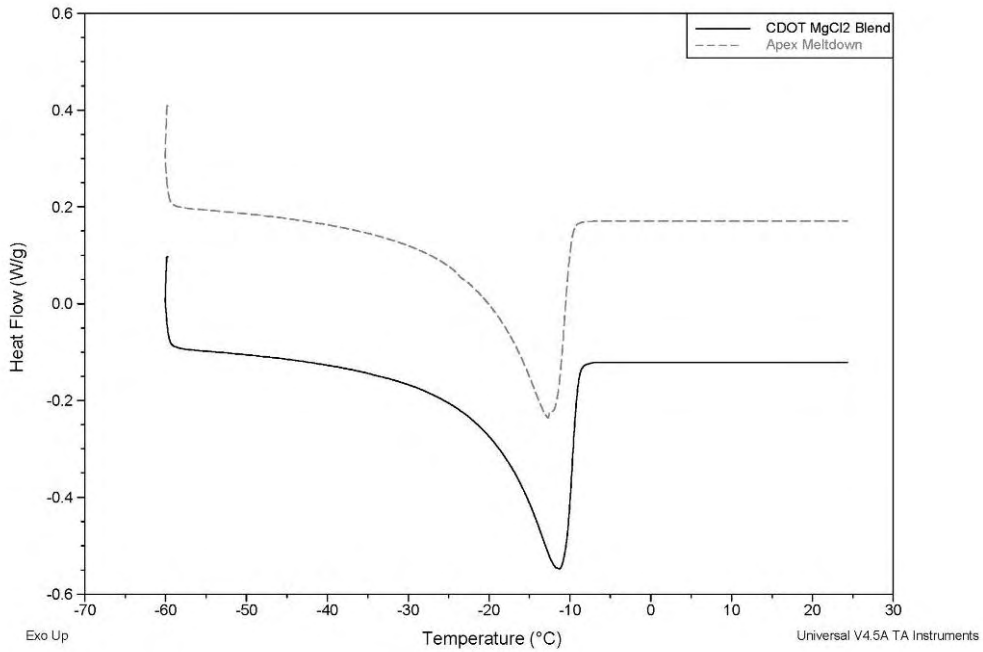


Figure 20 (A)

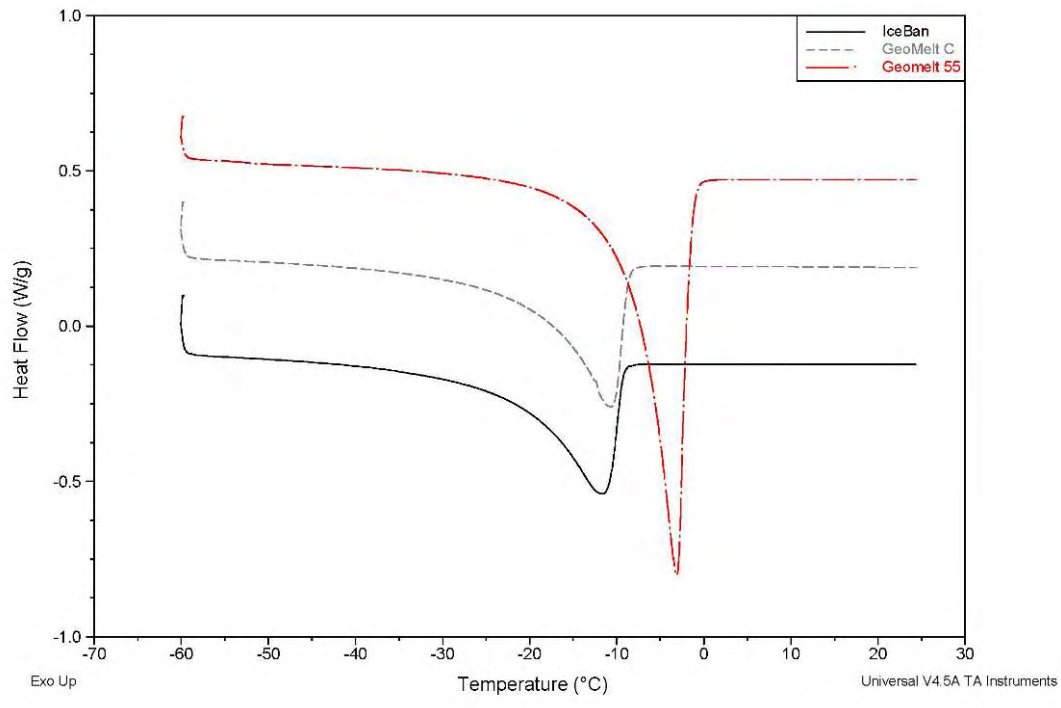


Figure 20 (B)

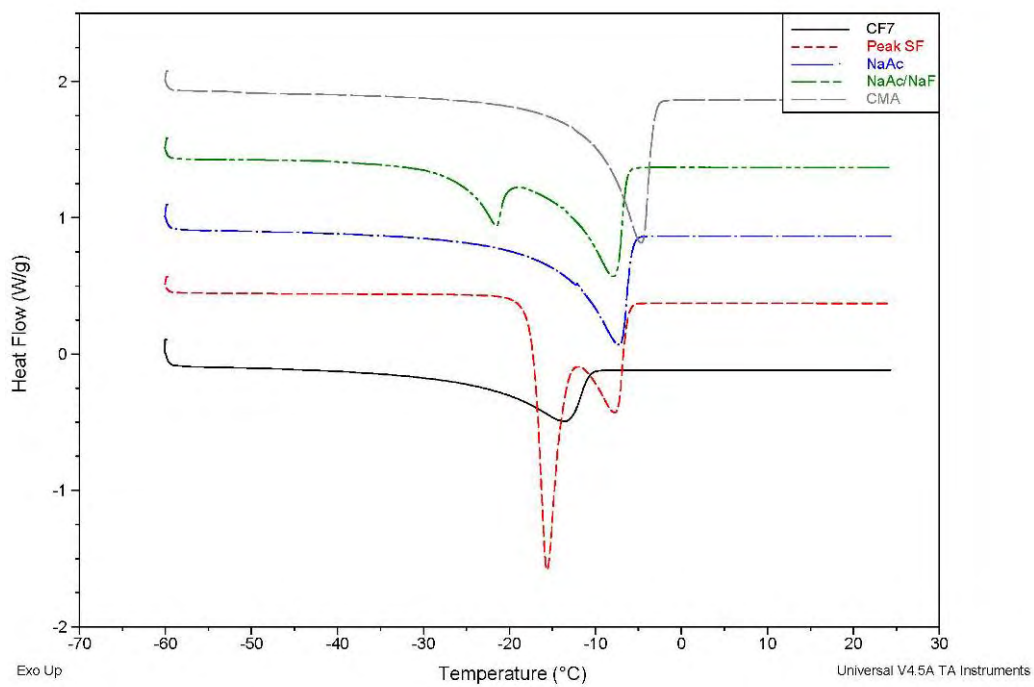


Figure 20 (C)

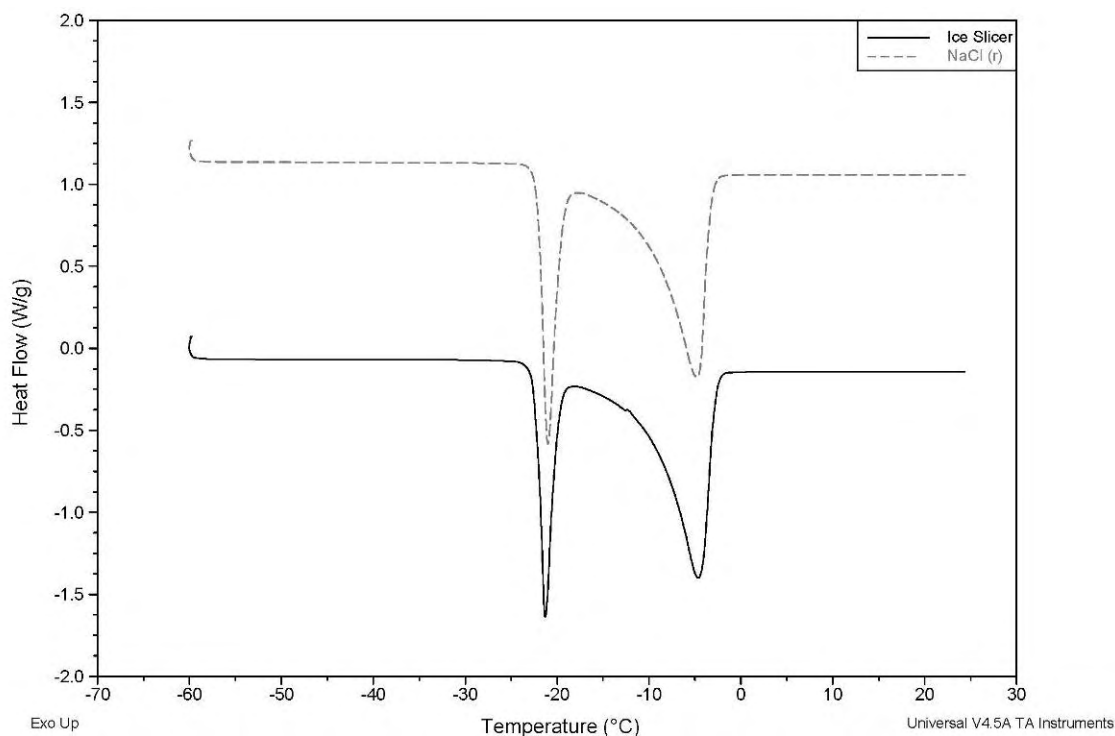


Figure 20 (D)

**Figure 20 DSC thermograms of the tested deicers grouped by deicer type: (A) magnesium-chloride-based deicers (B) agricultural co-product-based deicers acetate- and formate-based deicers and (D) sodium-chloride-based deicers.**

Table 12A shows the characteristic temperature and heat flow data for the tested deicers obtained from the DSC thermograms. It can be seen that CF7 had the coldest effective temperature, followed by Apex Meltdown. Table 12B shows the ice melting capacity of the tested deicers from the SHRP test. It can be seen that reagent-grade NaCl (r,s) and IceSlicer had the highest ice melting capacities. In general, the SHRP ice melting data had more variance than the DSC data, as indicated by the higher coefficients of variance (CoV).

**Table 12 (A) Effective temperature and heat flow of deicers (based on the DSC thermograms); (B) Ice melt capacity for a limited number of deicers at T=0, -5, -18°C (32, 23, -0.4°F).**

(A)

Deicer	Original state	Characteristic Temperature Peak			Second Peak Temperature			Heat flow, H (J/g)		
		Average (°C)	CoV	Average (°F)	Average (°C)	CoV	Average (°F)	Average	CoV	ΔH
CDOT MgCl <sub>2</sub> blend	liquid	-11.24	-0.4%	11.77				95.05		
Apex Meltdown	liquid	-11.47	-4.3%	11.35				97.53		
IceBan	liquid	-11.03	-4.7%	12.15				97.26		
CF7	liquid	-13.91	-2.8%	6.96				90.46		
Geomelt C	liquid	-10.69	-4.1%	12.76				108.87		
Geomelt 55	liquid	-3.26	-6.4%	26.13				169.57		
IceSlicer*	solid	-4.55	-1.5%	23.81	-21.25	-0.4%	-6.25	191.77	1.0%	263
NaCl (reagent)*	solid	-4.71	-1.9%	23.52	-21.02	-0.2%	-5.84	179.70	3.2%	253
NAAC	solid	-7.34	-2.3%	18.79				164.60		
Peak SF	solid	-8.14	-7.6%	17.35	-24.56	-10.3%	-12.21	43.55	4.2%	290
NaAc/NaF	solid	-7.73	-1.8%	18.09				205.77		
CMA	solid	-4.73	-1.1%	23.49				179.67		

(B)

Deicer	Original state	Ice Melting Capacity (g ice/g deicer)					
		T=0 °C (32°F)		T=-5 °C (23°F)		T=-18 °C (-0.40°F)	
		Average	CoV	Average	CoV	Average	CoV
CDOT MgCl <sub>2</sub> blend	liquid	8.68	1.9%	2.95	8.5%	1.80	10.0%
IceBan	liquid	7.87	6.3%	2.57	9.8%	1.37	18.0%
IceSlicer*	solid	10.93	11.8%	5.24	6.0%	0.73	27.6%
NaCl (reagent)*	solid	10.70	4.3%	8.48	15.7%	1.43	17.6%
NAAC	solid	9.17	2.7%	5.27	2.9%	0.00	0.0%
Peak SF	solid	8.27	19.2%	4.73	8.0%	0.00	0.0%

In Table 12A, the change in heat flow (ΔH) was calculated by subtracting the total heat of fusion for pure water (334 J/g) from the measured heat flow of the characteristic peak. Statistical analysis revealed (Equation 1) the following correlation between the DSC data (°C) and the SHRP data at 0°C (32°F):

$$\text{Ice Melting Capacity} = 0.66 \times T + 8.58 \times \text{Log}_{10}(\Delta H) - 4.86 \quad (R^2=0.91) \quad (1)$$

The positive coefficient associated with  $\text{Log}_{10}(\Delta H)$ , i.e., 8.58, is consistent with the notion that the more powerful a deicer is, the less external heat it needs to melt the ice

(and thus the higher value in  $\Delta H$ ). The high *R*-square value confirms that there is a strong correlation between the DSC data and the SHRP ice melting capacity at 0°C. The less-than-one *R*-square can be attributed to experimental error, especially in the SHRP test, the different behavior between solid and liquid deicers in the SHRP test, etc. As such, DSC may hold the promise of a reliable standard test protocol to assess the deicer performance under certain road weather conditions.

The eutectic temperature of a deicer is the temperature at which crystallization completes and the product becomes solid. A deicer featuring lower eutectic temperature does not necessarily have lower effective temperature or higher ice melting capacity. Therefore, the DSC thermogram provides a much better indication of deicer performance than the widely used eutectic curve (eutectic temperature as a function of deicer concentration). In fact, based on the DSC thermograms of deicers at different concentrations, one can generate a more useful curve of effective temperature vs. deicer concentration, or even predicted ice melting capacity vs. deicer concentration, which is part of an ongoing study at our laboratory sponsored by the Clear Roads program.

### **7.3. Concluding Remarks**

Understanding the performance characteristics and negative impacts of deicers is critical to effective and responsible winter maintenance operations. This section utilized five tests to quantify the performance of identified deicers. The SHRP ice melting, penetration and undercutting tests together identified the four best-performing deicers, which were all liquids, including CDOT MgCl<sub>2</sub> blend, Apex Meltdown, IceBan, and CF7. The results from the ice melting and ice penetration tests agreed with those of Nixon et al. (2007). The DSC test showed that CF7 had the coldest effective temperature, followed by the Apex Meltdown. The tribometer test revealed that IceBan led to the lowest friction coefficients on both the ice and the deiced concrete, meaning more slippery conditions, whereas IceSlicer had the greatest variance of friction coefficients on the ice. In addition



to identifying two promising test methods (DSC and tribometer), the laboratory data shed light on the complexity and challenges of evaluating the performance of various deicers.

#### 7.4. References

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## **CHAPTER 8. DEICER IMPACTS: LABORATORY AND FIELD STUDIES**

### **8.1. Background**

In the last two decades, the growing use of deicers for snow and ice control has raised concerns about their effects on motor vehicles, transportation infrastructure, and the environment. Over five billion dollars are spent each year by state and local agencies to repair infrastructure damage caused by snow and ice control operations (1).

According to a recent study by Levelton Consultants (2007) (2), deicing products used in the field are selected based on two main criteria—cost and performance under various road weather conditions—while generally there are more factors that need to be considered. Even though the hidden costs of road salts to the infrastructure and surrounding environment can be substantial (3), such costs are often ignored in formulating highway winter-maintenance strategies. Some products for snow and ice control may cost less in regard to materials, labor and equipment, but cost more in the long run as a result of their corrosion and environmental impacts. Considerable amount of research is needed in order to fill the knowledge gap and establish a scientifically robust, defensible decision-making process for winter maintenance (3).

In this project, we conducted a series of laboratory tests to evaluate the performance and impacts of several alternative deicers compared with traditional chloride-based deicers. The research methodology and findings are presented as follows.

## 8.2. Freeze/Thaw Resistance of PCC in the Presence of Deicers

### 8.2.1. Weight loss and macroscopic observations of freeze/thaw specimens

The weight loss of PCC specimens following the SHRP H205.8 laboratory test is a good indicator of the freeze/thaw resistance of PCC in the presence of various solutions. Experimental results show that the concrete mix itself had high freeze/thaw resistance in the absence of deleterious deicers. As shown in Figure 21, the impact of deicers on the structural integrity of PCC fell into three groups. In the first group, the PCC specimens in the presence of de-ionized water, the CMA solid deicer, and the CDOT  $MgCl_2$  liquid deicer showed minimal amount of weight loss and little visual deterioration of the concrete. In the second group, the PCC specimens in the presence of KFm and the NaAc/NaFm blend deicer showed a moderate amount of weight loss and noticeable deterioration of the concrete. Finally, the PCC specimens in the presence of NaCl, the NaCl-based deicer (IceSlicer), or the KAc-based deicer (CF7) showed a significant amount of weight loss and marked visual deterioration of the concrete. It should be cautioned that in the field environment, the deicer impact on the durability of concrete may not follow a similar pattern, as it is further complicated by the concentration and longevity of deicers, the chemical composition and microstructure of the concrete, and the temperature cycles experienced by the concrete.

Regarding the relatively negative impact of  $MgCl_2$  as compared to NaCl on PCC durability, the SHRP H205.8 test results of diluted deicers (~0.85%  $MgCl_2$  vs. ~3% NaCl) from this study differed from the AS C 666 freeze/thaw test results of concentrated deicers (14%  $MgCl_2$  vs. 18% NaCl) reported by Sutter et al. (4). In the previous study (4), concrete prisms of 4" diameter  $\times$  2" height (10cm  $\times$  5cm) subjected to 300 freezing/thawing cycles in 14%  $MgCl_2$  expanded considerably with 0.17% length change and reported 3.5% mass gain and 50% loss in the dynamic modulus of elasticity, whereas those exposed to 18% NaCl did not expand more than 0.04% and reported 0.5% mass

gain and approximately 5% loss in the dynamic modulus of elasticity. In contrast, our data indicated much more deleterious impacts by 3% NaCl than 0.85% MgCl<sub>2</sub> on PCC durability. Even though cement chemistry, aggregate properties, concrete permeability, air content, and the micro-cracking level of concrete might have played some role in the difference between the two studies, we argue that the key was the difference in the deicer solution concentration. The concentrations we used better simulate the field exposure scenario, where the liquid MgCl<sub>2</sub> deicer (27% to 29%) or the solid NaCl deicer (99%) applied on pavement is dramatically diluted in the long term (a 100-to-3 dilution ratio was assumed in this study). On the other hand, the AS C 666 test utilized larger PCC specimens and more freezing/thawing cycles, which might have better simulated the field experience of concrete structures and pavements than the SHRP H205.8 test.

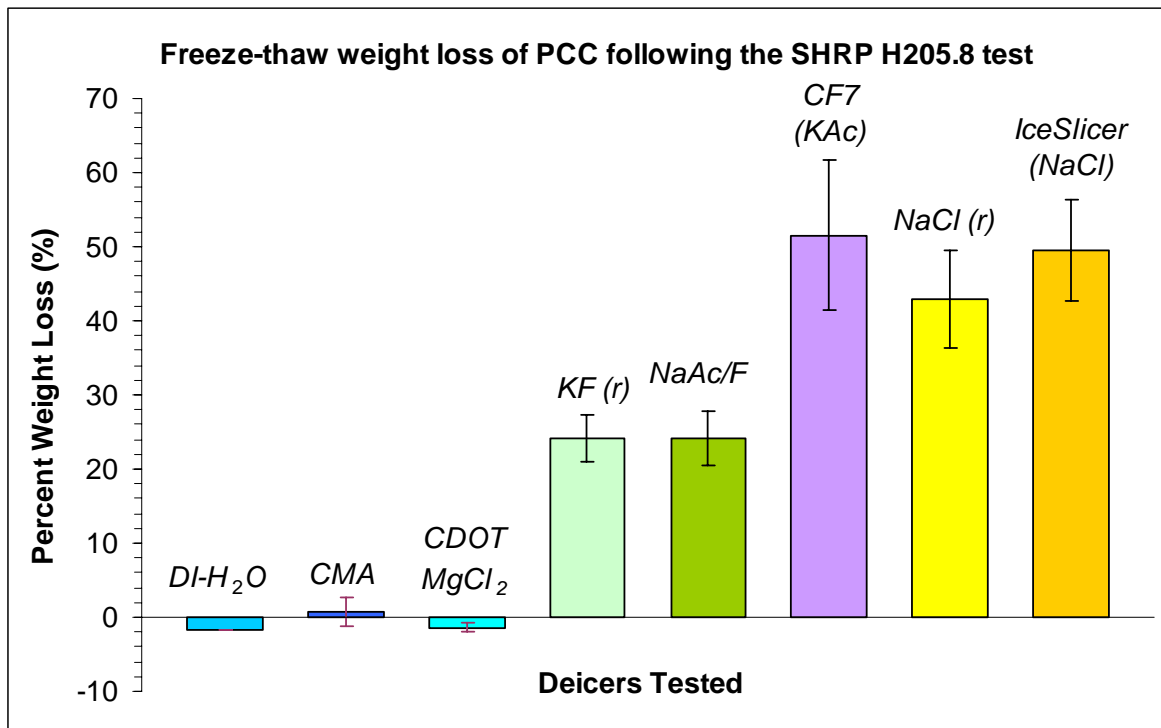


Figure 21 (a)

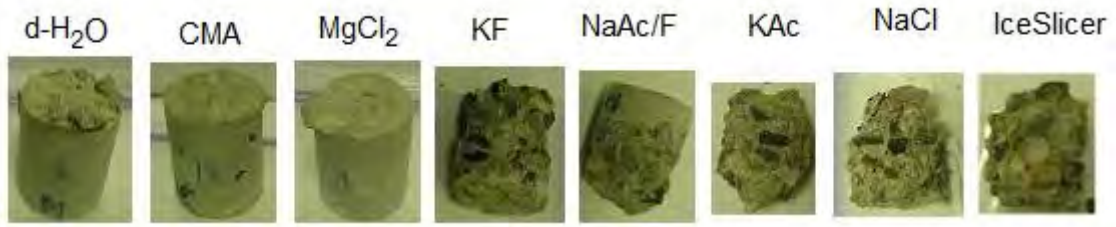


Figure 21 (b)

**Figure 21 Weight loss (a) and typical digital photos (b) of portland cement concrete specimen following the SHRP H205.8 freeze/thaw test in the presence of various solutions.**

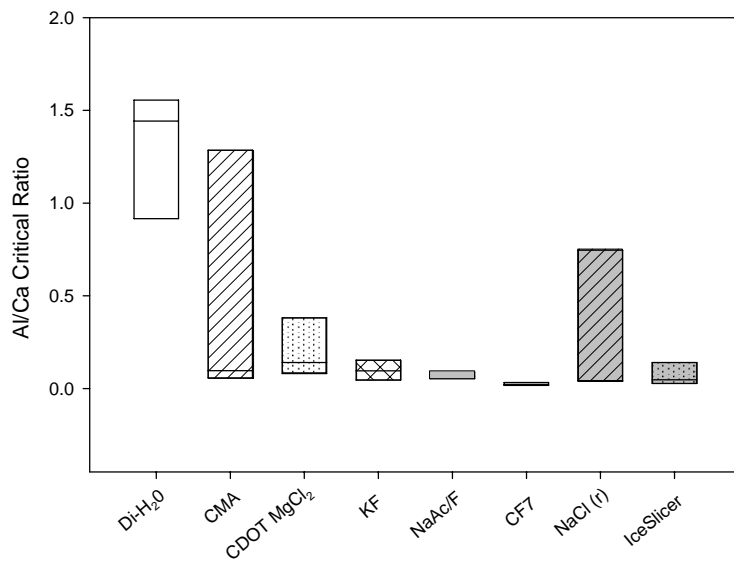


Figure 22 (a)

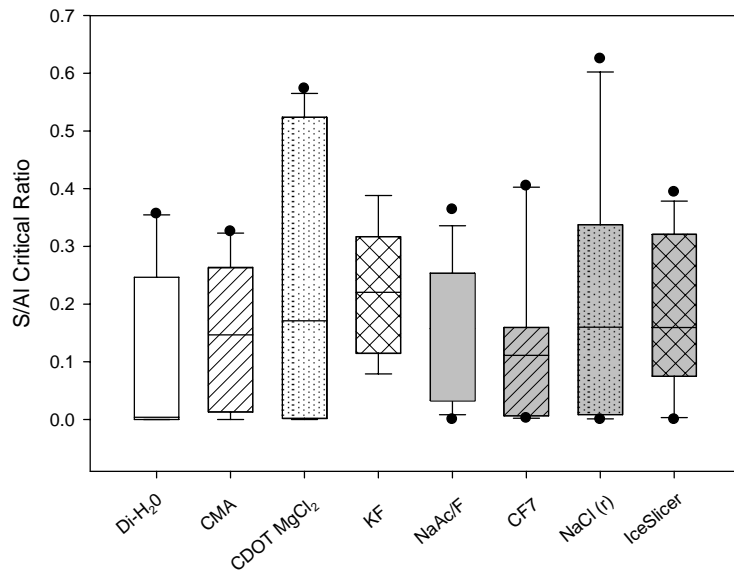


Figure 22 (b)

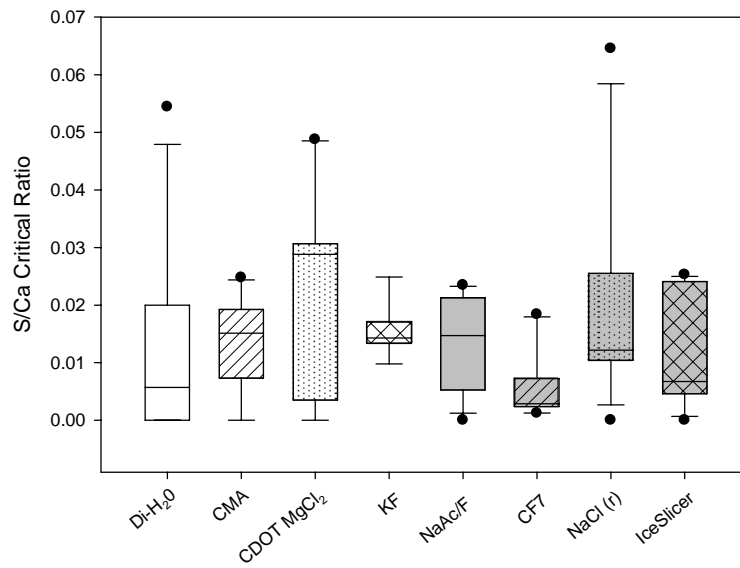


Figure 22 (c)

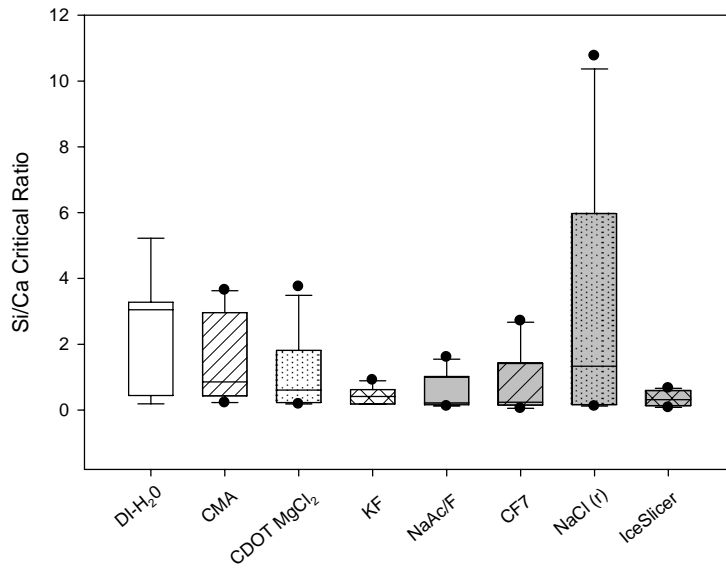


Figure 22 (d)

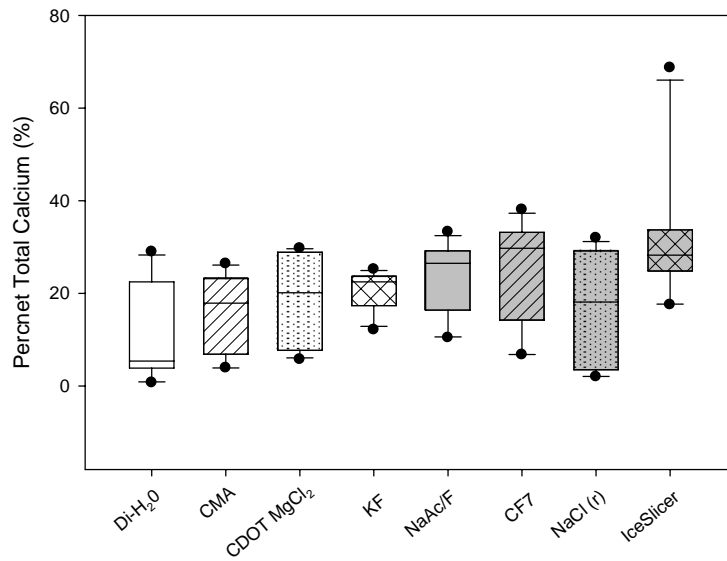


Figure 22 (e)

**Figure 22 Chemical composition of PCC samples following the SHRP H205.8 freeze/thaw test in the presence of various solutions, with box plots illustrating the EDX data collected from multiple locations on the sample. (a) Al/Ca; (b) S/Al; (c) S/Ca; (d) Si/Ca; and (e) percent total Ca.**

At least two mechanisms were at work in how the deicers affected the freeze/thaw resistance of PCC. First, in the case of NaCl, KAc, NaAc/NaFm, and KFm, the presence of deicer significantly increased the salinity of the concrete pore solution and thus the number of freezing/thawing cycles, which greatly exacerbated the physical distresses in the concrete. We hypothesize that the  $\text{Na}^+$  and  $\text{K}^+$  cations derived from deicers increased the salinity of the concrete pore solution more than the  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  cations derived from deicers, since these smaller cations can easily exchange with the cations in the cement paste and greatly enhance the solubility of cations and anions from cement hydrates including portlandite ( $\text{Ca}(\text{OH})_2$ ), calcium silicate hydrates (C-S-H) and calcium aluminosulfate hydrates. Second, the presence of each deicer altered the chemical composition of the cement paste to varying degrees, as discussed in the following sections. Such chemical changes may lead to altered microstructure of the concrete matrix and buildup of stresses inside. There was a third mechanism suggesting that the NaAc crystal growth inside the pores reduced the water penetration into concrete (5); such a beneficial role of NaAc observed for the poor-quality concrete ( $w/c=0.65$  and non-air-entrained), however, was not evident in this study.

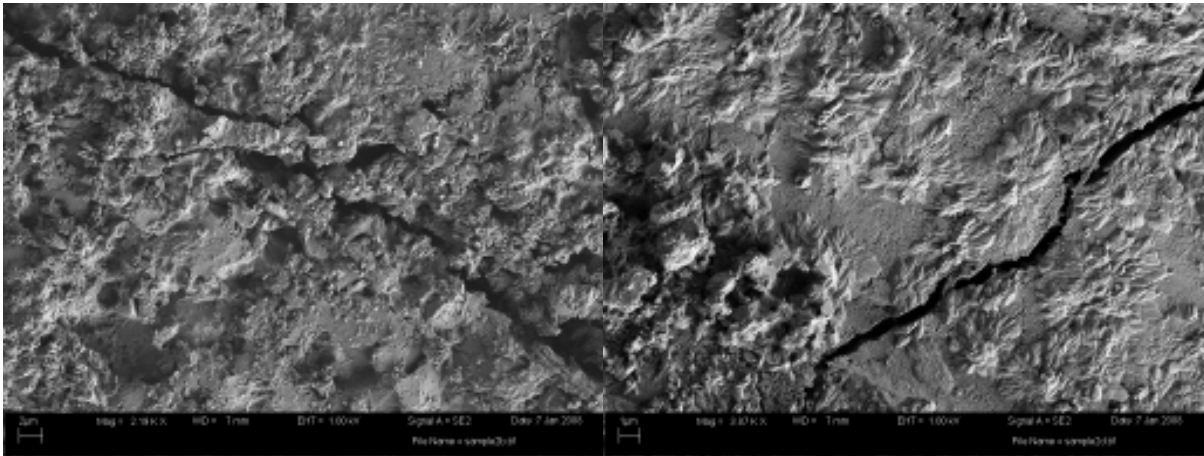


Figure 23 (a)

Figure 23 (b)



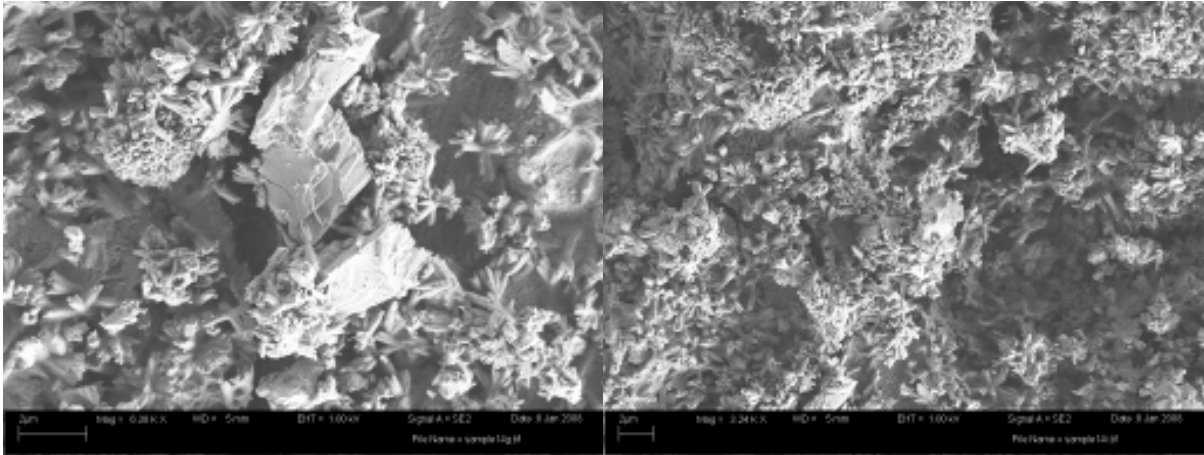


Figure 23 (c)

Figure 23 (d)

**Figure 23 Representative SEM images of PCC samples following the SHRP H205.8 freeze/thaw test in the presence of various solutions. (a) de-ionized water, 2190 times magnification; (b) de-ionized water, 3870 times magnification; (c) CMA, 6380 times magnification; and (d) CMA, 3240 times magnification.**

### *8.2.2. Effect of de-ionized water on the surface chemistry of PCC*

For the PCC specimens subjected to freeze/thaw cycling in the presence of de-ionized water, the high Si/Ca ratios and very low calcium contents in them (Figures 22d and 22e) were caused by the significant leaching of  $\text{Ca}^{2+}$  from the cement paste to the concrete pore solution and eventually to the de-ionized water featuring an extremely low ionic strength. Based on the box plots of critical elemental ratios (Figures 22a–22c), the high Al/Ca ratios (0.8–1.6) suggest the loss of  $\text{Ca}^{2+}$  from either calcium aluminate monosulfate hydrates (AFm phases) or calcium aluminate trisulfate hydrates (AFt phases), whereas the very low S/Al ratios (0.01–0.25) and very low S/Ca ratios (0.001–0.02) suggest the loss of  $\text{SO}_4^{2-}$  from AFm or AFt phases. Compact or honeycombed structures characteristic of type II C-S-H can be seen in Figure 23a. Despite the dissolution of  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$ , the rosette structures characteristic of AFm phases remained, as shown in

Figure 23b. Overall, the examined PCC surfaces were dominated by AFm phases and calcium-rich type II C-S-H, whereas structures of portlandite, silicate-rich type I C-S-H, or AFt phases were not observed. In the presence of de-ionized water, the residual AFt phases from cement hydration might have further evolved to become AFm phases. It is interesting to note that the chemical changes in the cement paste caused minimal amount of weight loss and little visual deterioration of the concrete (Figure 21).

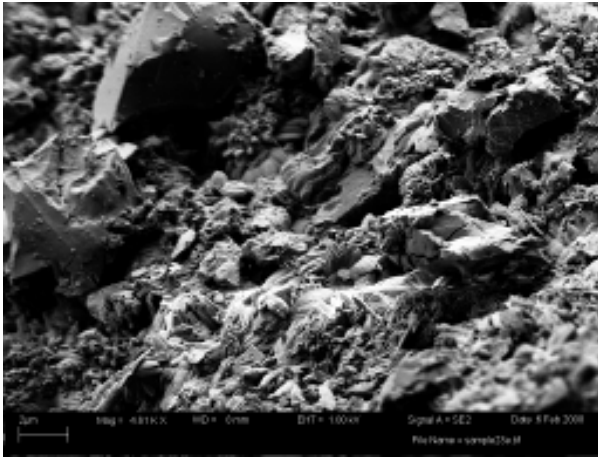


Figure 24 (a)

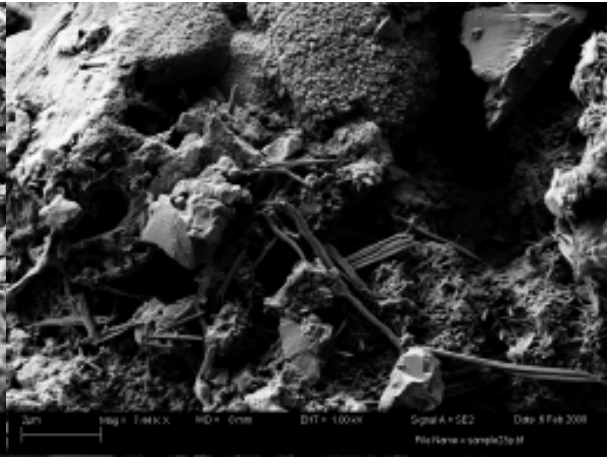


Figure 24 (b)

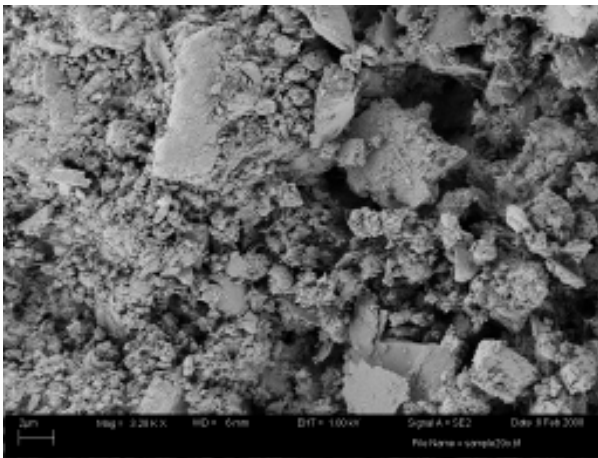


Figure 24 (c)

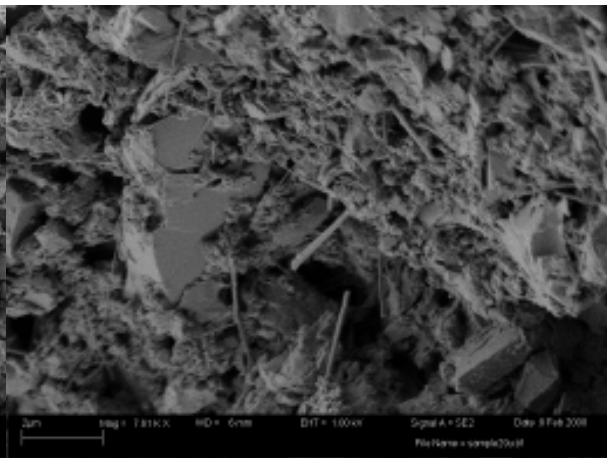


Figure 24 (d)

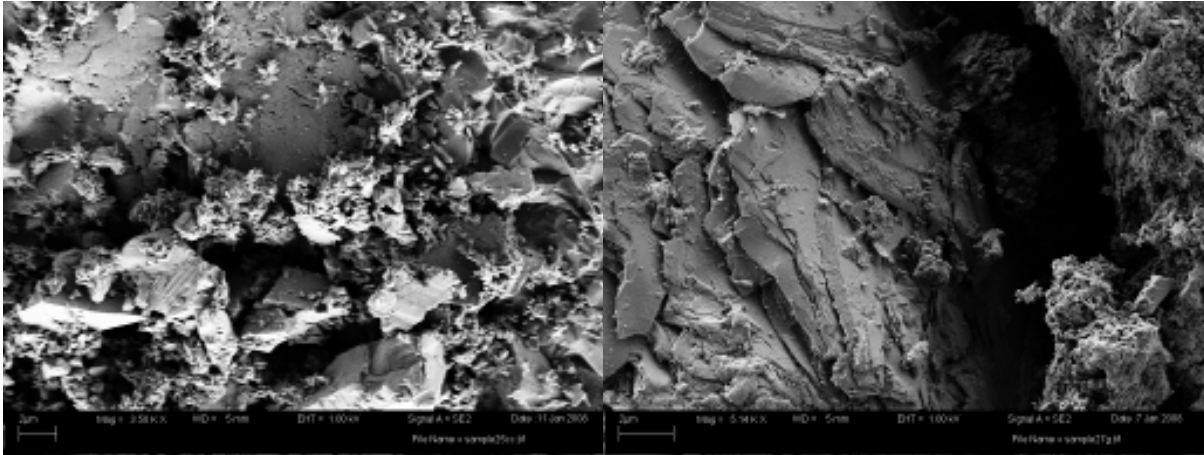


Figure 24 (e)

Figure 24 (f)

**Figure 24 Representative SEM images of PCC samples following SHRP H205.8 freeze/thaw test in the presence of various solutions. (a) KFm (r), 4610 times magnification; (b) KFm (r), 7440 times magnification; (c) NaAc/NaFm, 3280 times magnification; (d) NaAc/NaFm, 7610 times magnification; (e) KAc, 3500 times magnification; and (f) KAc, 5140 times magnification.**

### ***8.2.3. Effect of acetate/formate-based deicers on the surface chemistry of PCC***

For the PCC specimens subjected to freeze/thaw cycling in the presence of ~3% CMA deicer solution, the relatively high Si/Ca ratios and low calcium contents in them (Figures 22d and 22e) were caused by the leaching of  $\text{Ca}^{2+}$  from the cement paste to the deicer solution. Based on the box plots of critical elemental ratios (Figures 22a–22c), the high end of Al/Ca ratios (0.1–1.3) suggests some loss of  $\text{Ca}^{2+}$  from AFm or AFt phases, whereas the very low S/Al ratios (0.03–0.27) and very low S/Ca ratios (0.008–0.018) suggest the loss of  $\text{SO}_4^{2-}$  from AFm or AFt phases. Platey structures, likely calcium acetate hydrate crystals as reported by Kawamura et al., (1994) (6), and spherulites characteristic of type I C-S-H can be seen in Figure 23c. Despite the dissolution of  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$ , the rosette structures characteristic of AFm phases remained, as shown in

Figure 23d. Overall, the examined PCC surfaces were dominated by silicate-rich type I C-S-H and AFm phases, whereas structures of AFt phases and calcium-rich type II C-S-H were not observed, likely preferentially dissolved by CMA. As shown in Figure 21, the chemical changes in the cement paste caused minimal amount of weight loss and little visual deterioration of the concrete, likely due to the limited duration of the freeze/thaw test. Nonetheless, the preferential dissolution of some cement hydrates by CMA explains the observed deterioration of the cement matrix and exposure of the aggregates in another laboratory study (7), where eight months of continuous exposure of good-quality concrete ( $w/c=0.45$  and air-entrained) to concentrated CMA solutions (25%) caused a significant decrease in load capacity, mass loss and severe visual degradation of the concrete. Cement mortar samples ( $w/c=0.485$ ) were also reported to lose cohesiveness and disintegrate completely after 30-day exposure to 28% CMA solution at room temperature, and the formation of calcium acetate hydrate phases were confirmed by X-ray diffraction results (6).

For the PCC specimens subjected to freeze/thaw cycling in the presence of ~3% KFM solution, the low Si/Ca ratios and reasonable calcium contents in them (Figures 22d and 22e) suggest little leaching of  $\text{Ca}^{2+}$  from the cement paste to the deicer solution. Based on the box plots of critical elemental ratios (Figures 22a–22c), the relatively low Al/Ca ratios (0.1–0.2) further confirms little leaching of  $\text{Ca}^{2+}$ , whereas the low S/Al ratios (0.12–0.33) and low S/Ca ratios (0.014–0.016) suggest the loss of  $\text{SO}_4^{2-}$  from AFm or AFt phases. Rosette structures characteristic of AFm phases can be seen in Figure 24a, whereas poorly crystalline fibers characteristic of AFt phases and honeycombed structures characteristic of calcium-rich type II C-S-H can be seen in Figure 24b. Overall, the examined PCC surfaces showed a very high presence of bladed calcium-rich crystals. We hypothesize that the exposure of the cement paste to potassium formate led to the preferential dissolution of silicate-rich type I C-S-H and the releasing of calcium sulfate ( $\text{CaSO}_4$ ) from AFm phases and promoted the formation of calcium formate hydrate crystals and AFt phases. The disintegration of the cement paste and the formation of new cement hydrates contributed to the moderate amount of weight loss and noticeable deterioration observed in the freeze/thaw specimens.

For the PCC specimens subjected to freeze/thaw cycling in the presence of ~3% NAAC + Peak SF (NaAc:NaFm~1:1) deicer solution, the low Si/Ca ratios and reasonable calcium contents in them (Figures 22d and 22e) suggest little leaching of  $\text{Ca}^{2+}$  from the cement paste to the deicer solution. Based on the box plots of critical elemental ratios (Figures 22a–22c), the low Al/Ca ratios (~0.1) further confirms little leaching of  $\text{Ca}^{2+}$ , whereas the low S/Al ratios (0.05–0.25) and low S/Ca ratios (0.006–0.022) suggest the loss of  $\text{SO}_4^{2-}$  from AFm or AFt phases. Overall, the examined PCC surfaces showed a very high presence of platey or bladed calcium-rich crystals and coarsening of the concrete pores (Figures 24c and 24d). Spiky sodium-rich crystals and honeycombed structures characteristic of calcium-rich type II C-S-H were present as well. We hypothesize that the exposure of the cement paste to sodium acetate and sodium formate led to the preferential dissolution of silicate-rich type I C-S-H and the releasing of calcium sulfate ( $\text{CaSO}_4$ ) from AFm and AFt phases and promoted the formation of calcium acetate and calcium formate hydrate crystals. The disintegration of the cement paste and the formation of new cement hydrates contributed to the moderate amount of weight loss and noticeable deterioration observed in the freeze/thaw specimens.

For the PCC specimens subjected to freeze/thaw cycling in the presence of ~1.5% CF7 (KAc) deicer solution, the relatively low Si/Ca ratios and relatively high calcium contents in them (Figures 22d and 22e) suggest little leaching of  $\text{Ca}^{2+}$  from the cement paste to the deicer solution. Based on the box plots of critical elemental ratios (Figures 22a–22c), the very low Al/Ca ratios (~0.02) further confirms little leaching of  $\text{Ca}^{2+}$ , whereas the low S/Al ratios (0.01–0.15) and low S/Ca ratios (0.004–0.008) suggest the loss of  $\text{SO}_4^{2-}$  from AFm or AFt phases. Overall, the examined PCC surfaces showed a high presence of lamellar structures (Figure 24f). In addition, compact structures characteristic of calcium-rich type II C-S-H can be seen in Figure 24e, along with platey calcium-rich crystals and residual rosette structures attributable to AFm phases deficient in  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$ . We hypothesize that the exposure of the cement paste to potassium acetate led to the preferential dissolution of silicate-rich type I C-S-H and the releasing of calcium sulfate

(CaSO<sub>4</sub>) from AFm and AFt phases, and promoted the formation of calcium acetate hydrate crystals and some lamellar structures. The disintegration of the cement paste and the formation of new cement hydrates contributed to the significant amount of weight loss and marked visual deterioration observed in the freeze/thaw specimens. In particular, the exfoliation of the lamella crystals might be responsible for expansion and subsequent cracking or spalling of the concrete, as suggested by a previous study (8).

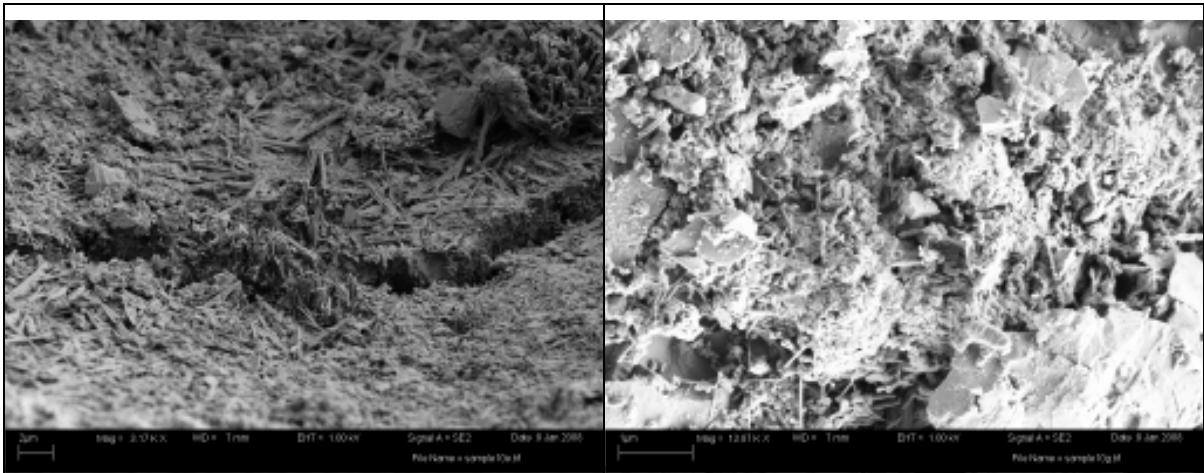


Figure 25 (a)

Figure 25 (b)

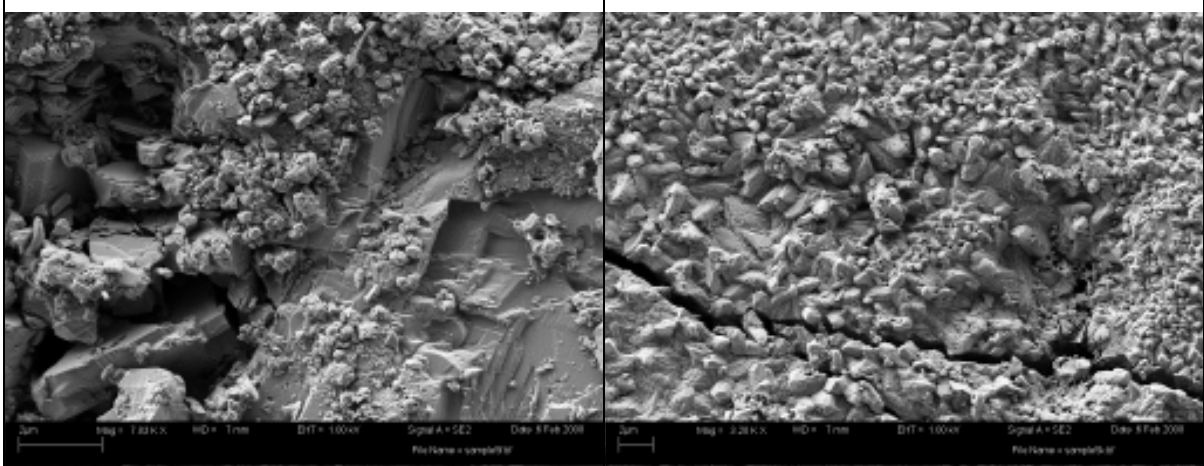
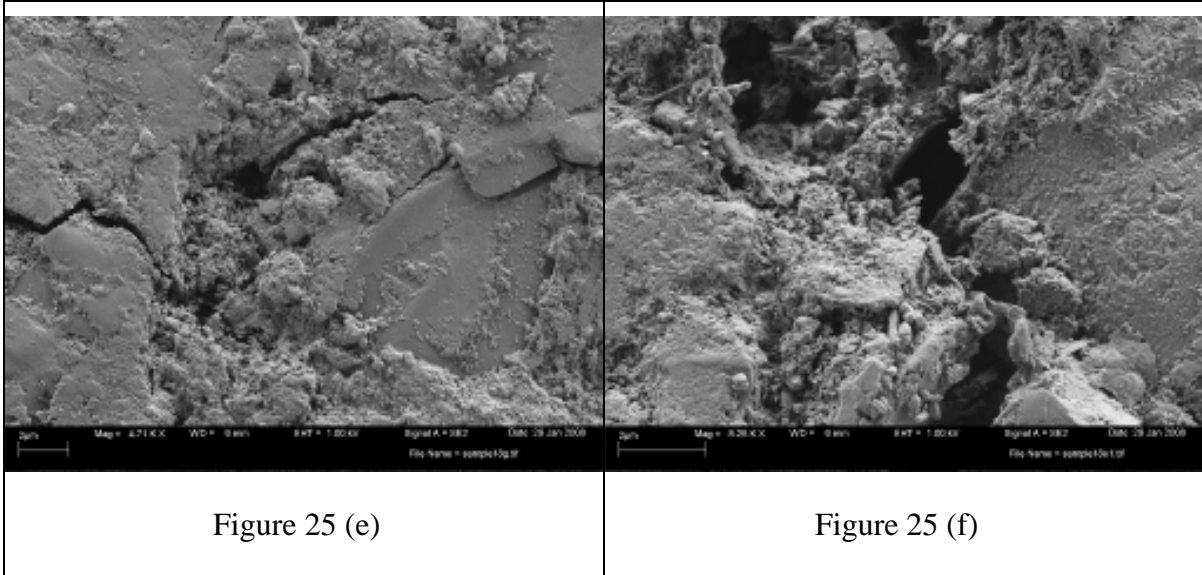


Figure 25 (c)

Figure 25 (d)

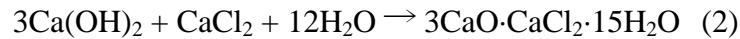
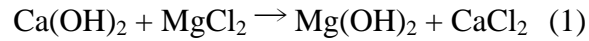


**Figure 25 Representative SEM images of PCC samples following the SHRP H205.8 freeze/thaw test in the presence of various solutions. (a) MgCl<sub>2</sub>, 3170 times magnification; (b) MgCl<sub>2</sub>, 13,870 times magnification; (c) NaCl (r), 7830 times magnification; (d) NaCl (r), 3200 times magnification; (e) IceSlicer, 7290 times magnification; and (f) IceSlicer, 8250 times magnification.**

#### ***8.2.4. Effect of chloride-based deicer on the surface chemistry of PCC***

For the PCC specimens subjected to freeze/thaw cycling in the presence of ~0.85% MgCl<sub>2</sub> deicer solution, the relatively low calcium contents in them (Figure 22e) indicate some leaching of Ca<sup>2+</sup> from the cement paste to the deicer solution. Based on the box plots of critical elemental ratios (Figures 22a–22c), the low end of S/Al ratios (0.02–0.52) and low S/Ca ratios (0.003–0.03) suggest the loss of SO<sub>4</sub><sup>2-</sup> from AFm or AFt phases, whereas the Al/Ca ratios were in the reasonable range of 0.1 to 0.4. The high Cl<sup>-</sup> signals on the examined PCC surfaces and the presence of layer structure of Friedel’s salt (calcium chloroaluminates) suggest partial substitution of the sulfate anion in AFm or AFt phases by the chloride anion (i.e., chloride binding). Overall, the examined PCC surfaces featured a high presence of fibrous crystals (Figure 5a) and needle-like crystals

(Figure 25b). Some platey calcium-rich crystals were also observed. The fibrous crystals were magnesium chloride hydroxide hydrates formed by the  $\text{Ca}^{2+}$  substitution for  $\text{Mg}^{2+}$  and  $\text{Cl}^-$  substitution for  $\text{SO}_4^{2-}$  in the cement hydrates, with pseudomorphs replacing the AFm and AFt phases observed. The needle-like crystals can be attributed to the formation of some hydrated magnesium oxychlorides similar to  $\text{Mg}_3(\text{OH})_2\text{Cl}\cdot 4\text{H}_2\text{O}$  crystals formed in the hardened Sorel cement paste (9). The presence of platey calcium-rich crystals can be attributed to the formation of hydrated calcium oxychloride phases, as reported previously (10). The structures of brucite were not observed on the examined PCC surfaces, even though they were observed in the outer layers of the specimens exposed to concentrated  $\text{MgCl}_2$  (6). These microscopic observations confirm the following reactions commonly accepted to be responsible for concrete degradation by  $\text{MgCl}_2$ :



In addition, previous studies suggest that  $\text{MgCl}_2$  can also react with the cementitious C-S-H phases and produce non-cementitious magnesium silicate hydrate (M-S-H) and  $\text{CaCl}_2$ , and thus significantly degrade the strength of the concrete. In the case of concentrated  $\text{MgCl}_2$ , the formation of brucite inside the concrete was accompanied with great expansive forces and subsequently aggravated concrete deterioration (11-13). As shown in Figure 21, the chemical changes in the cement paste caused minimal amount of weight loss and little visual deterioration of the concrete, likely due to the limited duration of the freeze/thaw test. Nonetheless, the physiochemical changes in the cement paste induced by  $\text{MgCl}_2$  explains the findings in another laboratory study (6), where concentrated  $\text{MgCl}_2$ -based deicers chemically attacked mortar and concrete, leading to volume change, loss of compressive strength, and microcracks.



For the PCC specimens subjected to freeze/thaw cycling in the presence of ~3% NaCl deicer solution, the low calcium contents and high Si/Ca ratios in them (Figure 22e) indicate leaching of  $\text{Ca}^{2+}$  from the cement paste to the deicer solution. Based on the box plots of critical elemental ratios (Figures 22a-22c), the high end of Al/Ca ratios (0.06-0.75) suggests loss of  $\text{Ca}^{2+}$  from AFm or AFt phases, whereas the low end of S/Al ratios (0.02-0.34) and low S/Ca ratios (0.01-0.025) suggest the loss of  $\text{SO}_4^{2-}$  from AFm or AFt phases. The  $\text{Cl}^-$  signals on the examined PCC surfaces suggest limited level of chloride binding. Compact or honeycombed structures characteristic of type II C-S-H and hexagonal portlandite crystals can be seen in Figure 25c. Residual rosette structures can be seen in Figure 25d, as a result of the dissolution of  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  decomposing AFm phases. Overall, the examined PCC surfaces were dominated by AFm phases and calcium-rich type II C-S-H, whereas structures of AFt phases and silicate-rich type I C-S-H were not observed. We hypothesize that the exposure of the cement paste to sodium chloride led to the preferential dissolution of silicate-rich type I C-S-H and the releasing of calcium sulfate ( $\text{CaSO}_4$ ) from AFm and AFt phases. While previous studies suggest that NaCl may react with portlandite and lead to portlandite dissolution and pH increase (5, 14-16), this process was found to be quite slow and might be masked by other short-term effects. The preferential dissolution of certain cement hydrates, along with exacerbated physical distresses in the freeze/thaw test, led to the significant amount of weight loss and marked visual deterioration of the concrete. This finding from diluted deicers differed from the study of concentrated deicers (6), where NaCl seemed to be more chemically benign to concrete than  $\text{MgCl}_2$ .

For the PCC specimens subjected to freeze/thaw cycling in the presence of ~3% IceSlicer (NaCl and other chlorides) deicer solution, the high calcium contents and low Si/Ca ratios in them (Figure 22e) indicate little leaching of  $\text{Ca}^{2+}$  from the cement paste to the deicer solution. Based on the box plots of critical elemental ratios (Figures 22a-22c), the low Al/Ca ratios (0.02-0.15) further confirms little leaching of  $\text{Ca}^{2+}$ , whereas low S/Al ratios (0.09-0.33) and low S/Ca ratios (0.005-0.024) suggest the loss of  $\text{SO}_4^{2-}$  from AFm or AFt phases. The  $\text{Cl}^-$  signals on the examined PCC surfaces suggest limited level of chloride binding. Overall, the examined PCC surfaces were dominated by compact or

honeycombed type II C-S-H phases with few resolvable crystals, whereas structures of AFt phases and silicate-rich type I C-S-H were not observed. Platey portlandite crystals and spiky sodium-rich crystals can be seen in Figures 25e and 25f, respectively. We hypothesize that the exposure of the cement paste to IceSlicer led to the preferential dissolution of silicate-rich type I C-S-H and the releasing of  $\text{SO}_4^{2-}$  from AFm and AFt phases. Similar to the reagent-grade NaCl, the diluted IceSlicer led to a significant amount of weight loss and marked visual deterioration of the concrete (Figure 21).

### ***8.2.5. Conclusions***

This work investigated the effect of diluted deicers on the durability of PCC. Based on the gravimetric and macroscopic observations of freeze/thaw specimens following the SHRP H205.8 laboratory test, de-ionized water, CMA solid deicer, and the CDOT  $\text{MgCl}_2$  liquid deicer were benign to the PCC durability, whereas KFm and the NaAc/NaFm blend deicer showed moderate amount of weight loss and noticeable deterioration of the concrete. NaCl, the NaCl-based deicer (IceSlicer), and the KAc-based deicer (CF7) were the most deleterious to the concrete.

It is interesting to note that all alternative deicers tested (except CMA) caused significant damage to the PCC. Since we did not use aggregates susceptible to alkali silica reactivity (ASR), the exacerbated deterioration of PCC in the presence of CF7, Peak SF, and NAAC merit further investigation since it can not be explained by the mechanism proposed by Rangaraju et al., (2005-6) (17-18).

In addition to exacerbating physical distresses, each investigated chemical or diluted deicer chemically reacted with some of the cement hydrates and formed new products in the pores and cracks, the composition of which may be determined by the thermodynamics of the chemical reactions. Some new reaction products were identified as oxychloride crystals, which according to previous research can be expansive. The

physiochemical changes of the cement paste induced by the deicers pose various risks for the concrete durability, the level of which depends on the kinetics of the chemical reactions.

This work provides new insights into the deicer/concrete interactions and highlights the need for bridging the gap between the laboratory data with the field experience. With the improved knowledge, more research should also be conducted on countermeasures in minimizing the deicer impact on concrete durability.

### **8.3. Deicer Corrosion to Metals**

#### ***8.3.1. Electrochemical testing of deicer corrosivity***

For deicers diluted at 3% by weight or volume (for solid and liquid deicers respectively), electrochemical polarization test results showed that acetate-based deicers (CF7 and NAAC) were much less corrosive to mild steel than chloride-based deicers (the CDOT MgCl<sub>2</sub> blend, IceSlicer, and IceBan). Steel is considered to be passive when its corrosion current density  $i_{\text{corr}}$  is lower than 0.1  $\mu\text{A}/\text{cm}^2$ , and active corrosion occurs when  $i_{\text{corr}}$  exceeds 1.0  $\mu\text{A}/\text{cm}^2$  (19). As such, it can be concluded that the acetate-based deicers were non-corrosive to mild steel whereas the chloride-based deicers (including IceBan) were very corrosive (see Table 13). Nonetheless, the galvanized steel in the acetate-based deicers was found to be corroding at comparably high rates as seen in the other deicers.

**Table 13 Electrochemical analysis of deicer effect to mild steel (ASTM A36) and galvanized steel (CDOT guardrail). The salt/sand blend has 10-25% NaCl by weight. MPY stands for milli-inch per year.**

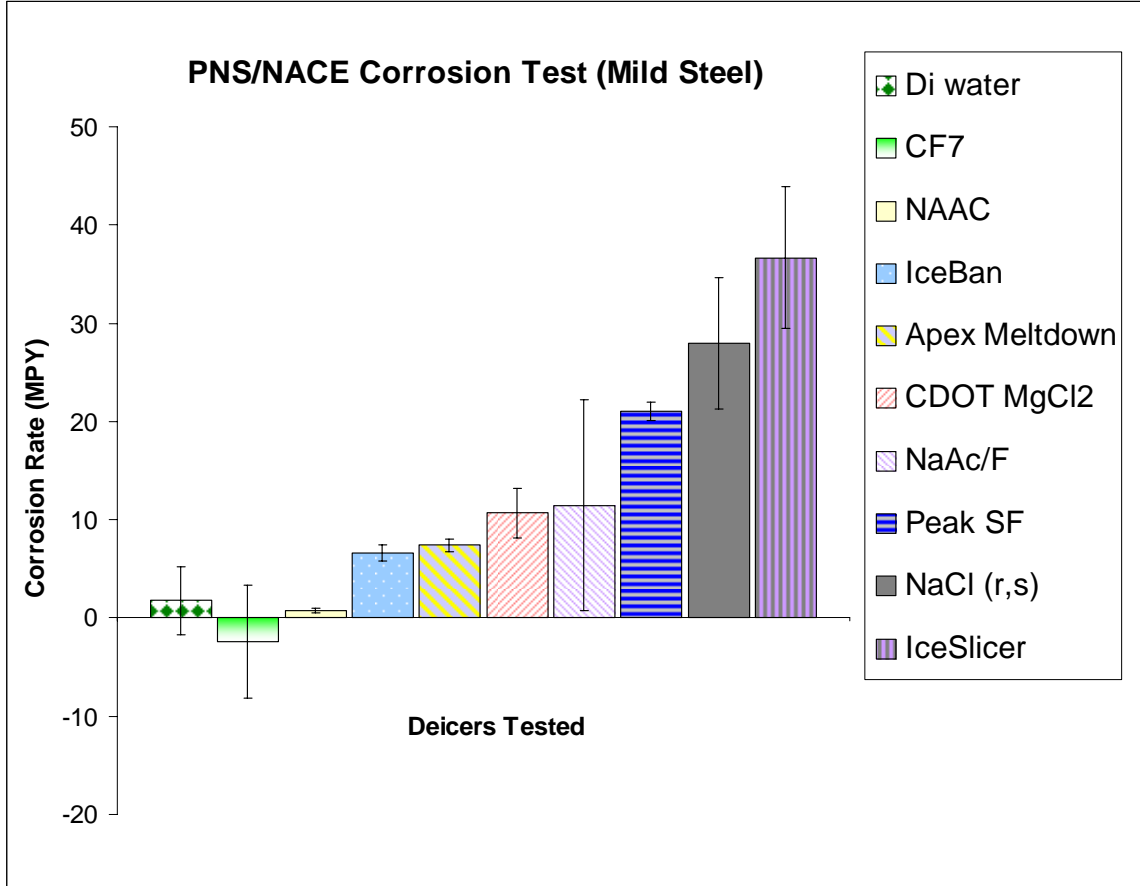
	Deicer	Corrosion Rate (MPY)	Impedence (kohm.cm <sup>2</sup> )	E <sub>corr</sub> (mV, SCE)	I <sub>corr</sub> (μA/cm <sup>2</sup> )
Mild Steel	MgCl <sub>2</sub>	2.7 ± 1.1	2.5 ± 0.5	-616.0 ± 1.8	6.0 ± 2.5
	IceBan®	4.7 ± 1.9	2.5 ± 0.5	-639.5 ± 6.0	10.2 ± 4.2
	IceSlicer®	8.1 ± 0.6	1.7 ± 0.1	-745.5 ± 3.0	17.8 ± 1.4
	KAc	2.5E-03 ± 9.1E-05	950.0 ± 50.0	-155.3 ± 30.2	5.5E-03 ± 2.0E-04
	NaAc	7.1E-03 ± 4.1E-03	316.7 ± 175.6	-204.3 ± 68.6	6.8E-02 ± 9.3E-02
	Salt/Sand	2.5 ± 0.6	2.1 ± 0.2	-764.3 ± 6.0	5.4 ± 1.3
	NaF	2.5E-03 ± 2.1E-04	87.0 ± 4.6	-199.5 ± 12.0	5.5E-03 ± 6.0E-04
	KF	8.5 ± 11.5	26.6 ± 48.9	-598.0 ± 316.5	19.8 ± 23.9
Galvanized Steel	MgCl <sub>2</sub>	1.7 ± 0.2	1.6 ± 0.3	-1037.5 ± 5.0	3.5 ± 0.6
	IceBan®	1.9 ± 0.7	2.1 ± 0.4	-1010.0 ± 8.2	4.4 ± 0.9
	IceSlicer®	0.9 ± 0.2	1.5 ± 0.0	-1037.5 ± 5.0	1.9 ± 0.4
	KAc	1.7 ± 0.6	3.9 ± 1.9	-1032.5 ± 5.0	3.0 ± 0.9
	NaAc	0.9 ± 0.2	8.9 ± 0.9	-1035 ± 19.1	1.8 ± 0.3
	Salt/Sand	0.8 ± 2.0E-02	0.7 ± 0.3	-1047.5 ± 5.0	1.6 ± 0.1
	NaF	5.2E-02 ± 5.9E-02	17.0 ± 8.5E-02	-1003.3 ± 8.3	0.2 ± 9.1E-02
	KF	1.6 ± 0.9	1.3 ± 8.5E-02	-1060.0 ± 0.0	4.1 ± 0.6

Data in Table 13 add to the existing knowledge base concerning the corrosive effects of deicers to metals and illustrates that the deicer products deemed non-corrosive to one metal may actually be corrosive to another metal. As such, it may be necessary to include the testing of more metal types of interest in the PNS/NACE test for deicer corrosivity, which currently only involves the testing of mild steel.

### 8.3.2. Gravimetric measurements of deicer corrosivity

To pass the Pacific Northwest Snowfighers (PNS) Association corrosion requirements, a deicer must be 70% less corrosive than salt, i.e., the reagent-grade NaCl. The existing PNS test (Modified NACE 0169-95 Test) is based on a gravimetric method that entails cyclic immersion of multiple parallel coupons for 72 hours on a custom design machine. The weight loss result in MPY (milli-inch per year) is translated into a percentage, or

percent corrosion rate (PCR), in terms of the solution corrosivity relative to a eutectic salt brine.



**Figure 26 Corrosion rate of mild steel as a function of deicer type, based on results from the PNS/NACE corrosion test.**

Figure 26 shows the corrosion rate of mild steel in various deicers, as obtained from the PNS/NACE test. The gravimetric test results showed that IceSlicer(non-inhibited), Peak SF, NAAC/Peak SF, and the CDOT MgCl<sub>2</sub> blend were very corrosive to mild steel and failed to pass the PNS specification of being 70% less corrosive than NaCl(r,s). Apex Meltdown and IceBan barely passed the PNS specification, whereas CF7 and NAAC demonstrated to be non-corrosive to mild steel. The IceSlicer used in this test was provided by CDOT and did not contain a corrosion inhibitor. We would suggest if CDOT

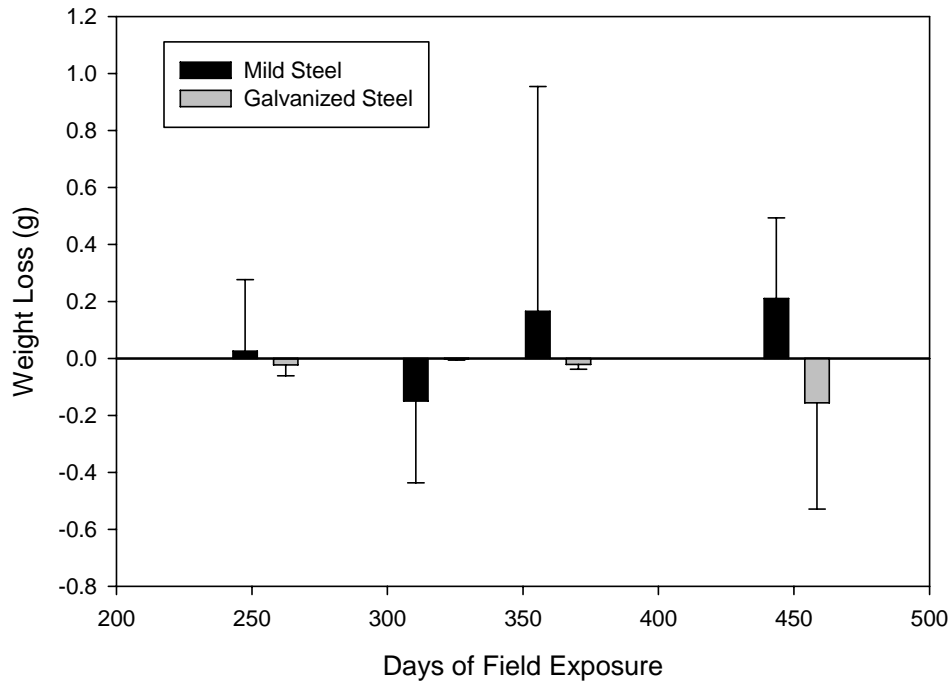
continues to use IceSlicer then switch to the inhibited versions (IceSlicer Elite and IceSlicer RS).

### ***8.3.3. Corrosion of Field Metal Samples***

At three field locations where chloride-based deicers were applied (Aspen, Greeley, and Castle Rock, Colorado), metal coupons of mild steel and galvanized steel were placed and collected over time. Once removed from the field the weight loss for each sample was determined. In the field the mild steel coupons developed a rust layer on the surface that increased over time, while the galvanized steel coupons showed little visible change over time, as shown in Figure 27.



**Figure 27 Metal coupons from the Aspen field site. The photo on the left was taken 7/8/2007 and the photo on the right was taken 3/10/2008. Mild steel is darker grey and the surface grew rustier over time. The galvanized steel is light grey and showed little visible change over time.**



**Figure 28 Mass change of mild steel and galvanized steel coupons from three field sites (Aspen, Greeley, and Castle Rock, Colorado) over time. A positive value means weight loss, while a negative value means weight gain. Metal samples were removed from the field at exposure time of 255, 318, 363, and 451 days, respectively.**

As shown in Figure 28, the mild steel samples generally lost weight over time and galvanized steel generally gained weight over time, both at an average rate of 0.09 MPY ( $0.05 \pm 0.06 \text{ g/m}^2/\text{day}$ ).

The corrosion rate for mild steel (0.09 MPY) was much lower than those observed in the PNS/NACE corrosion test or the electrochemical test. The difference is explained as follows. First, the laboratory tests provide instantaneous or 72-hour-average corrosion rates for the metal coupons in early contact with the corrosive deicer solution; such rates are expected to drop significantly once the corrosion product forms on the metal surface

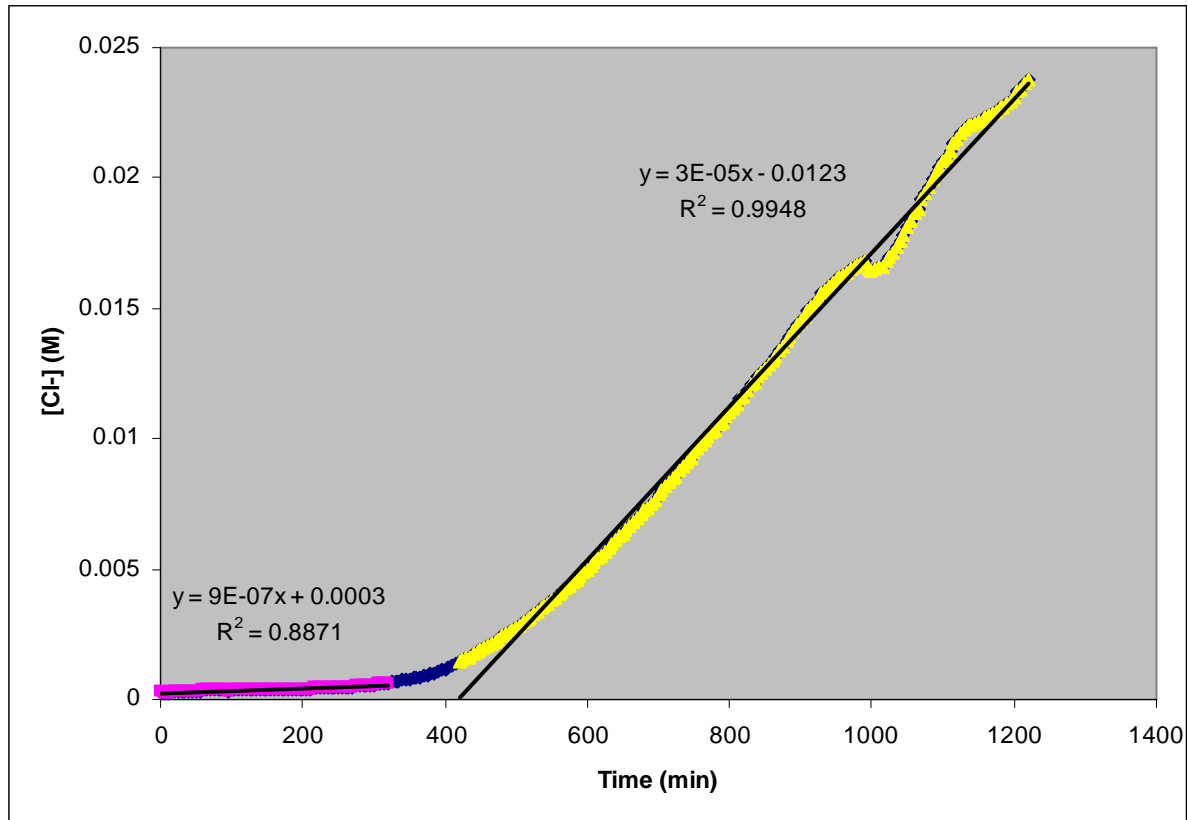
to slow down its corrosion by serving as a physical barrier and a corrosion inhibitor. Second, the laboratory test simulates the field exposure of metals to deicers in an accelerated manner, as it involves cyclic or continuous immersion of the metals in 3% deicer solutions. In the field, the metal samples most likely only came into spray/mist contact with the deicers and for an overall much smaller percent of the time.

## **8.4. Ingress of Chloride-based Deicer into Concrete**

### ***8.4.1. Laboratory Testing of Chloride Diffusion in Concrete and Service Life Implications***

Figure 29 illustrates the typical results obtained from the electromigration test. The breakthrough time  $t_0$  is the point after which the  $\text{Cl}^-$  concentration in the destination solution (anolyte) increases linearly with time, i.e., the intersection of the two fitted straight lines in Figure 9. The electromigration test for all samples was stopped when the chloride concentration in the destination compartment showed a clear bilinear pattern.





**Figure 29 Evolution of chloride concentration over time in the destination compartment, with data obtained from the electromigration test of 3% NaCl through concrete.**

The method used to calculate the apparent diffusion coefficient  $D$  of  $\text{Cl}^-$  in cement mortars is described as follows. Under an externally imposed electric field with an intensity of  $E$ , the mobility of ions (the average velocity of the ions per unit of electric field) is related to the diffusion coefficient through the Nernst-Einstein equation (3):

$$v = \frac{zFD}{RT} \quad (3)$$

Where  $z$ ,  $F$ ,  $R$  and  $T$  are charge number, Faraday constant, gas constant and absolute temperature (20), respectively. The chloride ion mobility can be calculated from the time  $t_0$  required for the chloride front to penetrate a depth  $d$  of the sample, following equation (4):

$$v = \frac{d}{t_0 E} \quad (4)$$

The chloride penetration time  $t_0$  was estimated from the monitored  $\text{Cl}^-$  concentrations in the anolyte (destination solution).  $t_0$  is the point after which the  $\text{Cl}^-$  concentration in the anolyte increases linearly with time.

Therefore, the diffusion coefficient  $D$  of  $\text{Cl}^-$  in cement mortars can be estimated by equation (5):

$$D = \frac{dRT}{t_0 E z F} \quad (5)$$

For the service life analysis of steel-reinforced concrete structures, it is assumed that the concrete cover depth is 3 inches (7.62 cm) in thickness. The value of  $C_s$ , which is used as the boundary condition on the concrete surface, is 23 wt.% for NaCl, 30 wt.% for  $\text{CaCl}_2$  and 30 wt.% for  $\text{MgCl}_2$  deicer solutions respectively. These values are chosen because they are very close to the saturated concentration for NaCl,  $\text{CaCl}_2$ , and  $\text{MgCl}_2$  in water respectively, thereby serving as the limiting concentrations for service life prediction. As for the IceBan, such a liquid deicer contains 25 wt.%  $\text{MgCl}_2$  (21). With the densities of the above solutions assumed to be identical to pure water, concentrations expressed in weight percent can be converted into mol/liter, leading to 3.93, 5.41, 6.30 and 5.25 M for  $[\text{Cl}^-]$  in NaCl,  $\text{CaCl}_2$ ,  $\text{MgCl}_2$  and IceBan deicer solutions, respectively. We conducted electromigration tests in the laboratory to measure the apparent chloride diffusion coefficient of various chlorides in portland cement mortar, which was  $1.27 \times 10^{-11}$ ,  $8.12 \times 10^{-12}$ ,  $1.51 \times 10^{-11}$ , and  $7.60 \times 10^{-12}$   $\text{m}^2/\text{s}$  for NaCl(r,s),  $\text{CaCl}_2$  (r,s), the CDOT  $\text{MgCl}_2$  blend, and IceBan respectively. It has been reported that the diffusion coefficients measured by the electromigration test are compatible with those measured in the natural diffusion test (22). Therefore, the obtained diffusion coefficients in portland cement mortar were used in service life prediction. The above diffusion coefficients were measured in cement mortar with the sand volume fraction of 0.446. The diffusion

coefficients in cement paste can therefore be inversely obtained from equation (5) in chapter 2. A typical CDOT concrete mixing design recipe includes 9.11 grams of water, 17.79 grams of cement powder, 31.13 grams of sand and 41.97 grams of aggregate, which leads to a concrete density of  $2.3246 \text{ g/cm}^3$ . Using a cement paste density of  $1.75 \text{ g/cm}^3$  for  $w/c=0.5$  (23), the total volume fraction of sand and coarse aggregate is estimated to be 0.74 if the sand and coarse aggregate are assumed to have the same density. Such a volume fraction as well as the derived diffusion coefficients in cement paste can be used to estimate the diffusion coefficients in cement concrete, leading to  $2.24 \times 10^{-12}$ ,  $1.433 \times 10^{-12}$ ,  $2.66 \times 10^{-12}$  and  $1.34 \times 10^{-12} \text{ m}^2/\text{s}$  for NaCl(r,s), CaCl<sub>2</sub> (r,s), the CDOT MgCl<sub>2</sub> blend, and IceBan respectively. The smaller the diffusion coefficient, the slower the deicer penetrates into the concrete, and ultimately the longer it takes for sufficient chlorides to reach the rebar surface and initiate its pitting corrosion.

When  $C_t$ ,  $C_s$ ,  $D_c$  and  $x$  are inserted into equation (2) in Chapter 2, the service life for a structure with 3-inch concrete cover continuously exposed to concentrated NaCl(r,s), CaCl<sub>2</sub> (r,s), the CDOT MgCl<sub>2</sub> blend, and IceBan can be estimated to be 4.76, 6.54, 3.32 and 7.07 years respectively. This assumes the service life as the time it takes for sufficient chlorides to reach the rebar surface and initiate its pitting corrosion, ignoring the additional time it takes for the corrosion to propagate before the actual failure of the steel-reinforced structure. If the surface chloride concentration is lowered by 15 times as a result of dilution, the corresponding service life is 148, 72.36, 27.56, and 83.41 years for reinforced structures exposed to NaCl(r,s), CaCl<sub>2</sub> (r,s), the CDOT MgCl<sub>2</sub> blend, and IceBan respectively. In the long run, such a dilution ratio is reasonable considering the loss of salts due to rainfall or roadway traffic and interactions with snow and ice on the winter roadway.

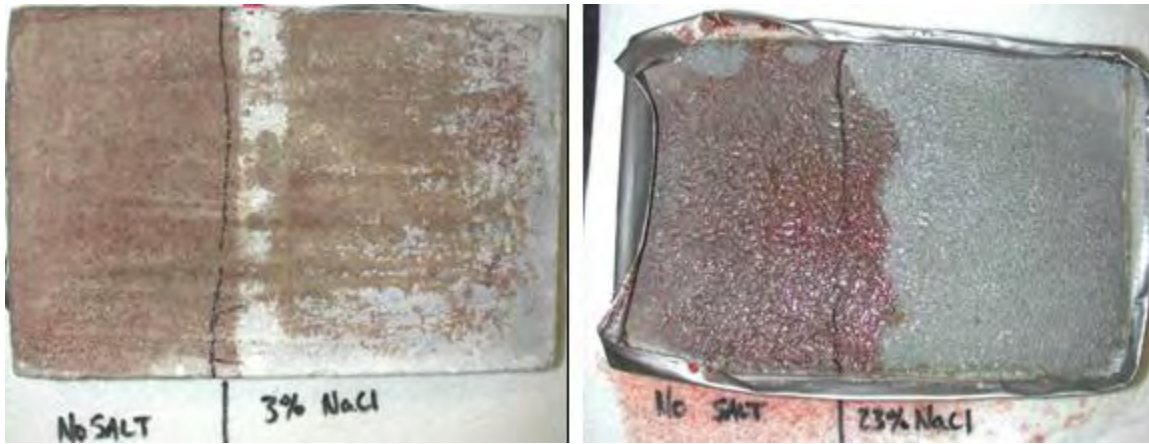
The above calculations are based on the assumption that the concrete is always saturated with water. In reality, however, this assumption is not valid. Take the area of Longmont in Colorado as an example; only 68 out of 365 days in the year 2007 were subject to precipitation (24). Accordingly, the service life calculated above should be roughly

amended by the multiplication of 5.37 to account for the drought seasons, which would greatly prolong the predicted service life of steel-reinforced concrete. Another important factor to consider, nonetheless, is the cracking of concrete, due to mechanical loadings, volumetric stability issues, or environmental loadings (25). The initiation and propagation of cracks in the concrete facilitates the ingress of chlorides onto the rebar surface and greatly shortens the predicted service life of steel-reinforced concrete in the chloride-laden environment.

Based on the results discussed above, we can conclude that the chloride diffusion coefficient in concrete is affected by the cations associated with the chloride anion and the additives in the deicer products. Based on the electromigration test of chloride diffusion coefficients in portland cement mortar, it was estimated that even for high-quality concrete, the implications of chloride-based deicers on the service life of steel-reinforced concrete might still be significant.

#### ***8.4.1. Field Concrete Samples***

Concrete samples that were placed out in the field were investigated for chloride ingress and physical damage. Following application of the indicator chemicals (first  $\text{AgNO}_3$  then  $\text{K}_2\text{CrO}_4$ ) on the concrete surface, the areas where no chloride was present turned a brick red-brown (Figure 30, left side labeled no salt) and the areas where chloride was present turned a bright yellow (right side labeled 3% and 23% NaCl). As can be seen in Figure 30, this test method was not very effective at the low chloride concentration of 3%, but very clearly worked at the elevated chloride concentration of 23%.



**Figure 30 Test concrete blocks used to show the color change that occurs from application of indicator chemicals when chloride is present at varying concentrations (3 and 23%), and when chloride is not present.**

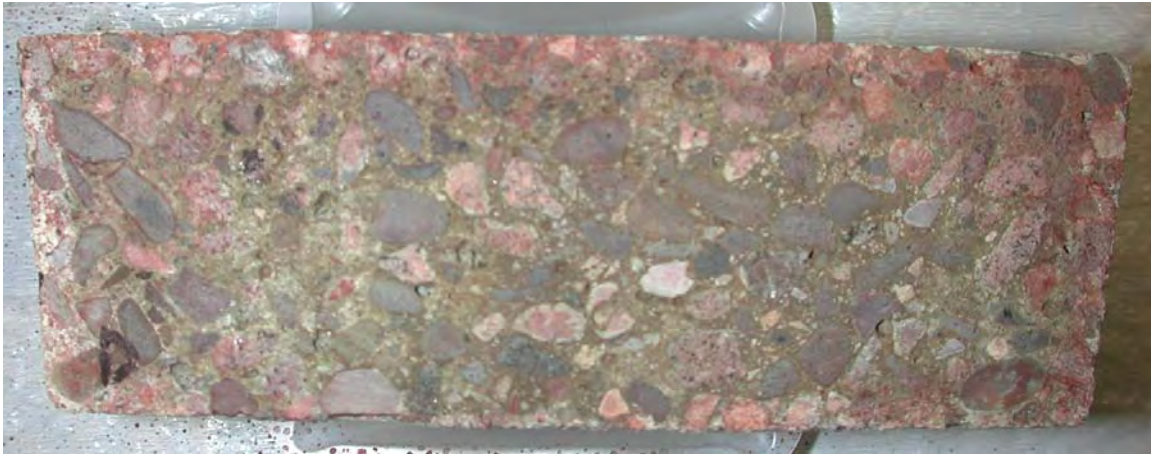
As shown in Table 14, concrete samples placed at the three field sites were collected after a varying number of days of field exposure. This was because the original concrete samples were removed from the Greeley and Castle Rock field sites by unknown activities.

**Table 14 The number of days the concrete samples were exposed to at each field site.**

Field Site	Number of Days of Field Exposure	
	Sample Collection 1	Sample Collection 2
Aspen	341	437
Castle Rock	193	289
Greeley	116	212

Over the course of more than one year of exposure at the field locations, concrete samples showed no surface scaling or cracking and little presence of chloride on the

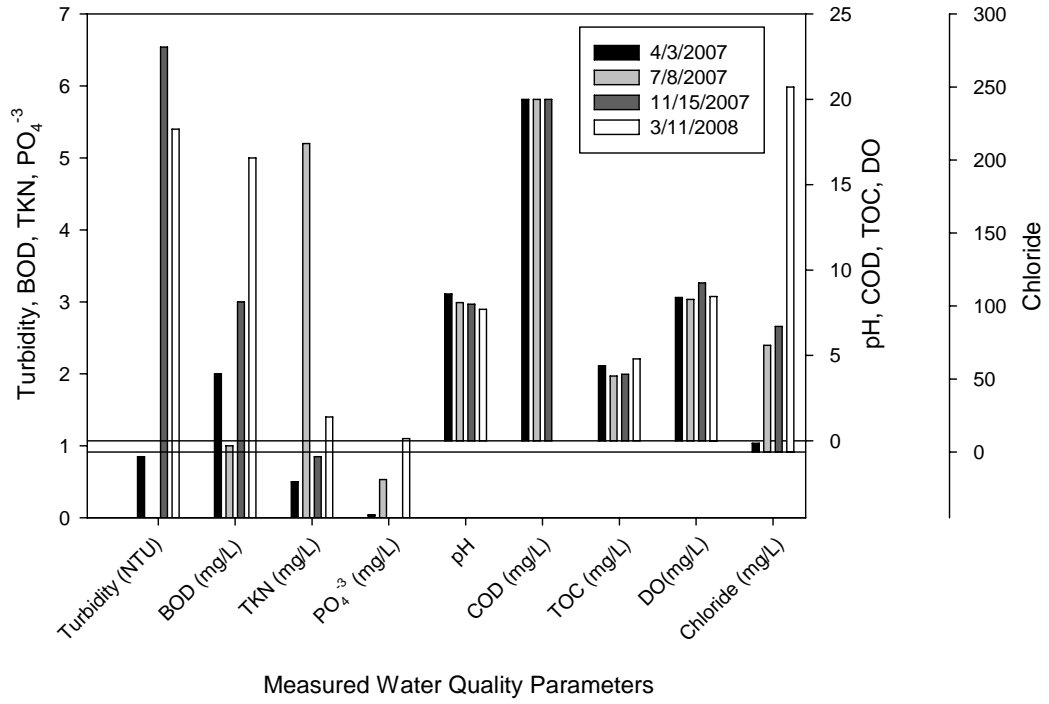
surface and little diffusion into the concrete. Figure 31 shows a typical cross-section of field concrete sample with color change due to the application of chloride indicator.



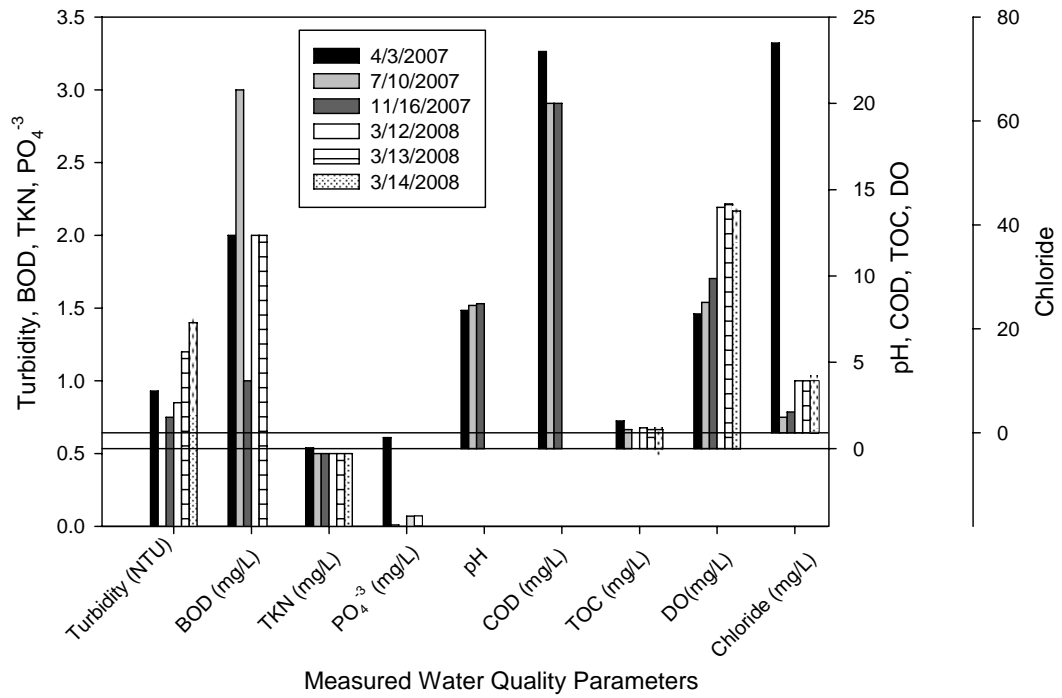
**Figure 31 A cross-section of a field concrete sample that was tested for the presence of chloride. The red-brown brick color indicated that the chloride penetration into concrete, if any, was below the detection limit.**

### **8.5. Water Quality near Colorado Highways**

Water samples were collected to assess the potential impacts of deicers on surface water adjacent to highways from applied deicers. Water sampling was conducted at each site (Greeley, Castle Rock, and Aspen, Colorado) in April 2007 at the same time of the deployment of the metal and concrete samples. Additional water samples were collected in July and November of 2007, and March 2008. During the March 2008 visit to Colorado we captured an entire storm event, pre-storm, during storm and post-storm at the Aspen field site. Measured water quality parameters include: ambient air temperature, humidity, water temperature, pH, turbidity, dissolved oxygen (DO), biological oxygen demand (BOD), chemical oxygen demand (COD), chloride, total Kjeldahl nitrogen (TKN), and orthophosphate ( $\text{PO}_4^{3-}$ ).

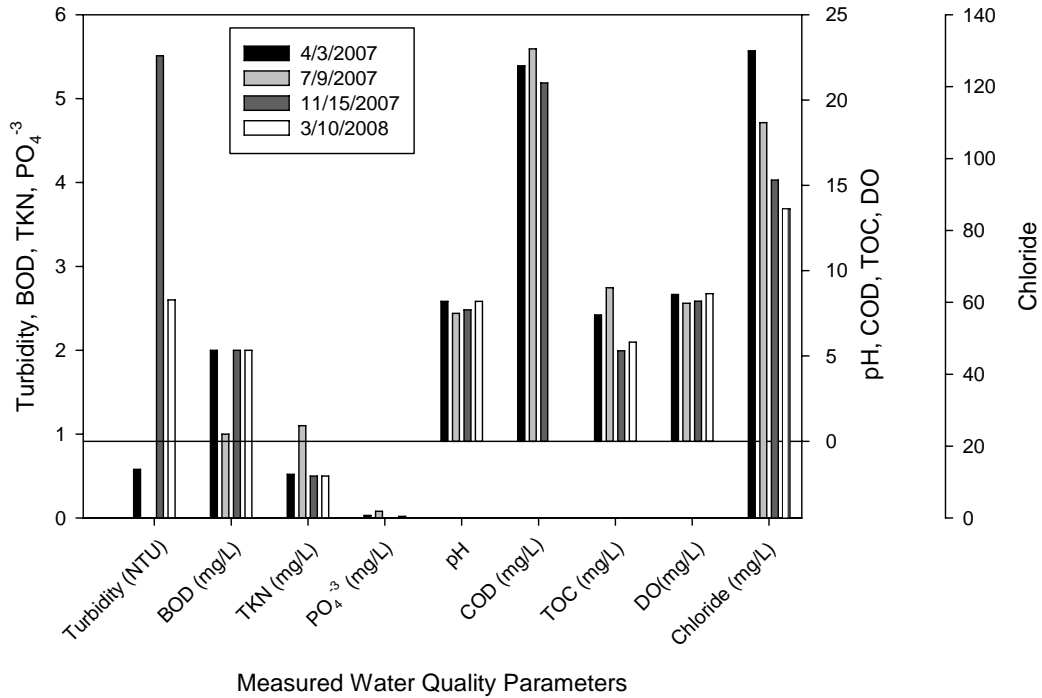


**Figure 32 Water quality data collected from the Greeley, Colorado field site located at the intersection of Hwy 34 and Business Route 34.**



**Figure 33 Water quality data collected from the Aspen, Colorado field site located north of Aspen on north bound Hwy 82 at the irrigation station.**





**Figure 34 Water quality data collected from the Castle Rock, Colorado field site located south of Castle Rock on north bound Hwy 25 at miles marker 167.**

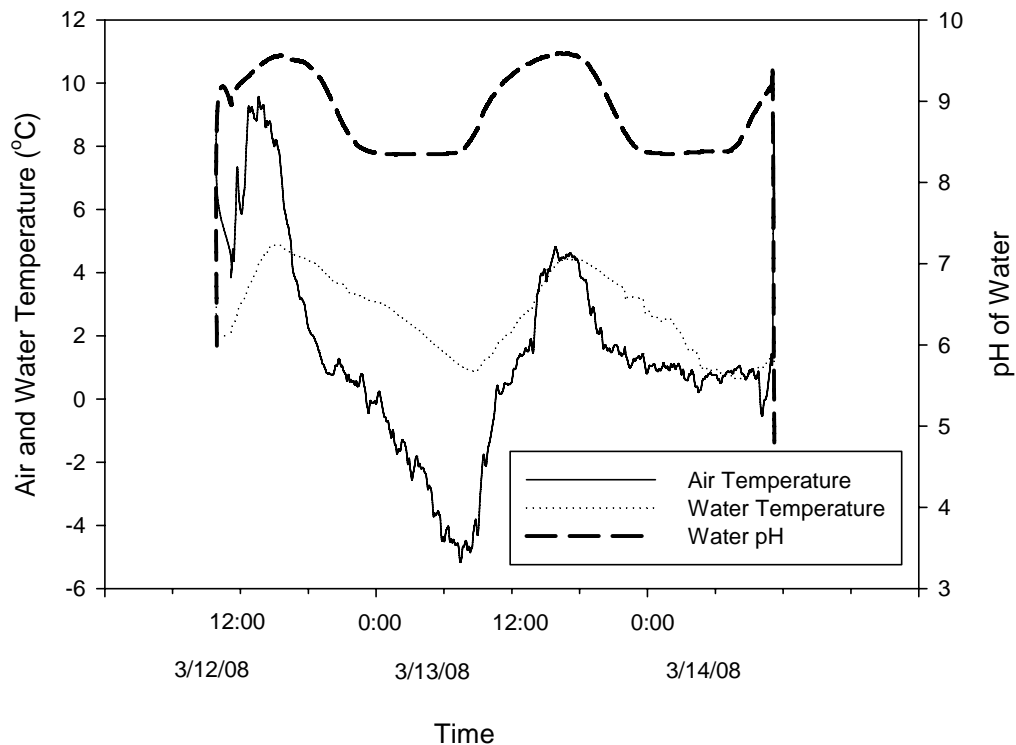
All measured water quality parameters were below Environmental Protection Agency (EPA) and Colorado State standards (for chloride both are currently 250 mg/L), with the exception of the Greeley chloride concentration from March 2008 (250 mg/L) (Figure 32). Ranges have been set for pH at 6.5-8.5 and 6.5-9.0 (by EPA and Colorado respectively), temperature, and DO (temperature dependent) and all other measured water quality parameters have no limits established (NLE). It is interesting to note the large variation in chloride and PO<sub>4</sub><sup>3-</sup> concentrations among the three sites, likely due to the inherent difference in site conditions. For instance, the daily mean discharge and air temperature at the Greeley site were 36,811 liter/second (1300 ft<sup>3</sup>/second) and 13.1°C (55.6°F), respectively, whereas those of the Aspen site was 1,076 liter/second (38 ft<sup>3</sup>/second) and 21.5°C (70.7°F). The lower flow rate at the Aspen site may have led to the higher chloride and PO<sub>4</sub><sup>3-</sup> concentrations there, as a result of less dilution.

Castle Rock consistently had the highest chloride and TOC concentrations (Figure 34). Greeley had the highest turbidity and elevated chloride concentrations but these were less than observed in Castle Rock.

The pre-, during, and post-storm event was captured at the Aspen field site March 12-14, 2008. Water samples were collected and sent for processing in addition to continuous collection of air and water temperature, relative humidity, pH, DO, and conductivity.

The chloride concentration for the Aspen site over time show the highest concentration of 75 mg/L in April 2007, with very low concentrations of 3 and 4 mg/L in July and November 2007, respectively (Figure 33). The captured storm event revealed pre-, during, and post-storm chloride concentrations of 10 mg/L. The first and highest chloride concentration measured may reflect spring flushing of streams putting more road salts into solution. The lack of change in chloride concentrations throughout the pre-, during, and post-storm event shows no immediate impact from chloride based deicers following application adjacent to water ways. The spike in chloride concentration seen in waterways following the first flushing event is quickly diluted as the water volume increases.

The pH of the water was continuously measured during the storm and ranged from 9.6 mid-day to 8.4 at night showing a consistent diel pattern (Figure 35). These values are slightly lower and higher than previously measured values and fall just outside what would be considered normal variation.. Parker et al., (2007) (26) has shown that daily cycles of temperature, oxidation–reduction, photosynthesis and respiration force cyclic chemical and physical changes in parameters such as pH, alkalinity, specific conductivity, dissolved oxygen, re-dox speciation, dissolved carbon dioxide, and dissolved and particulate trace and major element concentrations. Any of the previously mentioned parameters could have influenced the pH values, and further data collection is necessary to determine why the values were outside of the normal range.



**Figure 35 Air and water temperature and water pH measure continuously pre-, during, and post-storm at the Aspen field site.**

The measured relative humidity pre-storm was approximately 40%, and then significantly increased as the storm began ranging from 75 to 95% through out the storm. The dissolved oxygen (DO) measured through the storm followed a diel pattern and had values slightly higher than was previously measured through water sampling. This is most likely due to different measurement techniques being used, the Colorado Department of Public Health and Environment laboratory measured DO for the water samples collected over time versus using a Campbell Scientific Data logger 1000X at the Aspen field site throughout the. pre-, during, and post-storm event. The water conductivity measured in the field was  $0.47 \pm 0.02$  mS/cm. The measured water turbidity was the only parameter that increased steadily throughout the storm (Figure 33). The change in turbidity is most likely due to increase water volume passed through the

Roaring Fork River because of the storm, which mobilizes additional particulate matter. Increased runoff from paved roads and city pipes can also increase water turbidity.

## **8.6. Concluding Remarks**

We conducted laboratory tests to investigate the effect of diluted deicers on the durability of PCC. Based on the gravimetric and macroscopic observations of freeze/thaw specimens following the SHRP H205.8 freeze/thaw laboratory test, de-ionized water, CMA solid deicer, and the CDOT MgCl<sub>2</sub> blend were benign to the PCC durability, whereas KFm and the NaAc/NaFm blend deicer (NAAC/Peak SF) showed moderate amount of weight loss and noticeable deterioration of the concrete. NaCl, IceSlicer, and CF7 were the most deleterious to the concrete. In addition to exacerbating physical distresses, each investigated chemical or diluted deicer chemically reacted with some of the cement hydrates and formed new products in the pores and cracks, the composition of which may be determined by the thermodynamics of the chemical reactions. Some new reaction products were identified as oxychloride crystals, which according to previous research can be expansive. This work provides new insights into the deicer/concrete interactions and highlights the need for bridging the gap between the laboratory data with the field experience. The physiochemical changes of the cement paste induced by the deicers pose various risks for the concrete durability, the level of which depends on the kinetics of the chemical reactions.

The corrosive effects of deicers to metals were investigated both in the laboratory and in the field. For deicers diluted at 3% by weight or volume (for solid and liquid deicers respectively), electrochemical polarization test results showed that acetate-based deicers (CF7 and NAAC) were much less corrosive to mild steel than chloride-based deicers (the CDOT MgCl<sub>2</sub> blend, IceSlicer, and IceBan) while comparably corrosive to galvanized steel. Gravimetric PNS/NACE test results showed that (non-inhibited) IceSlicer, Peak SF, NAAC/Peak SF, and the CDOT MgCl<sub>2</sub> blend were very corrosive to mild steel and failed

to pass the PNS specification of being 70% less corrosive than NaCl(r,s). Apex Meltdown and IceBan barely passed the PNS specification, whereas CF7 and NAAC demonstrated to be non-corrosive to mild steel. At three field locations where chloride-based deicers were applied (Aspen, Greeley, and Castle Rock, Colorado), the mild steel coupons developed a rust layer on the surface that increased over time, while the galvanized steel coupons showed little visible change over time. Metal samples were removed from the field after 255, 318, 363, and 451 days. In general the mild steel samples lost weight over time and galvanized steel gained weight over time, both at an average rate of 0.09 MPY ( $0.05 \pm 0.06 \text{ g/m}^2/\text{day}$ ).

Based on the electromigration test of chloride diffusion coefficients in portland cement mortar, it was estimated that even for high-quality concrete, the implications of chloride-based deicers on the service life of steel-reinforced concrete might still be significant.

Over the course of more than one year of exposure at the field locations, concrete samples showed no surface scaling or cracking and little presence of chloride on the surface and little diffusion into the concrete.

At three field locations where chloride-based deicers were applied (Aspen, Greeley, and Castle Rock, Colorado), water samples were collected periodically to assess potential impacts of deicers on surface water adjacent to highways. Measured water quality parameters include: ambient air temperature and humidity, water temperature, pH, turbidity, dissolved oxygen (DO), biological oxygen demand (BOD), chemical oxygen demand (COD), chloride, total Kjeldahl nitrogen (TKN), and orthophosphate ( $\text{PO}_4^{3-}$ ). All relevant water quality parameters were below Environmental Protection Agency (EPA) and Colorado State standards (for chloride both are currently 250 mg/l), with the exception of the Greeley chloride concentration from March 2008 (250 mg/l). The field data also showed no immediate impact from chloride-based deicers following application adjacent to waterways. It is interesting to note the large variation in chloride and  $\text{PO}_4^{3-}$

concentrations among the three sites, likely due to the inherent difference in site conditions (flow rate, air temperature, etc.).

## 8.7 References

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## CHAPTER 9. POTENTIAL INTERACTIONS BETWEEN DEICERS

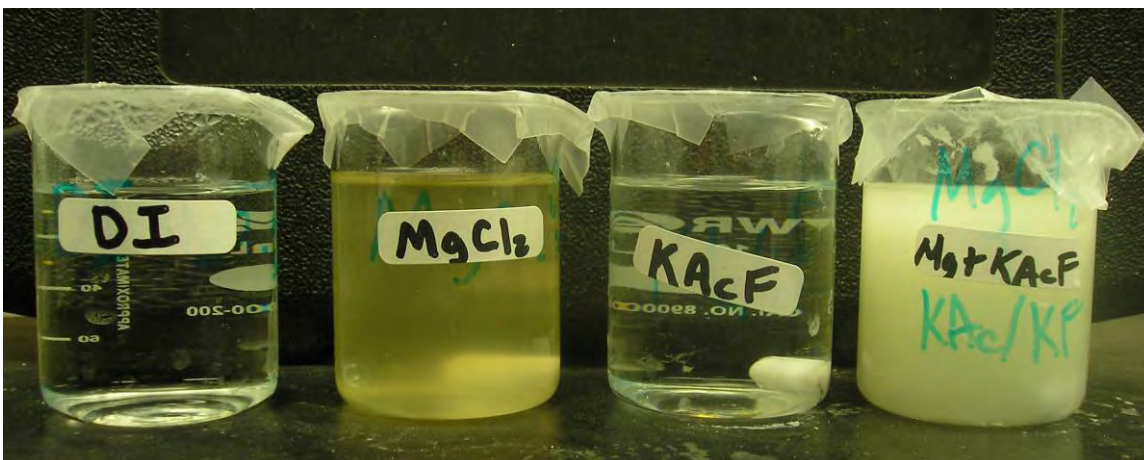
### 9.1 Background

There has been concern of potential chemical and physical reactions between different deicers and that some reaction products may clog the equipment used for anti-icing, impact the road surface where deicers overlap, and decrease the performance of deicers. For CDOT, this concern stemmed from observations that when potassium acetate (KAc) and magnesium chloride ( $\text{MgCl}_2$ ) were used after one another in unwashed holding tanks, a cottage-cheese-like substance formed and clogged the equipment. Such observations logically led to questions as to whether this same reaction or others would occur in the highway environment and how this reaction might be prevented.

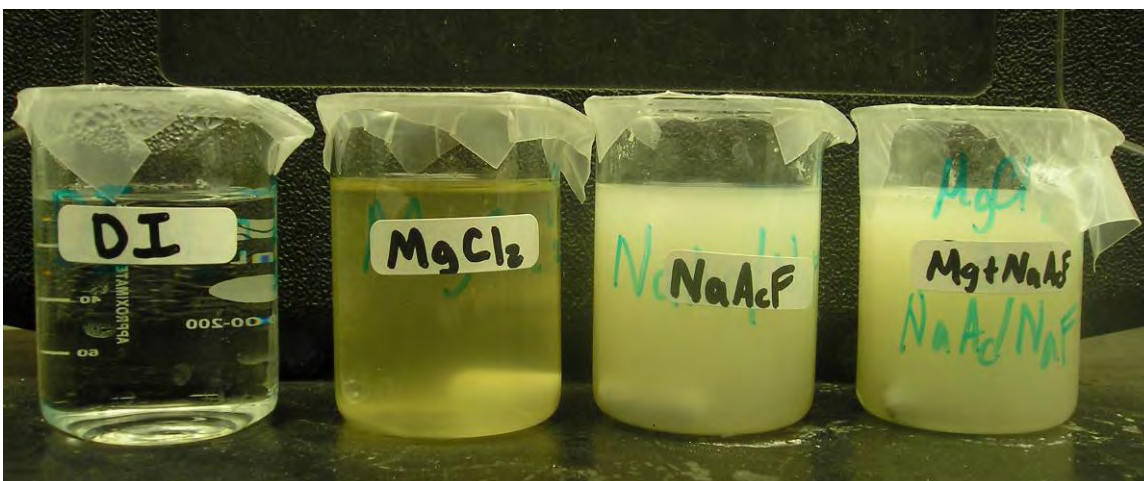
### 9.2 Results and Discussion

It is interesting to note that the temperature of deicer blend solutions was slightly higher than the ambient air temperature, likely due to the heat generated from the mixing of deicer solutions. The average ambient air temperature was  $22.6 \pm 1.0^\circ\text{C}$  ( $72.7^\circ\text{F}$ ) and average deicer solution temperature was  $24.8 \pm 1.1^\circ\text{C}$  ( $76.6^\circ\text{F}$ ). The relative humidity ranged from 35–52% with an average of 44%. No color changes of the deicer solutions were observed over time.

Figure 36A shows the parent solutions of de-ionized (DI) water, the CDOT  $\text{MgCl}_2$  liquid deicer, and KAc(CF7)/KFm, and then the 50:50 mixed solution of  $\text{MgCl}_2$ +KAc(CF7)/KFm. The observed milky appearance of the  $\text{MgCl}_2$ +KAc/KFm blend cannot be explained by the DI water, the CDOT  $\text{MgCl}_2$  deicer, or KAc/KFm parent solution, unlike in Figure 36B where the milky appearance of the  $\text{MgCl}_2$ +NaAc/NaFm blend can be potentially attributed to the NaAc (NAAC)/NaFm(Peak SF).



(A)

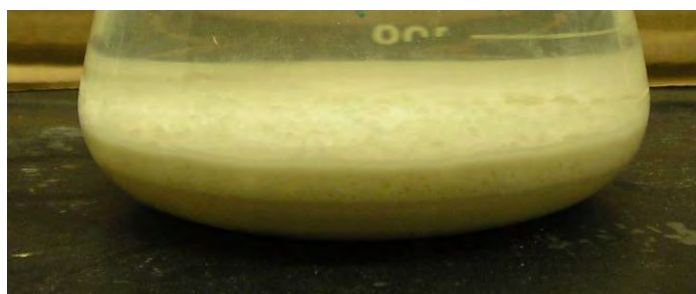


(B)

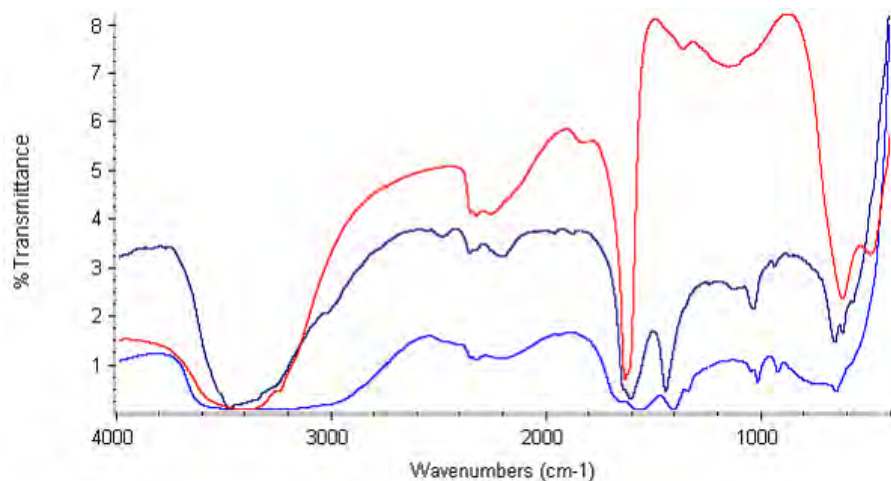
**Figure 36 Photographs of parent solutions and mixed deicers (A) de-ionized water (DI),  $MgCl_2$ , KAc/KFm, and  $MgCl_2+KAc/Fm$ , and (B) DI,  $MgCl_2$ , NaAc/NaFm, and  $MgCl_2+NaAc/NaFm$  taken on the last day of the experiment (Day 7).**

When allowed to sit without stirring, the  $MgCl_2+NaAc$  (NAAC),  $MgCl_2+NaFm$  (Peak SF),  $MgCl_2+KAc$  (CF7), and  $MgCl_2+KFm$  deicer blend solutions formed precipitates on the bottom of the beaker (Figure 37). Precipitates did not form when  $MgCl_2$  was mixed

with NaAc/NaFm or KAc/KFm, though the solutions were milky in appearance. To determine whether a physical or chemical reaction occurred to form the precipitates, samples of each solution were collected and FTIR was performed to provide insight on the potential reaction products. The FTIR spectroscopy was used to analyze the precipitate that developed after mixing  $MgCl_2$  deicer with acetate- and formate-based deicers, test specimens of which were prepared by compressing the solid powder with reagent-grade solid potassium bromide.

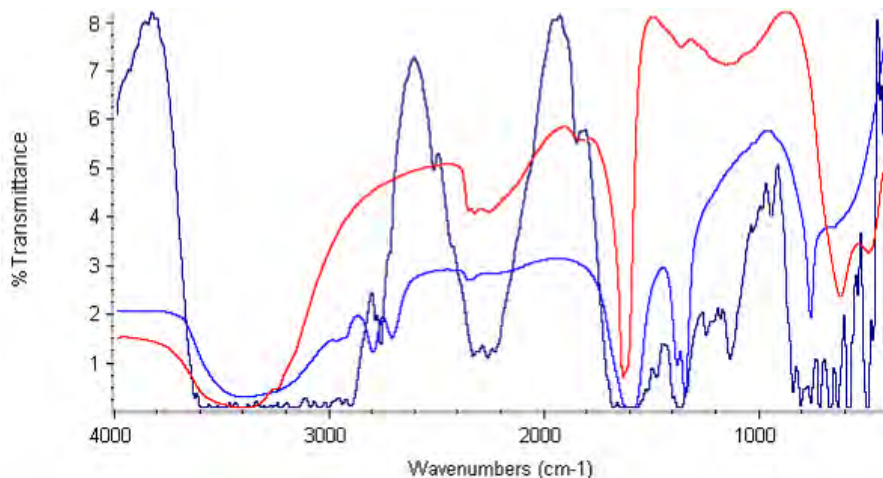


**Figure 37 Photograph of precipitate that formed from a mixture of  $MgCl_2$ +NaAc deicer solutions after sitting un-agitated for one hour.**



**Figure 38 FTIR spectra of the parent materials  $MgCl_2$  (red, top) and KAc (bottom, light blue) and their combined product  $MgCl_2$ +KAc (middle, dark blue).**

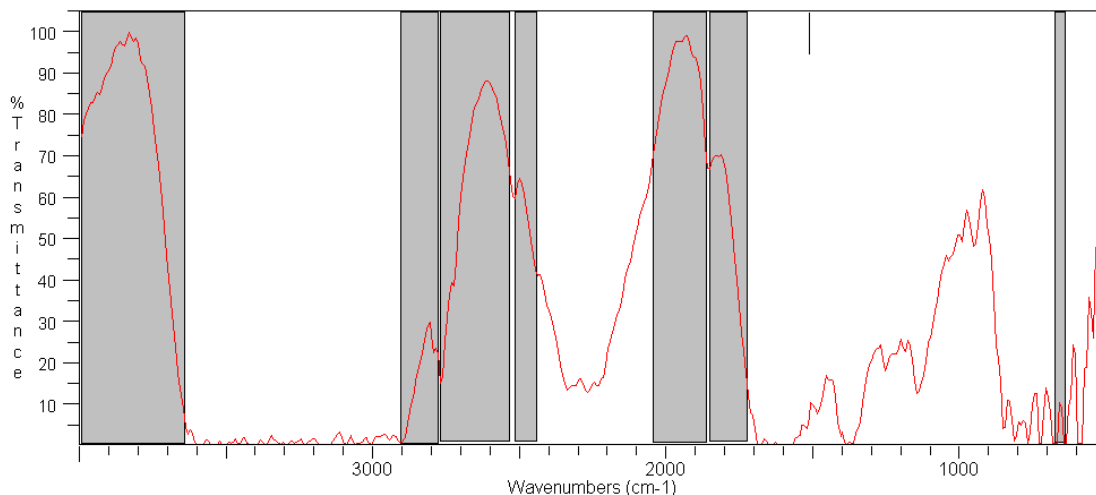
Figure 38 shows the FTIR spectra of the parent materials and combined products of  $\text{MgCl}_2 + \text{KAc}$ . In the FTIR spectrum of the  $\text{MgCl}_2 + \text{KAc}$  blend, all peaks present can be attributed to one or both of the parent solutions. Since no new chemical groups appeared to have formed, the precipitate is most likely magnesium acetate ( $\text{Mg}(\text{Ac})_2$ ) formed by the reaction of  $\text{MgCl}_2$  with  $\text{KAc}$  (see their solubility data in Table 15).



**Figure 39 FTIR spectra of the parent materials  $\text{MgCl}_2$  (red), and  $\text{KFm}$  (light blue) and their combined product  $\text{MgCl}_2 + \text{KFm}$  (dark blue).**

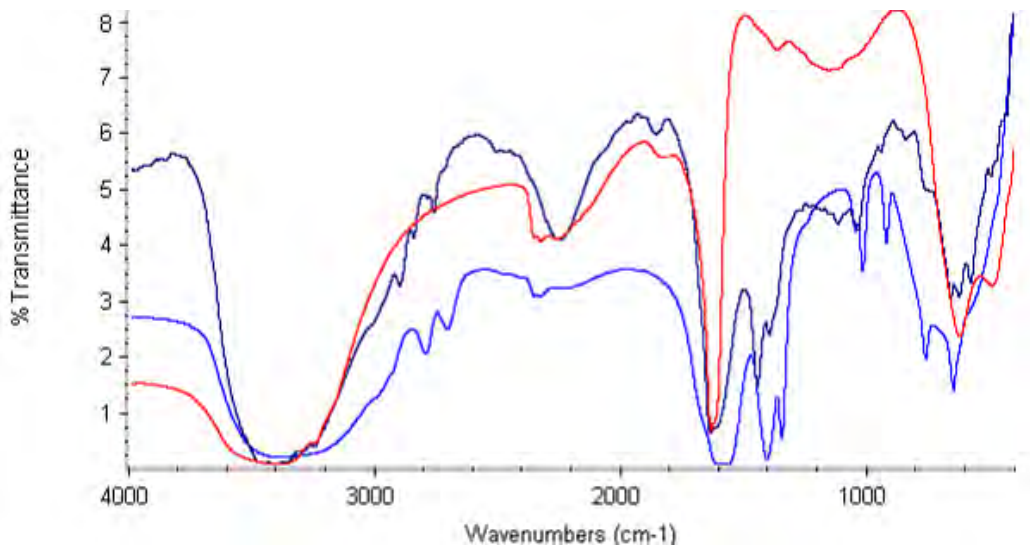
Figure 39 shows the FTIR spectra of the parent materials and the combined products of  $\text{MgCl}_2 + \text{KFm}$ . In the FTIR spectrum of the  $\text{MgCl}_2 + \text{KFm}$  blend, there exist characteristic peaks that are not present in the parent solutions. The highlighted regions shown in Figure 40 indicate the peaks that cannot be attributed to the parent solutions. The wavenumber region from  $3600$  to  $3800\text{cm}^{-1}$  is characteristic of aliphatic isocyanates with nitrogen-carbon-oxygen (NCO) functional groups. The wavenumber region from  $2500$  to  $2600\text{cm}^{-1}$  is characteristic of aliphatic thiols/mercaptans with sulfur-hydrogen (SH) based functional groups. The wavenumber regions  $2000\text{cm}^{-1}$  and  $2800\text{cm}^{-1}$  are characteristic of aliphatic isothiocyanates with nitrogen-carbon-sulfur ( $\text{N}=\text{C}=\text{S}$ ) functional groups. The precipitate is most likely magnesium formate ( $\text{Mg}(\text{Fm})_2$ ) formed by the reaction of

MgCl<sub>2</sub> with KFm (see their solubility data in Table 15), along with some additives in the parent solutions.



**Figure 40 FTIR spectrum of MgCl<sub>2</sub>+KFm. The highlighted regions show the presence of functional groups not present in the parent solutions.**

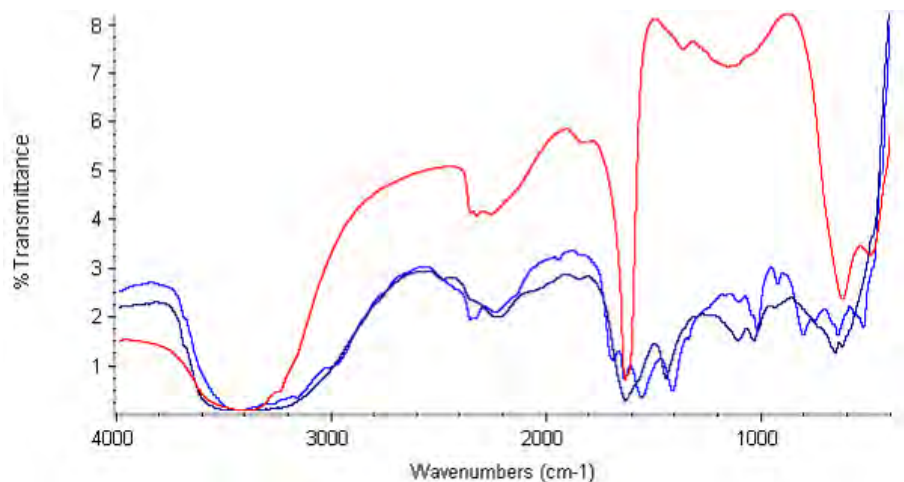
Figure 41 shows the FTIR spectra of the parent materials and the combined products MgCl<sub>2</sub>+KAc/KFm. In the FTIR spectrum of the MgCl<sub>2</sub>+KAc/KFm blend, all peaks present can be attributed to one or both of the parent solutions. Since no new chemical groups appeared to have formed, the only possible reaction products contributing to the milky appearance would be Mg(Fm)<sub>2</sub> and Mg(Ac)<sub>2</sub> formed by the reaction of MgCl<sub>2</sub> with KFm or KAc (see their solubility data in Table 15).



**Figure 41 FTIR spectra of the parent materials MgCl<sub>2</sub> (red) and KAc/KFm (light blue) and their combined product MgCl<sub>2</sub>+KAc/KFm (dark blue).**

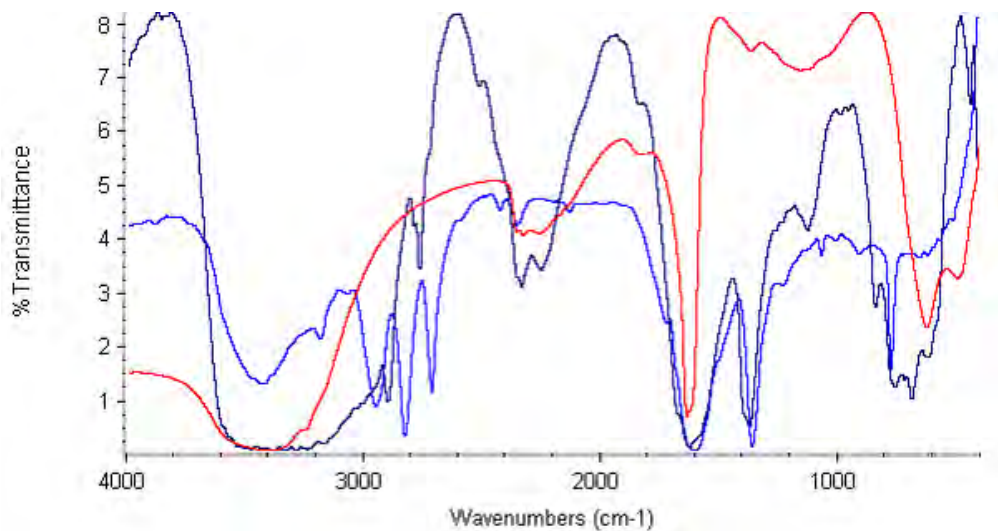
Figure 42 shows the FTIR spectra of the parent materials and the combined products of MgCl<sub>2</sub>+NaAc. In the FTIR spectrum of the MgCl<sub>2</sub>+NaAc blend, all peaks present can be attributed to one or both of the parent solutions. Since no new chemical groups appeared to have formed, the precipitate is most likely Mg(Ac)<sub>2</sub> formed by the reaction of MgCl<sub>2</sub> with KAc (see their solubility data in Table 15).



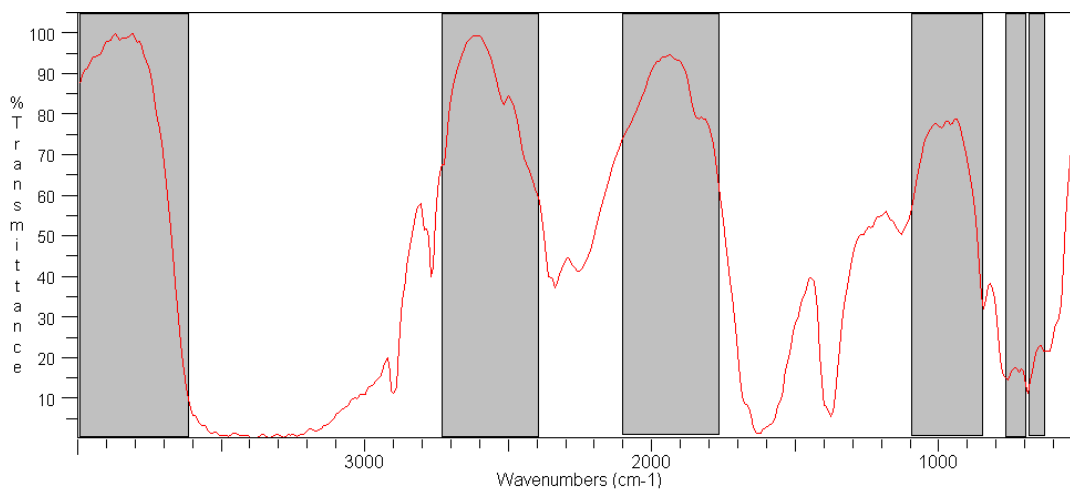


**Figure 42 FTIR spectra of the parent materials  $\text{MgCl}_2$  (red, top) and  $\text{NaAc}$  (light blue) and their combined product  $\text{MgCl}_2+\text{NaAc}$  (dark blue).**

Figure 43 shows the FTIR spectra of the parent materials and the combined products of  $\text{MgCl}_2+\text{NaFm}$ . In the FTIR spectrum of the  $\text{MgCl}_2+\text{NaFm}$  blend, there exist characteristic peaks that are not present in the parent solutions. The highlighted regions shown in Figure 44 indicate the peaks that cannot be attributed to the parent solutions. It is interesting to note that the highlighted regions seen in Figure 44 are very similar to those in Figure 40. The wavenumber region from  $3600$  to  $3800\text{cm}^{-1}$  is characteristic of aliphatic isocyanates with nitrogen-carbon-oxygen (NCO) functional groups. The wavenumber regions from  $700$  to  $800$  and  $2500$  to  $2600\text{cm}^{-1}$  are characteristic of aliphatic thiols/mercaptans with sulfur-hydrogen (SH) based functional groups. The wavenumber region from  $600$  to  $700\text{cm}^{-1}$  may represent either aliphatic secondary amines with nitrogen-based functional groups or inorganic sulfates with sulfur-oxygen (SO) functional groups. The precipitate is most likely  $\text{Mg}(\text{Fm})_2$  formed by the reaction of  $\text{MgCl}_2$  with  $\text{KFm}$  (see their solubility data in Table 15), along with some additives in the parent solutions.



**Figure 43 FTIR spectra of the parent materials  $\text{MgCl}_2$  (red) and NaFm (light blue) and their combined product  $\text{MgCl}_2+\text{NaFm}$  (dark blue).**

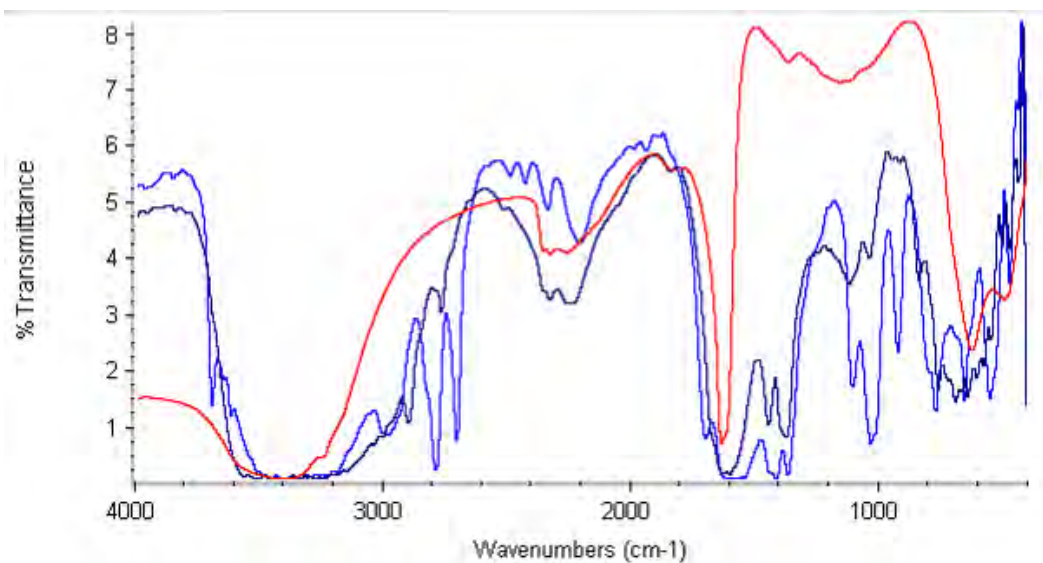


**Figure 44 FTIR spectrum of  $\text{MgCl}_2+\text{NaFm}$ . The highlighted regions show the presence of functional groups not present in the parent solutions.**

Figure 45 shows the FTIR spectra of the parent materials and the combined products of  $\text{MgCl}_2+\text{NaAc}/\text{NaFm}$ . In the FTIR spectrum of the  $\text{MgCl}_2+\text{NaAc}/\text{NaFm}$  blend, all peaks present can be attributed to one or both of the parent solutions. Since no new chemical



groups appeared to have formed, the only possible reaction products contributing to the milky appearance would be  $\text{Mg}(\text{Fm})_2$  and  $\text{Mg}(\text{Ac})_2$  formed by the reaction of  $\text{MgCl}_2$  with  $\text{KFm}$  or  $\text{KAc}$  (see their solubility data in Table 15).



**Figure 45 FTIR spectra of the parent materials  $\text{MgCl}_2$  (red) and  $\text{NaAc}/\text{NaFm}$  (light blue) and their combined product  $\text{MgCl}_2+\text{NaAc}/\text{NaFm}$  (dark blue).**

The nitrogen- and sulfur-based functional groups observed in the  $\text{MgCl}_2+\text{KFm}$  and  $\text{MgCl}_2+\text{NaFm}$  precipitates may be derived from corrosion inhibitors and additives added to the deicers for enhanced performance (Figures 40 and 44). Their characteristic peaks were not shown in the parent solutions likely due to the fact that their concentrations were too low to be detected. Once precipitated out of the mixed deicer solution, however, they exceeded the detection limits by FTIR.

Another less likely mechanism that may account for the precipitates out of the mixed deicer solutions is described as follows. By combining magnesium chloride with acetate- and formate-based deicers, the solution may become supersaturated leading to the precipitation of the salts. Magnesium chloride is present in solution at 27–29% while the acetate- and formate-based deicers are present in solution at 45–50%, representing the

majority of chemicals in the solution. To determine what potential products precipitated out of solution one needs to consider the solubility of various salts (as shown in Table 15) and the pH of the mixed solution.

**Table 15 (A) Solubility of the major chemical present in the deicer solutions and (B) solubility of potential reaction products formed.**

(A)

Deicer	Major Chemical Present	Solubility (g/100g water)*	Temperature Measured at
CF7	potassium acetate	256	20 °C
NAAC	sodium acetate	46.5	20 °C
MgCl <sub>2</sub>	magnesium chloride	54.3	20 °C
NaF	sodium formate	97	20 °C
KF	potassium formate	78	20 °C

(B)

Deicer	Major Chemical Present	Solubility (g/100g water)*	Temperature Measured at
NA	magnesium acetate	53.4	20 °C
NA	magnesium formate	14.4	20 °C
NA	sodium chloride	36	25 °C
NA	potassium chloride	36	25 °C

\* Referenced from MSDS.

Table 15A provides a list of the solubility of the major chemical present in each deicer solution and Table 15B provides a list of the solubility of potential reaction products that could form in solution. In general, chlorides, acetates and formates are soluble in water to varying degrees with a few exceptions that do not apply here. Table 16 provides a list of the pH of all deicers used in the experiment.

**Table 16 pH of deicer solutions.**

Deicer	Major Chemical Present	pH
CF7	potassium acetate	11
NAAC	sodium acetate	9.3
Peak SF	sodium formate	9.3
KF	potassium formate	9
NAAC+Peak SF	sodium acetate/formate	9.5
CF7+KF	potassium acetate/formate	10.5
MgCl <sub>2</sub>	magnesium chloride	6.5 to 8.5

Since the precipitated material could potentially clog anti-icing systems, we recommend that DOTs routinely clean out the liquid-holding tanks prior to introducing different liquid deicer products. To shed more light on the potential interactions between deicers, additional research should focus on how the formation of such precipitates affects the deicing performance and corrosivity of the product, as well as the friction coefficient of the treated pavement.

## CHAPTER 10. CONCLUSIONS, RESEARCH NEEDS AND IMPLEMENTATION RECOMMENDATIONS

### 10.1. Conclusions

In this project, we conducted a series of literature reviews, agency surveys, laboratory tests and field investigation to evaluate the performance and impacts of several alternative deicers and traditional chloride-based deicers. The key findings and conclusions are presented as follows.

1. All deicers available on the market have various impacts, the level of which depends on many factors including the application rate of deicers, the winter precipitation rate, the specific road environment of the application, the traffic volume, etc.
2. Based on the literature review, deicers may pose detrimental effects on portland cement concrete (PCC) infrastructure and thus reduce concrete strength and integrity (as indicated by expansion, mass change and loss in the dynamic modulus of elasticity). Such risks of deicers on the durability of PCC structures and pavements exist through three main pathways: 1) physical deterioration of the concrete through such effects as salt scaling; 2) chemical reactions between deicers and cement paste (a cation-oriented process, esp. in the presence of  $Mg^{2+}$  and  $Ca^{2+}$ ); and 3) deicers aggravating aggregate-cement reactions (including an anion-oriented process in the case of chlorides and acetates/formates affecting ASR; and a cation-oriented process in the case of  $CaCl_2$  and  $MgCl_2$  affecting ACR). The proper use of air entrainment, high-quality cementitious materials and aggregates, and mineral admixtures is promising in mitigating the deicer impact on PCC.
3. Based on the literature review, deicers may pose detrimental effects on asphalt pavement. While their impact on skid resistance is still inconclusive, deicers are known to affect pavement structure and cause loss of the strength and elasticity of asphalt concrete. Exposure to freeze/thaw cycles and deicers was found to affect the

viscosity of the recovered asphalt binder and the gradation of recovered aggregates. Formate/ acetate-based deicers were found to significantly damage asphalt pavements, through the combination of chemical reactions, emulsifications and distillations, as well as generation of additional stress inside the asphalt concrete. In order to manage deicer effects on asphalt concrete, it is recommended to: 1) follow best possible practices in asphalt mix design and paving (e.g., low void contents); 2) use binders with high viscosity or polymer-modified binders; 3) use alkaline aggregates or high-quality (sound) aggregates (avoid limestone filler or heavily contaminated RAP when acetates/formates are used as deicers); and 4) test the compatibility of the materials in advance.

4. Based on the literature review, deicers may cause corrosion damage to the transportation infrastructure such as reinforced or pre-stressed concrete structures and steel bridges. The relative corrosivity of deicers is dependent on many details related to the metal/deicer system. Therefore, no general conclusions should be made when ranking corrosion risks of different deicer products. Instead, it is important to note the test protocol employed, the metal coupons tested, the deicer concentrations, the test environment, etc. It is also extremely difficult to relate laboratory test results of corrosion resistance to the actual field performance of metals. There are many ways to manage the corrosive effects of deicers, such as: selection of high-quality concrete, adequate concrete cover and alternative reinforcement, control of the ingress and accumulation of deleterious ions or molecules from deicers, injection of beneficial ions or molecules into concrete, and use of non-corrosive deicer alternatives and optimal application rates.
5. Deicers can have significant impacts on the environment, and the impacts are dependent on a wide range of factors unique to each formulation and the location of application. Further testing is necessary for many of the deicers, and for this information to be made available to the public. To minimize the environmental impacts of deicer, it is crucial to make informed decisions by utilizing available resources including existing test methods and the PNS-approved deicer list. By identifying sensitive areas and species and setting limits for air and water quality, minimum impact requirements can be established which all deicers must meet, so

that a toolbox approach may be implemented. Despite the potential damaging effects, the use of deicers for snow and ice control can reduce the need for applying abrasives, and thus pose less threat to the surrounding vegetation, water bodies, aquatic biota, air quality, and wildlife.

6. As a result of our survey of deicer performance and impacts, a total of 24 deicer users participated with one from Finland, and one from New Zealand, and the rest from the United States representing 15 different states and agencies. Solid salt ( $\text{NaCl(s)}$ ) is most frequently used, followed by abrasives, then magnesium chloride ( $\text{MgCl}_2$ ), agriculturally based (Agr-based)<sup>6</sup>, calcium chloride ( $\text{CaCl}_2$ ), and then other deicers. It is interesting to note that less than 25% of the survey respondents used alternative deicers such as potassium acetate (KAc), sodium acetate (NaAc), calcium magnesium acetate (CMA), and potassium formate (KFm), whereas conventional deicers such as abrasives and chlorides are still most widely used. The Agr-based products were perceived by users to be the most advantageous, with abrasives being the least and no significant difference between chlorides and acetates/formates. Acetates and formates were perceived by users to have the least impacts and chlorides the most. Based on user perception, the most promising deicers identified were as follows: NaAc, Ice B'Gone, CMA, De-ice, KFm, Clearlane, IceSlicer, unspecified Agr-based, and calcium chloride liquid. The worst deicers identified were as follows: sodium chloride & abrasives and specifically corn and sugar beet based deicers. One caveat is that the surveys results may be skewed due to a limited number of people provided the rankings or a limited number of criteria were ranked, especially when it comes to acetates, formates, or agr-based deicers.
7. According to our survey of CDOT winter maintenance practices,  $\text{NaCl (s)}$  cost \$20.00 to \$42.00 per ton delivered to all regions in Colorado, whereas  $\text{MgCl}_2 (l)$  cost \$0.53 to \$0.84 per gallon delivered. These two deicers were mostly used and also consistently the most affordable. The application rate for  $\text{NaCl (s)}$  generally

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<sup>6</sup> Agricultural-based deicers must contain some quantity of bio-based product, for example corn or sugar beet co-products and may also contain chlorides, acetates, and/or formates.

ranged from 100 to 500 lb/l-m, whereas that for  $MgCl_2$  (l) ranged from 20 to 100 gallons/l-m. The application rates were reported to increase with the traffic volume and the intensity of the storm.

8. According to our survey of CDOT deicer priorities, CDOT personnel rankings for deicer performance attributes varied greatly, most likely due to the difference in their job descriptions. The high ice melting capacity, low material cost per lane mile, ease of application, and low cost of application equipment were ranked as having the greatest relevance. The deicer corrosion to metals were consistently ranked as highly relevant, with the low corrosion effect on rebar or dowel bars and slow penetration into concrete ranked as the highest. Deicer impacts on concrete and asphalt pavements were ranked by survey respondents as having great relevance. Survey respondents also ranked some deicer impacts on the environment, including impact to water quality and air quality as highly relevant.
9. We conducted laboratory tests to evaluate the performance of several alternative deicers compared with traditional chloride-based deicers. The SHRP ice melting, penetration and undercutting tests together identified four best performing deicers that were all liquids, including the CDOT  $MgCl_2$  blend,  $MgCl_2$ -based Apex Meltdown,  $MgCl_2$ -and-Agr-based IceBan, and KAc-based CF7. The differential scanning calorimetry (DSC) test showed that CF7 had the coldest effective temperature, followed by Apex Meltdown. The tribometer test revealed that IceBan led to the lowest friction coefficients on both the ice and the deiced concrete, whereas NaCl-based IceSlicer had the greatest variance of friction coefficients on the ice. In addition to identifying two promising test methods (DSC and tribometer), the laboratory data shed light on the complexity and challenges in evaluating the performance of various deicers.
10. We also conducted laboratory tests to investigate the effect of diluted deicers on the durability of PCC. Based on the gravimetric and macroscopic observations of freeze/thaw specimens following the SHRP H205.8 freeze/thaw laboratory test, de-ionized water, CMA solid deicer, and the CDOT  $MgCl_2$  blend were benign to the PCC durability, whereas KFm and the NaAc/NaFm blend deicer (NAAC/Peak SF)

showed moderate amount of weight loss and noticeable deterioration of the concrete. NaCl, IceSlicer, and CF7 were the most deleterious to the concrete. In addition to exacerbating physical distresses, each investigated chemical or diluted deicer chemically reacted with some of the cement hydrates and formed new products in the pores and cracks, the composition of which may be determined by the thermodynamics of the chemical reactions. Some new reaction products were identified as oxychloride crystals, which according to previous research can be expansive. This work provides new insights into the deicer/concrete interactions and highlights the need for bridging the gap between the laboratory data with the field experience. The physiochemical changes of the cement paste induced by the deicers pose various risks for the concrete durability, the level of which depends on the kinetics of the chemical reactions.

11. The corrosive effects of deicers to metals were investigated both in the laboratory and in the field. For deicers diluted at 3% by weight or volume (for solid and liquid deicers respectively), electrochemical polarization test results showed that acetate-based deicers (CF7 and NAAC) were much less corrosive to mild steel than chloride-based deicers (the CDOT MgCl<sub>2</sub> blend, IceSlicer, and IceBan) while comparably corrosive to galvanized steel. Gravimetric PNS/NACE test results showed that (non-inhibited) Iceslicer, Peak SF, NAAC/Peak SF, and the CDOT MgCl<sub>2</sub> blend were very corrosive to mild steel and failed to pass the PNS specification of being 70% less corrosive than NaCl(r,s). Apex Meltdown and IceBan barely passed the PNS specification, whereas CF7 and NAAC demonstrated to be non-corrosive to mild steel. At three field locations where chloride-based deicers were applied (Aspen, Greeley, and Castle Rock, Colorado), the mild steel coupons developed a rust layer on the surface that increased over time, while the galvanized steel coupons showed little visible change over time. Metal samples were removed from the field after 255, 318, 363, and 451 days. In general the mild steel samples lost weight over time and galvanized steel gained weight over time, both at an average rate of 0.09 MPY (0.05±0.06 g/m<sup>2</sup>/day).
12. Based on the electromigration test of chloride diffusion coefficients in portland cement mortar, it was estimated that even for high-quality concrete, the implications



of chloride-based deicers on the service life of steel-reinforced concrete might still be significant. While diffusion rates of acetate/formate based deicers were not measured, these products can impact steel reinforced PCC but to a much lesser extent than chloride based deicers.

13. Over the course of more than one year of exposure at the field locations, concrete samples showed no surface scaling or cracking and little presence of chloride on the surface and little diffusion into the concrete.
14. At three field locations where chloride-based deicers were applied (Aspen, Greeley, and Castle Rock, Colorado), water samples were collected periodically to assess potential impacts of deicers on surface water adjacent to highways. All relevant water quality parameters were below Environmental Protection Agency (EPA) and Colorado State standards (for chloride both are currently 250 mg/l), with the exception of the Greeley chloride concentration from March 2008 (250 mg/l). The field data also showed no immediate impact from chloride-based deicers following application adjacent to waterways. It is interesting to note the large variation in chloride and  $\text{PO}_4^{3-}$  concentrations among the three sites, likely due to the inherent difference in site conditions (flow rate, air temperature, etc.).
15. When allowed to sit without stirring at room temperature, the  $\text{MgCl}_2+\text{NaAc}$  (NAAC),  $\text{MgCl}_2+\text{NaFm}$  (Peak SF),  $\text{MgCl}_2+\text{KAc}$  (CF7), and  $\text{MgCl}_2+\text{KFm}$  deicer blend solutions formed precipitates on the bottom of the beaker. Precipitates did not form when the CDOT  $\text{MgCl}_2$  liquid deicer was mixed with NAAC/ Peak SF or CF7/KFm, though the solutions were milky in appearance. To determine whether a physical or chemical reaction occurred to form the precipitates, samples of each solution were collected and FTIR was performed to provide insight on the potential reaction products. The precipitates were most likely  $\text{Mg}(\text{Ac})_2$  and/or  $\text{Mg}(\text{Fm})_2$  formed by the reaction of  $\text{MgCl}_2$  with NaAc, NaFm, KAc, or KFm. The nitrogen and sulfur based functional groups observed in the  $\text{MgCl}_2+\text{KFm}$  and  $\text{MgCl}_2+\text{NaFm}$  precipitates may be derived from corrosion inhibitors and additives added to the deicers for enhanced performance.

16. The literature reviews and laboratory data both shed light on the complexity and challenges in evaluating various deicers. To facilitate scientifically sound decision-making, we propose a systematic approach to integrate the information available regarding various aspects of deicers and to incorporate agency priorities, which is expected to help transportation agencies in selecting or formulating their snow and ice control materials. We described a *deicer composite index* that would allow winter maintenance managers to numerically evaluate deicers based on their agency priorities or local needs and constraints. The *deicer composite index* for each deicer product is calculated by multiplying the relevant *decision weights* by the *attribute values* indicating where the product's cost, performance or impacts fall in the specific category or subcategory. The *deicer composite index* was calculated to be 46.6, 57.1, and 46.5 for non-inhibited NaCl, inhibited liquid MgCl<sub>2</sub>, and K- or Na-acetate/formate deicers, respectively. This illustrates the challenges still faced by the highway maintenance agencies, given that none of the deicers evaluated is close to being perfect (which would have a *deicer composite index* of 100). With the CDOT user priorities, the inhibited liquid MgCl<sub>2</sub> deicer products present a better alternative than either the non-inhibited NaCl or the K- or Na-acetate/formate deicers.

## 10.2. Research Needs

While this research helps shed more light on various aspects related to deicer performance and impacts, it also identifies some key knowledge gaps and research needs, as summarized below.

1. Research is needed to determine if and how the application of MgCl<sub>2</sub> affects Colorado's roads and bridges. The first step can be developing an exposure map showing the history of MgCl<sub>2</sub> applications on CDOT concrete pavements and bridge decks. Then, field core samples can be collected and examined to determine, characterize and describe any damage that can be attributed to the application of MgCl<sub>2</sub>. Finally, a forecasting tool needs to be made available to plan for long-range

CDOT infrastructure repair and replacements, taking into account the impacts of winter maintenance activities.

2. Additional research is needed to investigate the proper use of air entrainment, high-quality cementitious materials and aggregates, and mineral admixtures in mitigating the deicer impact on PCC and in enhancing the overall durability of PCC. The inter-relationships among these countermeasures need to be explored and optimized.
3. Accelerated laboratory tests of PCC durability in the presence of deicers need to be established in order to realistically simulate the field experience of PCC structures and pavements in the highway environment. Such tests are expected to be implemented both in assessing the potential impacts of deicer products and in assessing the durability of conventional and unconventional concrete mixes.
4. Research is needed to identify, evaluate and optimize various ways to mitigate the impacts of deicers on asphalt pavement, especially those of acetate/formate-based deicers.
5. Accelerated laboratory tests of asphalt concrete durability in the presence of deicers need to be established in order to realistically simulate the field experience of asphalt pavements in the highway environment. Such tests are expected to be implemented both in assessing the potential impacts of deicer products and in assessing the durability of conventional and unconventional asphalt pavements.
6. Additional research is needed to investigate the proper use of corrosion inhibitors, mineral admixtures, concrete sealers, and electrochemical rehabilitation in mitigating the deicer impact on reinforced or pre-stressed concrete structures. The inter-relationships among these countermeasures need to be explored and optimized.
7. Accelerated laboratory tests of metallic corrosion in the presence of deicers need to be established in order to realistically simulate the field experience of motor vehicles and steel bridges in the highway environment. Such tests are expected to be implemented both in assessing the potential impacts of deicer products and in assessing the effectiveness of surface treatment of metals.

8. Long term in-situ research is needed to further assess the impacts of winter maintenance practices on water quality adjacent to highways. The first step could identify point-source locations for in-situ water quality monitoring, followed by an assessment of CDOT practices in terms of material storage and best management practices (BMPs) in place so that further recommendations could be made.
9. Research is needed to establish a set of guidelines for anti-icing and deicing best practices on CDOT roadways, while taking into account the typical road weather scenarios seen in Colorado and the typical deicer products used. The FHWA anti-icing guidelines need to be updated and customized to the CDOT rules of practice. The research results are expected to assist the implementation of Maintenance Decision Support System (MDSS) for CDOT snow and ice control operations.
10. A tribometer-based standard laboratory test needs to be established for assessing the impact of anti-icing chemicals on the friction coefficient of dry pavement and for assessing the anti-icing and deicing performance of deicers. The latter can be done by monitoring the temporal evolution of friction coefficient of the treated pavement. To enhance statistical reliability of test results and to better simulate the field scenarios, the tribometer test reported in this project needs significant improvements, such as: using a rubber tip in place of the steel tip for friction measurements; controlling the air temperature as well as the pavement temperature; potentially controlling the wind speed, radiation, and relative humidity of the test environment.
11. To shed more light on the potential interactions between deicers, additional research should focus on how the formation of formed precipitates affects the deicing performance and corrosivity of the product as well as the friction coefficient of the treated pavement.
12. While there is an increasing amount of information available regarding various aspects of deicers, how to use the information is a challenge for winter maintenance decision-makers. Additional research is needed to establish a methodology consisting of various standard laboratory tests of deicer performance and impacts in order to generate data to be used in a multi-variable objective optimization process.

The research results will be implemented to help CDOT maintenance managers select or formulate their snow and ice control materials to best meet area-specific priorities and constraints.

### **10.3. Implementation Recommendations**

In light of the research findings from this project, we provide the following recommendations for implementation:

1. Determine whether a second round (an additional two-year project) is warranted to further investigate corrosion-inhibited chlorides, agr-based products, and other proprietary brands of deicers.
2. Continue the use of inhibited NaCl and inhibited MgCl<sub>2</sub> deicers until better deicer alternatives are identified.
3. Explore new technologies such as MDSS, automatic vehicle location (AVL), in-place anti-icing pavement, fixed automated anti-icing technology (FAST), and thermal deicing to minimize the salt usage while maintaining the desired levels of service.
4. Optimize application rate through anti-icing practices, AVL, vehicle-based sensor technologies, MDSS, and road weather information systems (RWIS).
5. Provide maintenance practitioners with sufficient opportunities for the training in and continuous learning of winter maintenance best practices.
6. Explore new technologies and methods to minimize the negative side effects of NaCl, MgCl<sub>2</sub>, and other deicers.
7. Encourage environmental compliance through the training in winter maintenance best practices and provide resources on region-specific BMPs that will meet compliance standards.
8. Explore options for infrastructure preservation including mix design specifications, electrochemical rehabilitation, concrete sealers, overlays, etc.

9. Routinely clean out the liquid-holding tanks prior to introducing different liquid deicer products to prevent precipitates from forming and clogging equipment.
10. Fund more research related to winter maintenance best practices in a proactive manner. Given the millions of dollars spent by CDOT for snow and ice control each winter season, such CDOT-sponsored research is expected to lead to implementable results addressing CDOT priorities and generate great return on investment. In addition to cost savings for the agency, benefits to the road users can be expected as a result of improved LOS, while environmental and infrastructure benefits can be expected as a result of reduced salt usage.

## APPENDIX A. (NATIONAL) DEICER/ANTI-ICER USER QUESTIONNAIRE

1. What deicing and/or anti-icing materials does your agency use for snow and ice control? Please check all that apply.

- Abrasives (Sand)
- Sodium Chloride (NaCl)
- Magnesium Chloride (MgCl<sub>2</sub>)
- Calcium Chloride (CaCl<sub>2</sub>)
- Potassium Acetate (KA)
- Calcium-Magnesium Acetate (CMA)
- Calcium-Magnesium-Potassium Acetate (CMAK)
- Sodium Acetate
- Sodium Formate
- Potassium Formate
- Sodium Acetate/Formate Blend
- Agr-based chemicals (e.g., those from the fermentation and processing of cane, beet sugar, corn, barley and milk). Please specify:
- Other. Please specify:

2. According to the field experience and research by your agency, please rank the deicers/anti-icers on a 1-5 scale in terms of their *advantages* (1 being the least merit and 5 being the best). Please fill in NA if sufficient information is not available.

Product	Low	Low	High ice	Ease of	Overall
	cost per	effective	melting	application	safety
	lane	temperature	capacity		benefits
	mile				for winter roads

Please provide additional comments:

3. According to the field experience and research by your agency, please rank the deicers/anti-icers on a 1-5 scale in terms of their *disadvantages* (1 being the least impact and 5 being the worst). Please fill in NA if sufficient information is not available.

Product	Corrosion to metals	Impact on concrete and asphalt pavements	Impact on water quality	Impact on soil, vegetation, wildlife and human health	Overall effects to structures and the environment
---------	---------------------	--	-------------------------	---	---

Please provide additional comments:

4. What successes and lessons has your agency learned from the use of deicers/anti-icers? What do you see as the promising alternative deicer/anti-icer in the near future?

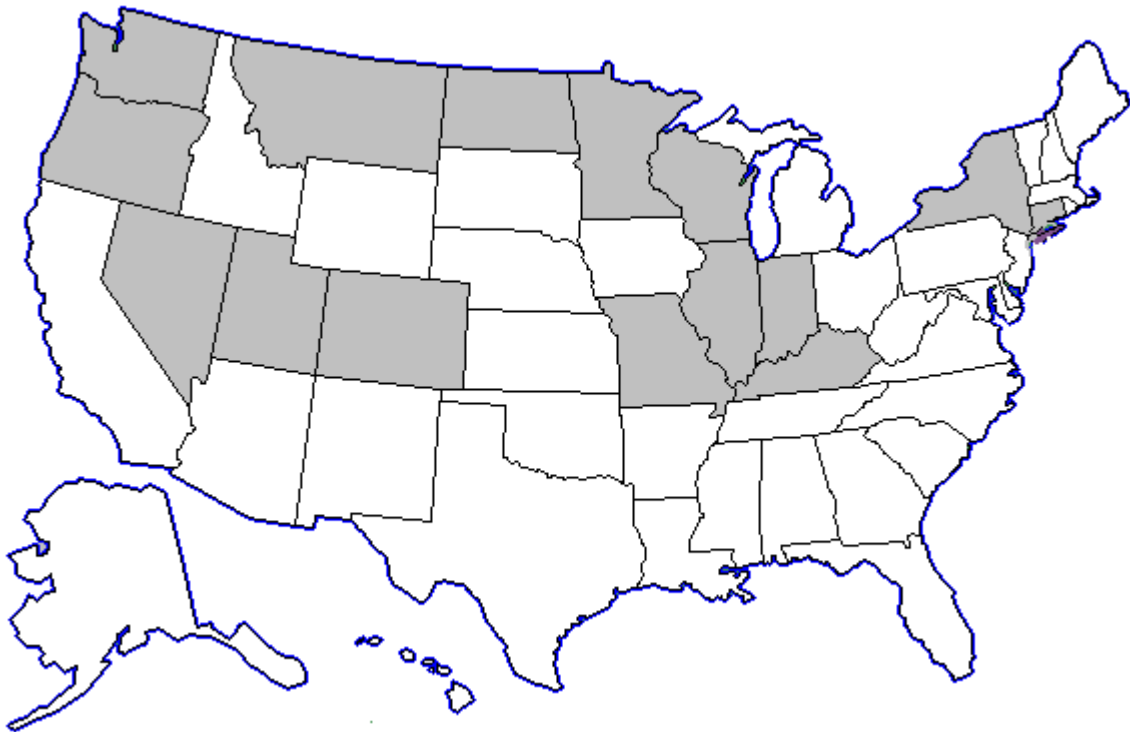
Please provide your name, title, agency, phone number and e-mail address so that if we have further questions we may contact you.

Thank you for your time!



## APPENDIX B. SPATIAL DISTRIBUTION OF DEICER USER RESPONDENTS

Finland	(n=1)
New Zealand	(n=1)
United States	(n=22)
Colorado	(n=1)
Connecticut	(n=1)
Illinois	(n=2)
Indiana	(n=5)
Minnesota	(n=2)
Missouri	(n=1)
Montana	(n=1)
Nevada	(n=1)
New York	(n=2)
North Dakota	(n=1)
Oregon	(n=1)
Utah	(n=1)
Virginia	(n=1)
Washington	(n=2)
Wisconsin	(n=1)



## **APPENDIX C. RESPONDING AGENCIES TO THE DEICER USER QUESTIONNAIRE**

Adams County Highway (Indiana)  
City Street Department (Jasper, Indiana)  
City Street Department (Jeffersonville, Indiana)  
Colorado Department of Transportation  
Director of Public Works (East Hartford, Connecticut)  
Finish Road Administration (Helsinki, Finland)  
Illinois Department of Transportation  
Indiana Department of Transportation  
Minnesota Department of Transportation  
Missouri Department of Transportation  
Montana Department of Transportation  
Nevada Department of Transportation  
New York State Department of Transportation  
Oregon Department of Transportation  
Public Works (Township of Hamilton, North Dakota)  
Public Works (Village of Wilmette, Illinois)  
Tippecanoe County Highway Department (Indiana)  
Transit New Zealand  
Utah Department of Transportation  
Virginia Department of Transportation  
Washington Department of Transportation  
Washington Street Department  
Wisconsin Department of Transportation

## APPENDIX D. CDOT DEICER USER SURVEY (2007)

### Purpose

This 16-question survey is designed to gather information from CDOT deicer users (winter maintenance professionals) for a CDOT research project entitled “*Evaluation of Alternate Anti-icing and Deicing Compounds Using Sodium Chloride and Magnesium Chloride as Baseline Deicers*”. The objective of this project is to evaluate potassium acetate and sodium acetate/formate blend deicers (or possibly potassium formate) as alternative anti-icing and deicing compounds relative to NaCl salt-sand mixtures and MgCl<sub>2</sub>, in terms of their effectiveness, performance, safety, ease of application, cost, impacts on pavements and structures, reactivity with other deicers, human health effects and environmental effects. The project consists of literature review, agency surveys, laboratory investigation as well as field investigation.

### Contact Information

Please complete the following information to aid in the processing of this survey:

Name: \_\_\_\_\_

Agency (Region)/Title: \_\_\_\_\_

Mailing Address: \_\_\_\_\_

City: \_\_\_\_\_ State: \_\_\_\_\_ Zip Code: \_\_\_\_\_

E-mail Address: \_\_\_\_\_

Phone Number: \_\_\_\_\_ - \_\_\_\_\_ - \_\_\_\_\_ Ext. \_\_\_\_\_

Fax Number: \_\_\_\_\_ - \_\_\_\_\_ - \_\_\_\_\_

Please return survey and any supporting documents to:

Xianming Shi, Ph.D.

Program Manager, Winter Maintenance & Effects

P.O. Box 174250, Western Transportation Institute

Montana State University

Bozeman, MT 59717-4250

Phone: (406) 994-6486

Fax: (406) 994-1697

Or email completed surveys to [Xianming\\_S@coe.montana.edu](mailto:Xianming_S@coe.montana.edu). The survey results will be available upon request.

Deadline for submission of survey is August 20, 2007.

**THANK YOU FOR YOUR PARTICIPATION IN THIS IMPORTANT SURVEY!**

*Please attach additional sheets if additional space is needed.*

Deicers: Storage, Transport, Handling and Application

1. Which of the following deicers<sup>1</sup> do you use? Please circle if the product used is in the liquid or solid form.

Potassium Acetate (KA)	liquid	solid
Sodium Acetate/Formate blends (NaAc/F)	liquid	solid
NaCl Salt-Sand mixtures	liquid salt	solid salt
Magnesium Chloride (MgCl <sub>2</sub> )	liquid	solid

Other:

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2. How would the deicers be stored, if obtained for your winter maintenance operations? (Inside/Outside? Agitated? Covered?). Please describe any challenges you experienced or anticipate for deicer storage.

KA      liquid      solid

---

NaAc/F    liquid      solid

---

NaCl Salt-Sand mixtures    liquid salt      solid salt

---

MgCl<sub>2</sub>    liquid      solid

---

Other:

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3. How would the deicers be transported to the storage site? Please comment whether you use brine maker to produce liquid deicers at CDOT facility. Please describe any challenges you experienced or anticipate for deicer transport and mixing.

KA      liquid      solid

---

NaAc/F    liquid      solid

---

NaCl Salt-Sand mixtures    liquid salt      solid salt

---

---

MgCl<sub>2</sub>    liquid            solid

---

---

Other:

---

---

4. How would the deicers be transported out into the field and deployed? Please describe any challenges you experienced or anticipate.

KA            liquid            solid

---

NaAc/F    liquid            solid

---

NaCl Salt-Sand mixtures    liquid salt            solid salt

---

MgCl<sub>2</sub>    liquid            solid

---

Other:

---

---

5. Is there any special handling procedures involved with the deicers? Please describe any challenges you experienced or anticipate.

KA            liquid            solid

---

NaAc/F    liquid            solid

---

NaCl Salt-Sand mixtures    liquid salt            solid salt

---

MgCl<sub>2</sub>    liquid            solid

---

Other:

---

---

6. What application rates would you typically use for each deicer, to provide a reasonable level of service for winter roads? Please describe any challenges you experienced or anticipate.

KA        liquid        solid

---

---

NaAc/F    liquid        solid

---

---

NaCl Salt-Sand mixtures    liquid salt        solid salt

---

---

MgCl<sub>2</sub>    liquid        solid

---

---

Other:

---

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7. How would the application rates vary for each deicer with regard to:

a. Traffic volume or roadway classification

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b. Pavement temperature and its trend

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c. Air temperature and its trend

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d. Type of precipitation and its intensity

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---

e. Humidity

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f. Wind speed and direction

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g. Other factors

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Equipment

8. What equipment would be required when using the deicers?

KA            liquid            solid

---

---

NaAc/F    liquid            solid

---

---

NaCl Salt-Sand mixtures    liquid salt            solid salt

---

---

MgCl<sub>2</sub>    liquid            solid

---

---

Other:

---

---

9. Please elaborate whether there would be a need for obtaining new equipment, or retrofitting the existing equipment, if you have to use a different deicer than what you use now.

---

---

Training

10. Please elaborate whether there would be a need for training in deicer transport, mixing, handling, storage, application etc., if you have to use a different deicer than what you use now.

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Costs

11. What concentrations would you typically require for each liquid deicer, for acceptable effectiveness?

KA:

NaAc/F:

Liquid NaCl (in Salt-Sand mixtures):

MgCl<sub>2</sub>:

Other:

12. Please provide cost information on the deicers including delivery to your site?

KA            liquid            solid

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---

NaAc/F    liquid            solid

---

---

NaCl Salt-Sand mixtures    liquid salt                    solid salt

---

---

MgCl<sub>2</sub>    liquid            solid

---

---

Other:

---

---

13. Please estimate the cost of equipment purchase or retrofitting, if you have to use a different deicer than what you use now.

KA            liquid            solid

---

---

NaAc/F    liquid            solid

---

---

NaCl Salt-Sand mixtures    liquid salt                    solid salt

---

---

MgCl<sub>2</sub>    liquid            solid

---

---

Other:

---

---

14. Please estimate the cost of training, if you have to use a different deicer than what you use now.

KA            liquid            solid

---

---

NaAc/F    liquid            solid

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NaCl Salt-Sand mixtures    liquid salt                    solid salt

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MgCl<sub>2</sub>    liquid            solid

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Other:

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Inhibitors

15. Do you purchase inhibitors to produce corrosion-inhibited deicers at CDOT facility? If so please list the products and the inhibitor dosage used. Also describe any challenges you experienced or anticipate (e.g. meeting CDOT specifications on heavy metal and phosphorus contents)

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Other

16. Please provide additional comments regarding the selection of deicers, considering cost per lane-mile, deicer performance, corrosion to metals, impact on concrete or asphalt pavements, environmental and human health effects, and research needs.

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THANK YOU!

**APPENDIX E. CDOT CRITERIA FOR DEICER SELECTION SURVEY  
(2008)**

Please rank the following criteria related to *deicer performance and impacts* on a scale of 1 to 10, with 10 being the most important and 1 being the least important. Please leave it blank if you are not familiar with a specific aspect or criterion. Your rankings will be used to develop a deicer selection decision making framework for your district or the entire CDOT, which may help assess which deicers would best suit your needs in the future.

Name: \_\_\_\_\_

Title/Job Description: \_\_\_\_\_

District/Location: \_\_\_\_\_

Hwy/Road Section: \_\_\_\_\_

Elevation: \_\_\_\_\_ ADT: \_\_\_\_\_

***Deicing Performance (on a scale of 1 to 10 for relevance)***

Low materials cost per lane mile: \_\_\_\_\_

Low cost for training: \_\_\_\_\_

Low cost for application equipment: \_\_\_\_\_

Low effective temperature: \_\_\_\_\_

High ice melting capacity: \_\_\_\_\_

Improved pavement friction: \_\_\_\_\_

Other (please specify \_\_\_\_\_): \_\_\_\_\_

Other (please specify \_\_\_\_\_): \_\_\_\_\_

***Corrosion to Metals (on a scale of 1 to 10 for relevance)***

Low corrosion effect on mild steel (e.g. steel bridge): \_\_\_\_\_

Low corrosion effect on galvanized steel (e.g. guardrail): \_\_\_\_\_

Low corrosion effect on aluminum (e.g. for vehicles): \_\_\_\_\_

Low corrosion effect on rebar or dowel bar: \_\_\_\_\_

Slow penetration into concrete (to initiate the corrosion of rebar or dowel bar): \_\_\_\_\_

Other (please specify \_\_\_\_\_): \_\_\_\_\_

Other (please specify \_\_\_\_\_): \_\_\_\_\_

***Impact on Pavements (on a scale of 1 to 10 for relevance, either on each category OR on every detailed parameter)***

*Low impact on concrete pavement:* \_\_\_\_\_

Impact on freeze-thaw resistance of concrete pavement: \_\_\_\_\_

Impact on silica reactivity (ASR) of concrete pavement: \_\_\_\_\_

Impact on alkali-carbonate reactivity (ACR) of concrete pavements: \_\_\_\_\_

Impact on scaling of concrete pavement: \_\_\_\_\_

Impact on strength properties of concrete pavement: \_\_\_\_\_  
Impact on expansion of concrete pavement: \_\_\_\_\_  
Other (please specify \_\_\_\_\_): \_\_\_\_\_

*Low impact on asphalt pavement:* \_\_\_\_\_

Impact on aggregates (including ASR) of asphalt pavement: \_\_\_\_\_  
Impact on asphalt binders: \_\_\_\_\_  
Impact on degradation and disintegration of asphalt pavement: \_\_\_\_\_  
Impact on strength properties of asphalt pavement: \_\_\_\_\_  
Other (please specify \_\_\_\_\_): \_\_\_\_\_

***Impacts on the Environment (on a scale of 1 to 10 for relevance, either on each category OR on every detailed parameter)***

*Low impact on water quality:* \_\_\_\_\_

Total Phosphate: \_\_\_\_\_  
Total Nitrogen: \_\_\_\_\_  
Total organic carbon (TOC): \_\_\_\_\_  
Total chloride: \_\_\_\_\_  
Biological oxygen demand (BOD): \_\_\_\_\_  
Chemical oxygen demand (COD): \_\_\_\_\_  
Aquatic toxicity: \_\_\_\_\_  
Other (please specify \_\_\_\_\_): \_\_\_\_\_

*Low impact on plants:* \_\_\_\_\_

Browning/Singe: \_\_\_\_\_  
Senescence/death: \_\_\_\_\_  
Root issues: \_\_\_\_\_  
Native species secession: \_\_\_\_\_  
Other (please specify \_\_\_\_\_): \_\_\_\_\_

*Low impact on soil:* \_\_\_\_\_

Conductivity: \_\_\_\_\_  
Heavy metal leaching: \_\_\_\_\_  
Microbes: \_\_\_\_\_  
Food web: \_\_\_\_\_  
Other (please specify \_\_\_\_\_): \_\_\_\_\_

*Low impact on wildlife:* \_\_\_\_\_

Attraction to wildlife (wildlife-vehicle collisions): \_\_\_\_\_  
Ingestion toxicity: \_\_\_\_\_  
Altered habitat and migratory paths: \_\_\_\_\_  
Other (please specify \_\_\_\_\_): \_\_\_\_\_

*Low impact on air quality:* \_\_\_\_\_

PM10: \_\_\_\_\_  
Other (please specify \_\_\_\_\_): \_\_\_\_\_

*Other (please specify \_\_\_\_\_): \_\_\_\_\_*

## APPENDIX F: ABBREVIATIONS AND ACRONYMS

AASHTO	American Association of State Highway & Transportation Officials
ACR	Alkali-carbonate reaction
ADT	Average daily traffic
AFm	Aluminate monosulfate hydrates
AFt	Aluminate trisulfate hydrates
AgNO <sub>3</sub>	Silver nitrate
ASR	Alkali-silica reaction
ASTM	American Society for Testing and Material
BOD	Biological oxygen demand
C	degrees Celsius
Ca(OH) <sub>2</sub>	Calcium hydroxide
CaCl <sub>2</sub>	Calcium chloride
CaMg(CO <sub>3</sub> ) <sub>2</sub>	Calcium magnesium carbonate
CDOT	Colorado Department of Transportation
CF7	Cryotech potassium acetate
CMA	Calcium magnesium acetate
CMA	Calcium magnesium acetate
CMAK	Calcium magnesium-potassium acetate
CO <sub>3</sub> <sup>2-</sup>	Carbonate
COD	Chemical oxygen demand
C-S-H	Calcium silicate hydrate
CSIL	Corrosion and Sustainable Infrastructure Laboratory
DI	de-ionized water
DO	Dissolved oxygen
DSC	Differential Scanning Calorimetry
E <sub>corr</sub>	Corrosion potential
EDX	Energy dispersive x-ray
EPA	Environmental Protection Agency
F	degrees Fahrenheit
FESEM	Field emission scanning electron microscopy
FTIR	Fourier Transform Infrared
<i>i</i> <sub>corr</sub>	Corrosion current density
IPRP	Innovative Pavement Research Program
ITS	Indirect tensile strength
ITZ	Interfacial zone
K <sub>2</sub> CrO <sub>4</sub>	Potassium chromate

KAc	Potassium acetate
KAc/F	Potassium acetate formate blend
KBr	Potassium bromide
KF	Potassium formate
KOH	Potassium hydroxide
MCDM	Multi-criteria decision making
MDT	Montana Department of Transportation
Mg(Ac) <sub>2</sub>	Magnesium acetate
Mg(F) <sub>2</sub>	Magnesium formate
Mg(OH) <sub>2</sub>	Magnesium hydroxide
MgCl <sub>2</sub>	Magnesium chloride
MP	Melting point
MPY	Milli inches per year
M-S-H	Magnesium silicate hydrate
N=C=S	nitrogen-carbon-sulfur with double bonds
NAAC	Cryotech sodium acetate
NaAc	Sodium acetate
NaAc/F	Sodium acetate formate blend
NACE	National Association of County Engineers
NaCl	Sodium chloride
NaF	Sodium formate
NaOH	Sodium hydroxide
NCE	No limits established
NCHRP	National Center for Highway Research Program
NCO	nitrogen-carbon-oxygen
OCP	Open circuit potential
OGBM	Open grade base material
OGFC	Open grade fine coarse
OGM	Open grade mixes
OGP	Open grade pavement
OH	Hydroxyl
PAH	Polyaromatic hydrocarbon
PCC	Portland cement concrete
PCR	Percent corrosion rate
Peak SF	The Blackfoot Company sodium formate
PM-10	Particulate matter less than 10 microns
PNS	Pacific Northwest Snowfighters
ppm	Parts per million
SCE	Saturated calomel electrode
SEM	Scanning electron microscope

SH	sulfur-hydrogen
SHRP	Strategic Highway Research Program
SMA	Stone matrix asphalt
SO	Sulfur-oxygen
SSD	Saturated surface dry
TKN	Total Kjeldahl Nitrogen
TMDL	Total maximum daily load
TOC	Total organic carbon
UV	Ultra violet
w/c	Water-to-cement ratio
WTI	Western Transportation Institute