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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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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 ($MgCl_2$) 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 tesst, 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.

Implementation:

- Continue the use of inhibited NaCl and inhibited $MgCl_2$ deicers until better deicer alternatives are identified;
- Explore new technologies to minimize the salt usage while maintaining the desired levels of service;
- Optimize deicer application rate;
- Provide maintenance practitioners with sufficient training/learning opportunities;
- Explore new technologies/methods to minimize the negative side effects of NaCl, $MgCl_2$, and other deicers;
- Encourage environmental compliance; Explore options for infrastructure preservation;
- Routinely clean out the liquid-holding tanks prior to introducing different liquid deicer products;
- Fund more research related to winter maintenance best practices in a proactive manner; and
- 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.

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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[1] 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

[1] 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, $CaCl_2$, and $MgCl_2$), $CaCl_2$ 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. $MgCl_2$ 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 $MgCl_2$, agricultural-byproduct-based (agr-based)[2], calcium chloride ($CaCl_2$), 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:

[2] 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® 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 $CaCl_2$ 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 $MgCl_2$ (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 NaCl (s) generally 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.

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 $MgCl_2$ 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 $MgCl_2$ 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 $g/m^2$/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 $MgCl_2$+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. Precipitates did not form when the CDOT $MgCl_2$ 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 $Mg(Ac)_2$ and/or $Mg(Fm)_2$ formed by the reaction of $MgCl_2$ with NaAc, NaFm, KAc, or KFm. The nitrogen and sulfur based functional groups observed in the $MgCl_2$+KFm and $MgCl_2$+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 $MgCl_2$, 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 $MgCl_2$ 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 $MgCl_2$ 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, $MgCl_2$, 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.