Performance and Impacts of Current Deicing and Anti-icing Products: User Perspective versus Experimental Data

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ABSTRACT

This paper reports on the relevant information collected to date through an ongoing twoyear research project funded by the Colorado Department of Transportation (CDOT) with the goal of identifying alternative deicers to chlorides. A nationwide survey was conducted of highway maintenance agencies 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. According to the results, most responding maintenance agencies still depend on chlorides and abrasives for snow and ice control. Less than 25% of the survey respondents used alternative deicers such as potassium acetate, calcium magnesium acetate, sodium acetate, and potassium formate. The average ranking results show agricultural product-based deicers being the most advantageous, abrasives being the least and no significant difference between chlorides and acetates/formates based on the perceived advantages. Users were also 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. The average ranking results show that acetates and formates in general were perceived to have the least impacts and chlorides the most. Literature and experimental data indicated that the negative impacts of acetates and formates were greater than perceived by survey respondents, especially with respect to damage to pavement, structures and water quality. As such, CDOT has decided not to use available potassium or other acetate compounds.

BACKGROUND

Transportation agencies are under increasing pressure to maintain high levels of service on roadways even during the winter months, while working with limited financial and staffing resources. In cold-climate regions such as the northern United States and Canada, large amounts of solid and liquid chemicals (known as deicers^{*}) as well as abrasives are applied onto winter highways to keep them clear of ice and snow. Deicers (mainly chloride-based salts) are 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 and distribute, and help them stay on roadways (prewetting). In recent years, there has been a transition from reactive strategies (e.g., deicing and sanding) to proactive strategies (e.g., anti-icing) adopted by transportation professionals across North America. The U.S. spends \$2.3 billion annually to keep roads clear of snow and ice [1]. For an average winter season, the Colorado Department of Transportation (CDOT) spends more than \$38 million for snow- and ice-control operations [2].

While such maintenance activities are essential to maintain winter roadway safety, mobility and productivity, the growing use of deicers has raised concerns about their effects on motor vehicles, transportation infrastructure, and the environment [3,4,5,6,7,8]. Each year the U.S. and Canada use approximately 15 million and 4-5 million tons of deicing salts, respectively [9]. Motorists and trucking associations have become wary of deicers on their vehicles as vehicular corrosion (even though generally cosmetic) has been documented. On average, deicer corrosion has been estimated to cost \$32 per year per vehicle [10]. In addition, chemicals may cause corrosion damage to the transportation infrastructure such as reinforced concrete structures and steel bridges [3]. The cost of installing corrosion protection measures in new bridges and repairing old bridges in the snowbelt states has been estimated to cost between \$250 million and \$650 million annually [11]. Parking garages, pavements, roadside hardware, and non-highway objects near winter maintenance activities are also exposed to the corrosive effects of road salts. Indirect costs are estimated to be greater than ten times the cost of corrosion maintenance, repair and rehabilitation [12].

When using road salts for snow and ice control, the average costs due to corrosion and environmental effects are estimated at three times as high as the nominal cost [13]. However, such hidden costs are often ignored in formulating highway wintermaintenance 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. Therefore, a systematic perspective should be utilized to ensure that any cost savings of winter maintenance practices would not be at the price of deteriorated infrastructure, impaired environment, or jeopardized traveler safety. 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. Considerable amount of research is still needed in order to fill the knowledge

^{*} For simplicity, the term *deicer* will be used to refer to all chemicals for anti-icing, deicing, and pre-wetting operations.

gap and establish a scientifically robust, defensible decision-making process for highway winter maintenance [13].

According to the field experience of CDOT, magnesium chloride (MgCl₂) outperformed the sodium chloride (NaCl) salt-sand mixture as a deicer. Compared with the salt-sand mixture, MgCl₂ seemed to be more effective, less toxic and to significantly decrease the amount of sediment entering Colorado's streams and particulates entering the air [14,15,16]. CDOT has thus shifted away from using primarily NaCl and sand to using liquid MgCl₂–based deicers for snow- and ice-control operations of state and national highway systems over the past several years. Based on more current research [4,17], however, MgCl₂ has been shown to have greater impacts on infrastructure and roadside vegetation than the salt-sand mixture. Some local governments in the state of Colorado have banned the use of MgCl₂ and returned to using salt-sand mixtures. Consequently, additional research studies on alternative deicers were deemed necessary [14].

New deicing chemicals, additives or mixtures are continually introduced into the market by manufacturers for use in snow- and ice-control operations. Research is needed to help users understand how a deicer product may work and examine its performance and impacts in a holistic view. This will lead to best practices by transportation agencies that *apply 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.

As a participant of both the *Pacific Northwest Snowfighters (PNS)* Association and *Clear Roads*, CDOT has been constantly examining best practices for snow and ice control. Over the last decade or so, the *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 the states of Washington, Oregon, Montana, Idaho, Colorado and the Canadian province of British Columbia. The PNS Association 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* 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, Michigan, Minnesota, Missouri, Ohio, Utah, Wisconsin, Wyoming and New York. Launched in 2004 by seasoned winter maintenance engineers, Clear Roads responds to a need for research based on practical experience.

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 [18]. To this end, a two-year study was initiated in 2006 by CDOT and has been conducted by the Western Transportation Institute at Montana State University-Bozeman (WTI) to identify noncorrosive, environmentally friendly, and cost-effective deicers with good performance in anti-icing and deicing. The overall goal of the project was 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 MgCl₂, 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. This paper reports on the relevant information collected so far through the ongoing research consisting of a synthesis of relevant literature coupled with laboratory tests and field investigations.

METHODOLOGY

Survey of Winter Maintenance Professionals

The purpose of the survey was to gain insight on the deicing and anti-icing products (deicers) 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 MgCl₂ 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 (<u>http://www.sicop.net/</u>), which has hundreds of subscribers including state and local DOT professionals, researchers and private sector specialists in highway winter maintenance issues.



Figure 1. Map of the U.S. with survey-respondent 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, one from New Zealand, and the rest representing 15 different U.S. states and agencies (Figure 1). 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.

Laboratory Testing

Ice Melting Capacity

Preliminary laboratory measurements of ice melting capacity of various deicers were conducted following the SHRP (Strategic Highway Research Program) H205.1 & 2 test methods. 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 brines, 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) Petrie® dish. Once frozen, ice extrusions protruding from the ice surface were melted. The sample was then refrozen and placed in the cold room of the MSU Cold Regions Lab for 24 hours to equilibrate. After equilibration with the desired temperature, 1 g of solid deicer 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 removal of brine, weight, and reintroduction was completed within one minute for each sample. Testing was conducted at -5°C (23°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 with the exception of 0.9 g of liquid deicer being distributed over the surface of the ice with a Pasteur Pipette[®]. Liquid chloride-based products were applied at 27-29% concentration, liquid acetate-based product was applied at 45-50% concentration, and liquid ag-based product was applied at the vendor-mixed concentration.

Corrosion to Metal

Corrosion to mild steel (A36) and galvanized guardrail steel (Trinity Highway Products) was measured using a Gamry Instruments® Potentiostat with an 8-channel Electrochemical Multiplexer ECMB. The deicers tested were chloride, acetate, and agbased. Deicer solutions were 3% by weight for solid and by volume for liquid samples. After the metal samples were cleaned with acetone and de-ionized water and dried, they were placed in the deicer solution and the open circuit potential (OCP) of metals was monitored for 48 hours. Each metal type and deicer solution was run in triplicate.

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 deicers. Weak polarization is an experimental technique that measures the current-potential plot of a metal in an electrolyte when an external potential signal (perturbation) is applied within ± 120 mV range of its corrosion potential (E_{corr}). Such current-potential plot is termed a potentiodynamic polarization curve when the external potential signal is applied at a certain sweeping rate. By measuring the polarization curve, the instantaneous corrosion rate of the metal in the electrolyte can be calculated and the corrosivity of the electrolyte can thus be evaluated.

Field Sampling

Water Sampling

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⁻) concentration, total Kjeldahl nitrogen (TKN), and $PO_4^{3^-}$. Data related to meteorological conditions, average daily traffic (ADT), and winter maintenance treatments of the roadways during storm events were also collected. Water samples were tested by the Colorado Department of Public Health and Environment.

Corrosion to Metal

Metal samples of mild steel (A36) and galvanized guardrail steel (Trinity Highway Products) were cut by CDOT at the Greeley, Colorado, machine shop to 25.4 mm × 50.8 mm, and brought back to the WTI Corrosion, Electrochemistry & Analysis Laboratory 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 samples was 33.6578 ± 0.6428 g, and of the galvanized guardrail was 31.1101 ± 1.1512 g. Samples were then placed on wooden boards and fixed in place with plastic coated wire, such that there was no metal-on-metal contact (to avoid galvanic corrosion). Samples were placed in the field at the three selected sites. A total of twelve samples, six each of mild steel and galvanized guardrail, were deployed at each site. Samples will be removed over time, cleaned and weighed to determine the weight loss.

Impact on Concrete

The concrete samples were made in Greeley, Colorado, with the help of CDOT personnel. Materials (type I Portland cement and aggregates with a maximum size of 9.5 mm or 3/8 inches) from the CDOT stockpiles were used to fabricate the samples. Nine samples were made based on the SHRP H205.8 standard method. Samples were mixed by hand because of the small batch size and carefully compacted to minimize the amount of air entrapped. 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. Samples will be collected over time, weighed, visually inspected for scaling, cracking, and other defects, and then brought back to WTI for further testing. Samples will be sliced into sections and the spatial distribution of chlorine and other elements within the selected section will be examined using the Energy Dispersive x-ray Spectroscopy (EDS) at the MSU Image and Chemical Analysis Laboratory. Furthermore, chloride concentration profiles (both water-soluble chloride and acid-soluble chloride) in the concrete samples will be obtained using chemical titration and/or Ag/AgCl chloride sensors at WTI. Such data will be fed into a finite element model developed at WTI to predict the rebar corrosion due to deicer ingress into concrete.

RESULTS AND DISCUSSION

Deicers Used by Respondents

The survey responses illustrate the deicer user perspectives, either from field experience or from user perception, which may not always coincide with data available from the literature and experiments.

Table 1. Deicers list	ed by respondents	as being used l	by their	organization,
showing the frequen	cy of use.			

De/Anti-icers 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 ₂	14	58
Calcium Chloride	CaCl ₂	11	46
Clearlane®	NaCl, MgCl ₂	3	13
IceSlicer®	NaCl, KCl, Mg Cl ₂	3	13
Calcium Magnesium Acetate	CMA	2	8
Potassium Acetate	K-acetate	6	25
Sodium Acetate	Na-acetate	2	8
Potassium Formate	K-formate	1	4
Agricultual Based	Ag-based	12 [†]	50

* Only counted if specified use in survey.

Ag based deicers included: Ice B'Gone® (n=2), Magic by Caliber® (n=1), beet and/or corn based (n=3), unspecified Ag-based as inhibitor mixed with MgCl₂ (n=2), unspecified Ag-based as inhibitor mixed with CaCl₂ and NaCl(l) (n=1), or an unspecified small amount of Ag-based listed generally as inhibitor (n=3), and Geomelt® (n=1).

The first question posed to survey participants sought feedback on the type of deicers that are currently used for winter road maintenance. Table 1 reports the number and percentage of respondents who listed each deicer. The data indicate that solid salt (NaCl(s)) is the most frequently used, followed by abrasives, then magnesium chloride (MgCl₂), agriculturally based (ag-based), calcium chloride (CaCl₂), with the other deicers

listed used with the least frequency. 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 the most widely used (likely due to cost considerations). The ag-based products listed by survey respondents were defined by the product's name or function. About half of the agriculturally derived products listed were added specifically as corrosion inhibitors, which are generally added at 5-15% by weight or volume.

User-Perceived Performance of Deicers

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 1-5 scale for each criterion, with 1 being the least advantageous and 5 being the most advantageous. The survey results are summarized in Figure 2.

Low Cost per Lane/mile

As shown in Figure 2A, chloride-based deicers were believed to have the lowest cost per lane/mile, whereas acetates/formates were considered to be most costly per lane/mile. Several respondents commented that while abrasives might be low in cost initially, high application rates and clean-up requirements due to repeat applications significantly increase the cost per lane/mile. One respondent commented that abrasives can be costly to crush and use if they stay on the road for only a short duration and pre-wetting can help them stay longer. Several respondents commented that NaCl continues to be the most economical product for winter operations.

Low Effective Temperature

As shown in Figure 2A, chlorides, acetates/formates, and ag-based deicers were all believed to perform similarly well as far as low effective temperature, whereas abrasives were considered to perform the worst in this category.

One respondent commenting on potassium acetate said that it was used as an antiicing 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 an ag-based (beet sugar) product had been very successful and very beneficial during colder temperatures. Yet another respondent commented that by adding 5-10% of ag-based or CaCl₂ deicer to liquid NaCl, the freezing point was lowered and it remained on the pavement longer. A fourth respondent commented that CMA had been a resounding success in their climate, where temperatures varied around zero each day, and they had managed to keep roads open longer or reopened them more quickly than with previous reliance on abrasives only. A fifth respondent commented that a commercially available NaCl-MgCl₂ blend had been very useful because it worked in very cold temperatures. Α.



Figure 2. User perceived ranking of deicers based on positive performance, on a scale of 1 to 5. A) In various performance categories, B) Average perceived ranking.

High Ice-Melting Capacity

As shown in Figure 2A, chlorides, acetates/formates, and ag-based deicers were all believed to have high ice-melting capacity, whereas abrasives were considered to have the least.

There were a few comments that may offer insight on this topic. One respondent commented 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 respondent 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 respondent commented that anti-icing liquid products could be used to "burn through" packed ice and snow up to four inches thick.



Figure 3. Ice-melting capacity of deicers measured at -5°C for reagent grade chlorides, chloride-based (CB), CMA, and ag-based (AB) deicers. Deicers not listed as reagent grade are commercially available products. The salt/sand blend is 10% salt by weight.

Figure 3 shows the ice-melting capacity of various deicers over time, at air temperature of -5 °C (23 °F) and relative humidity of 26.6±6.6%. Reagent (r) grade (NaCl, CaCl₂, and MgCl₂) chlorides and commercially available products, chloride-based (CB) and ag-based (AB) were tested. The reagent grade chlorides were tested to compare the performance of pure chloride salts to commercially available deicers that are generally a combination of chlorides and additives. The reagent grade products and CB2

(chloride-based commercially available product no. 2) outperformed the other 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, with the exception of CB2. Solid reagent grade chemicals generally melted more ice in the first 30 minutes, after which point 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 10 minutes, after which point the rate of melting leveled off. The exceptions to this were the CMA-based product where after 30 minutes more ice began melting, and the salt-sand mixture where after 20 minutes ice melting occurred for 10 minutes before leveling. It was noted that for the reagent grade liquid MgCl₂, the liquid brine actually refroze after application and had minimal to no ice-melting capacity at -5°C.

In general, based on this preliminary data, there was no significant difference in the ice-melting capacity of the tested chloride-based deicers (with the exception of CB2), the CMA product, and the the ag-based product, which was consistent with the user perception. It is important to note that these results were collected at air temperature of -5 °C (23 °F) and relative humidity of $26.6 \pm 6.6\%$ in well-controlled laboratory conditions. The patterns may change when tested under different environmental parameters.

Ease of Application

As shown in Figure 2A, there was no perceived difference in the ease of application of deicers.

Overall Safety Benefits for Winter Roads

As shown in Figure 2A, ag-based deicers were ranked as having the highest overall safety impacts to wintery roads and abrasives the lowest, but the differences were not statistically significant.

Survey respondents' comments on this topic with regard to abrasives include abrasives used prior to icing of the roads create its own hazard by reducing 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 commented that use of chloride-based deicers may attract animals to roadways and perhaps increase the number of vehicle-animal collisions. One respondent commented that potassium acetate application on bridges reduces crashes on the bridges, but that the crashes migrated down the road and now appear to be less severe.

Summary of Respondents Ranking of Deicers Based on Positive Performance

Figure 2B shows the user-perceived average ranking of all five categories by deicer type, with the ag-based products being the most advantageous and abrasives being the least and no significant difference between chlorides and acetates/formates.

User-Perceived Impacts of Deicers

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, and provide any further comments on the topic. The rankings were on a 1-5 scale for each criterion, with 1 having the least impact and 5 having the most impact. The survey results are summarized in Figure 4.

Corrosion to Metal

As shown in Figure 4A, acetates/formates were believed to be the least corrosive to metal, whereas chloride-based deicers were considered to be the most corrosive. This is consistent with research findings from the literature review. 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 solution [19]. Chloride ingress through concrete to reinforcing metal is one of the primary forms of environmental attack for reinforced concrete bridges, which leads to rebar corrosion and a subsequent reduction in the strength, serviceability, and aesthetics of the structure [20]. Pure CMA was demonstrated capable of effectively inhibiting chloride-induced corrosion of reinforcing steel, but CMA as an additive to NaCl did not inhibit the rebar corrosion in concrete [21]. One study confirmed that sodium acetate, urea and CMA were only marginally effective as corrosion inhibitors for reinforced concrete [22].

Table 2. Electrochemical analysis of deicer effect to mild steel (A36) and galvanized steel (guardrail). The salt/sand blend has 10-25% NaCl by weight. Deicers used in this experiment were commercially available and included chloride-based (CB), acetate-based (AB), and ag-based (AB) products.

Deicer	Corrosion Rate (MPY)	Impedence (kohm.cm ²)	Ecorr (mV)	lcorr (µA.cm ²)
CB3 (liquid)	2.7 ± 1.1	2.5 ± 0.5	-616.0 ± 1.8	6.0 ± 2.5
ন্তু AB1 (solid)	4.7 ± 1.9	2.5 ± 0.5	-639.5 ± 6.0	10.2 ± 4.2
ස් CB2 (liquid)	8.1 ± 0.6	1.7 ± 0.1	-745.5 ± 3.0	17.8 ± 1.4
펄 KAc (liquid)	2.5E-03 ± 9.1E-05	950.0 ± 50.0	-155.3 ± 30.2	5.5E-03 ± 2.0E-04
E NaAc (solid)	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
ਰੂ CB3 (liquid)	1.7 ± 0.2	1.6 ± 0.3	-1037.5 ± 5.0	3.5 ± 0.6
ຜູ້ AB1 (solid)	1.9 ± 0.7	2.1 ± 0.4	-1010.0 ± 8.2	4.4 ± 0.9
G CB2 (liquid)	0.9 ± 0.2	1.5 ± 0.0	-1037.5 ± 5.0	1.9 ± 0.4
KAc (liquid)	1.7 ± 0.6	3.9 ± 1.9	-1032.5 ± 5.0	3.0 ± 0.9
🚊 NaAc (solid)	0.9 ± 0.2	8.9 ± 0.9	-1.0 ± 2.0E-02	1.8 ± 0.3
^O Salt/Sand	0.8 ± 2.0E-02	0.7 ± 0.3	-1.0 ± 5.0E-03	1.6 ± 0.1



Figure 4. User-perceived ranking of deicers based on negative impacts, on a scale of 1 to 5. A) In various performance categories, B) Average perceived ranking.

For deicers diluted at 3% by weight or volume (for solid and liquid deicers respectively), electrochemical testing of their corrosion to mild steel and galvanized steel showed that acetate-based deicers were much less corrosive to mild steel than either chloride-based or ag-based deicers. Steel is considered to be passive when its corrosion current density $i_{corr} < 0.1 \ \mu A/cm^2$, and active corrosion occurs when $i_{corr} > 1.0 \ \mu A/cm^2$ [23]. As such, it can be concluded that the acetate-based deicers were non-corrosive to mild steel whereas the chloride-based deicers and the ag-based deicer were very corrosive (as shown in Table 2). Nonetheless, the galvanized steel in the acetate-based deicers was found to be corroding at comparably higher rates than seen in the other deicers. It is hypothesized that, compared with the chloride-based deicers, the formation of corrosion product reduced the corrosion of mild steel in the acetate-based deicers by increasing its corrosion potential (E_{corr}), and the formation of corrosion product (especially zinc acetate) aggravated the corrosion of galvanized steel (containing the sacrificial zinc) in the acetate-based deicers while decreasing its E_{corr} .

The patterns of deicer corrosion to galvanized steel apparently contradicted the user perspective. It should be cautioned that no conclusions can be drawn without stating the specific deicer product and its concentration, the test protocol used (PNS/NACE, SAE, ASTM, or electrochemical test), or the type of metal tested. Furthermore, the short-term laboratory test data may not reflect the long-term corrosion behavior of metals in the field where they are exposed to deicers and other environmental conditions.

Impacts on Concrete and Asphalt Pavements

As shown in Figure 4A, acetates/formates were believed to have the least impact on concrete and asphalt pavements, while chloride deicers were ranked as having the greatest impacts. This contradicts the research findings from the literature. While chloride-based deicing salts can exacerbate the scaling problem as concrete experiences freeze-thaw cycles, the use of properly cured, air-entrained Portland cement concrete 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 [24,25,26,27,28,29,30]. Numerous research studies have shown that MgCl₂, when used as a deicer, causes much more severe deterioration to concrete than NaCl or CaCl₂. This is due to the reaction between Mg^{2+} and the hydrated products in cement paste [31,32,33,34]. It has also been found that concrete exposed to CaCl₂ deteriorated in a similar pattern to that exposed to MgCl₂, although at a slower and less severe pace [35]. CaCl₂ and MgCl₂ do not have as obvious an effect on ASR as NaCl.

Both MgCl₂ and CaCl₂ deicers are known to deteriorate concretes containing reactive dolomite aggregates by accelerating the alkali-carbonate reaction (ACR) [32,33]. No literature was found to report potential effects 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 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 [36,37,38].

While chlorides have little negative impact on asphalt pavements, asphalt durability problems due to the use of acetate/formate 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 [39,40]. 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, with damage caused at the site of airplane deicing costing an estimated \$10-60 million to repair at one airport (Colorado Springs Airport), part of which may be attributable to poor construction. Recent laboratory research at WTI has found that acetates can cause significant emulsification of asphalt and thus strength loss in asphalt concrete [41].

Impacts on Water Quality

As shown in Figure 4A, acetate/formate deicers were believed to have the least impacts to water quality, while abrasives were perceived to have the greatest impact. This is not consistent with findings from the literature. Acetates and formates are known to have a high BOD [42,43], generally higher than chlorides but less than urea and glycol, which can lead to oxygen depletion in the water. They are also known to increase turbidity and water hardness in both surface and ground waters [44]. Chloride-based deicers also increase water hardness in both surface and ground waters. Chloride effects on surface water also include density stratification in small receiving waters which can cause anoxic conditions at depth [45].

One 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 commented that they 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. Another respondent commented that deicing products typically contain additives that can affect the potential for environmental impacts, that some corrosion inhibitors are organic-based and may contribute to this problem, and that it is desirable for deicers to contain fewer additives that contribute to elevated BOD and COD and do not introduce phosphorus into the environment. The same respondent said that it is critical that deicers should not be overapplied, especially in areas near surface waters.

Water samples are being collected from three field sites in Colorado over the course of a year and a half to try and capture the potential deicer effects on the quality of surface water adjacent to CDOT highways. As shown in Figure 5, preliminary data showed that all parameters of interest complied with the Environmental Protection

Agency (EPA) and Colorado State standards[†]. It is interesting to note the large variation in chloride and PO_4^{3-} 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 ft³/second) and 13.1°C (55.6°F), respectively, whereas those at the Aspen site were 1,076 liter/second (38 ft³/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_4^{3-} concentrations there, as a result of less dilution.



Water Quality Parameters

Figure 5. Water quality data collected from Greeley, Aspen and Castle Rock, Colorado, in April 2007.

[†] EPA and Colorado state standards for chloride are currently 250 mg/L. Ranges have been set for pH (6.5-8.5 and 6.5-9.0, respectively), temperature, and DO (temperature dependent), and all other parameters have no limits established (NLE).

Impacts on Soil, Vegetation, Wildlife, and Human Health

As shown in Figure 4A, acetate/formate deicers were believed to have the least impact on soil, vegetation, wildlife and human health, while abrasives and ag-based deicers were perceived to have the greatest impacts. This is consistent with the research findings from the literature. Both acetates/formates and chlorides can affect soil through the potential mobilization of heavy metals into adjacent waters and increase soil pH [45,46]. 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 [42].

At high concentrations, acetates and formates can affect vegetation by reducing seed germination rates, lowering biomass yield, and by leaf browning and senescence. At low concentrations they can act as a fertilizer [44]. Chloride-based deicers can affect vegetation by leaf singing, browning and senescence [45]. Elevated salt concentrations can cause osmotic stress in vegetation. Salt-tolerant vegetation is available for most ecoregions to mitigate some of these effects.

Acetate/formate deicers may affect aquatic organisms via the elevated BOD, which can cause anoxic conditions in water as well as stimulated growth of bacteria and algae [44]. Potassium acetate and sodium acetate are slightly more toxic than CMA when directly consumed [42]. Chlorides are known to have minimal to no effects to aquatic organisms unless concentrations are extremely elevated, but concentrations of 250 mg/l or greater can lead to changes in community structures and food web dynamics [47]. 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.

Overall Effects to Structures and the Environment

As shown in Figure 4A, abrasives and acetates/formates were believed to have the least overall effects to structures and the environment, while chlorides in general were perceived to have the greatest effect.

One respondent commented that while salt brine systems are the most economical set-up, they are not as environmentally safe. Another respondent commented that the agbased (beet juice) product is the most appealing as far as safety and environmental issues are concerned. A third respondent commented that allowing snow-pack 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 4B shows the user-perceived average ranking of all five categories by deicer types, with acetates and formates in general perceived to have the least impacts and chlorides the most.

FUTURE WORK

Additional work planned for this CDOT research project includes further testing of the ice-melting capacity of deicers at -18, -5, and 1.5°C (-0.5, 23, 35°F) to better capture their ice-melting capacities at temperatures typically seen in Colorado between October and April (-18 to 18 °C), following the SHRP H 205.1 & 2 test methods. The iceundercutting and ice-penetration capabilities of deicers will also be tested following the SHRP test methods. In addition, the differential scanning calorimetry (DSC) thermogram of deicer solutions will be tested to gain insight on their effective temperature range and ice-melting capacity at certain concentrations. In the WTI laboratory, electrochemical testing of deicer corrosion to metal will be continued using deicers based on formate or acetate/formate blends. The gravimetric corrosion test using the PNS/NACE modified test method will be conducted for all deicers of interest. Furthermore, the impact of deicers on concrete will be investigated in the laboratory. For the field investigation, water samples will be taken periodically and analyzed until April 2008 to capture the potential deicer effects on water quality at the three Colorado field sites, with some sampling to capture an entire storm from pre-storm to post-storm. The field metal and concrete samples will be periodically removed and analyzed to examine the deicer corrosion to metal and deicer impact on concrete. Laboratory testing of the pavement friction coefficient following deicer application will be conducted using a tribometer.

CONCLUDING REMARKS

This paper reports on the information related to deicer performance and impacts through an ongoing CDOT research project consisting of a synthesis of relevant literature coupled with laboratory tests and field investigations. 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 is the most frequently used, followed by abrasives, then MgCl₂, agbased, CaCl₂, and other deicers. Less than 25% of the survey respondents used alternative deicers such as potassium acetate, sodium acetate, 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. Figure 2B shows the user-perceived average ranking of all five categories by deicer, with the ag-based products being the most advantageous and abrasives being the least, and no significant difference between chlorides and acetates/formates. Generally speaking, user perspectives related to deicer performance were consistent with the literature and experimental data.

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. Figure 4B 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. Literature and experimental data indicated that the negative impacts of acetates and formates were greater than perceived by survey

respondents, especially with respect to damage to pavement, structures and water quality. As such, CDOT has decided not to use available potassium or other acetate compounds.

One caveat is that the survey results may be skewed due to the limited number of people who provided the rankings, limited number of criteria ranked, and possible lack of scientific data or field experience by the road maintenance professionals who responded. 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 fewer rankings provided for acetates, formates, or ag-based deicers, as such products are relatively new to practitioners and their long-term impacts are not as well-known. Continued laboratory and field investigation of the CDOT research project are expected to shed more light on the performance and impact of various deicers currently on the market.

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