



## Longevity of Corrosion Inhibitors and Performance of Deicer Products under Storage or after Pavement Application

**Xianming Shi, Ph.D., P.E.**  
Corrosion & Sustainable Infrastructure Lab  
Montana State University



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## Team Members

- Xianming Shi, Ph.D., P.E. (PI)
- Laura Fay, M.Sc. (Co-PI)
- Keith Fortune
- Robert Smithlin
- Matthew Johnson
- Marijean M. Peterson, M.Sc.
- Andrew Creighton
- Zhengxian Yang, M.Sc.
- Doug Cross




## Outline

- Introduction
- Inhibitor Longevity and Deicer Performance *under Storage*
- Inhibitor Longevity and Deicer Performance *after Pavement Application* during Winter Storms
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## Introduction

- Direct cost of inhibited chemicals can be much higher than that of the non-inhibited chemicals.
- How long the corrosion inhibitors and the deicer products remain effective during storage and on the pavement once applied during the winter storm?






## Critical Questions Asked

1. Longevity of the inhibitors and the duration in which they persist with the deicer (both under storage and after pavement application);
2. Possible effects of temperature, UV intensity, exposure, and dilution on inhibitors in common chloride deicers and deicer performance;
3. Cost-effectiveness of including inhibitors in deicers;
4. Any inhibitor effect on freezing point suppression or deicer effectiveness; and
5. The most effective deicer for different winter weather scenarios.

## Inhibitor Longevity and Deicer Performance under Storage

- Multiple established analytical methods to monitor the temporal evolution of deicer properties
  - Periodical, random sampling
  - Chloride & inhibitor concentrations
  - corrosion parameters  $E_{corr}$  & PCR
  - pH, electrical conductivity
  - performance parameters  $T_c$  &  $IMC_{30°F, 60min}$

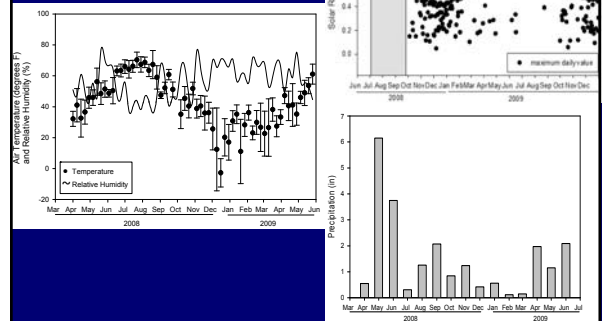
mixed 1/4" for 1 hr (1<sup>st</sup> mon)  
20min. for 1 hr thereafter

### Deicers for the Field Storage Study

Deicer Product	Salt Concentration (by vendor)	Corrosion Inhibitor Concentration (by vendor)	Salt Concentration (by WTI)	Corrosion Inhibitor Concentration (by WTI)	Inhibitor to Chloride Ratio
NaCl+GLT	specified 23%	5%	19.3%	4.3%	1:4.5
CCB	31+%	12%	42.4%*	11.1%	1:3.8
FreezGard	29-31%	1.7%	36.1%*	2.4%	1:15.0
IceSlicer	NA	1.5%	NA	0.2%*	NA

\* These reported concentrations are likely higher than the actual concentrations, for unknown reasons. Note that the salt concentrations reported by WTI were calculated based on the elemental concentrations of cations (Na, Ca, or Mg) measured using the inductively-coupled plasma (ICP), whereas the vast majority of the salt concentrations reported in this project were calculated based on ion-selective sensor measurements of chloride concentration. There could be cations that are associated with the corrosion inhibitor or other additives, instead of the Cl<sup>-</sup> anions.

### Field Storage Site Conditions

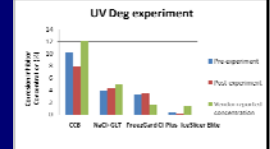


### Key Findings of Storage Study (1)

- None of liquid deicers lost their quality over the 14 months of storage (mixed or non-mixed). The NaCl-based solid deicer did not lose its quality over the 12 months of storage (covered or uncovered).
- No significant degradation of corrosion inhibitor or loss of chlorides was seen during the months of field storage.
- During the 14-month field monitoring, NaCl+GLT was the only liquid deicer to have non-passing corrosion scores, suggesting potential shelf-life issues.

### Accelerated UV-Deg Study

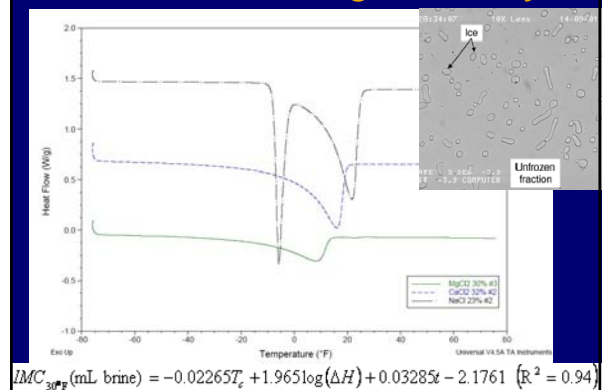
- Effect of *T*, *UV intensity*, & *time* on the resulting [inhibitor]: insignificant for the NaCl+GLT & FreezGard deicers but significant for the CCB deicer
- For the CCB deicer, the blocking of UV light by the storage tanks was likely beneficial in preventing its inhibitor degradation over the 14-month field storage.



### Inhibitors Showed No Side Benefits

Deicer Products	Characteristic Temperature ( <i>T<sub>c</sub></i> , °F)	ΔH (J/g)
NaCl+GLT (with 4.3% inhibitor)	21.4	201
Non-inhibited 23% straight salt brine (provided by the MDT)	21.4	192
Non-inhibited 23% NaCl brine (made from reagent-grade NaCl)	21.8	180
Corrosion inhibitor (GLT) only	34.2	0.1
CCB (CaCl <sub>2</sub> -based, with 11.1% inhibitor)	13.7	191
Non-inhibited CCB brine (provided by the vendor)	11.5	202
Corrosion inhibitor only	31.9	87
FreezGard (MgCl <sub>2</sub> -based, with 2.4% inhibitor)	11.2	210
Non-inhibited FreezGard Brine (provided by the vendor)	10.3	215
Corrosion inhibitor only	32.6	169

### Differential Scanning Calorimetry



### Key Findings of Storage Study (2)

- ANN: finding meaningful, logical results from the noisy data w.r.t. the corrosion experiments.
- ANN (R<sup>2</sup> 0.84): correlate the corrosion data from the **electrochemical test method** with those from **PNS/NACE test method**.
- ANNs (R<sup>2</sup> 0.91 & 0.98): correlate the deicer composition (*deicer type, [Cl<sup>-</sup>], [inhibitor], pH, & electrical conductivity*) w/ deicer corrosivity (in **PCR**) and performance (in **T<sub>c</sub>**) respectively.

### Key Findings of Storage Study (3)

- The **electrochemical test** could be used as a quality assurance tool for rapid assessment of deicer corrosivity to mild steel.
  - High  $E_{corr}$  ~ low corrosivity (**PCR**) values.
  - $E_{corr} > -562$  mV<sub>SCE</sub> ~ **PCR** < 30
  - $E_{corr} < -562$  mV<sub>SCE</sub> ≠ **PCR** > 30

### Inhibitor Longevity and Deicer Performance after Pavement Application

- Field Operational Tests at TRANSEND Test-bed
- Properties of deicer residuals
  - Chloride & inhibitor **concentrations**
  - corrosion parameters  $E_{corr}$  & **PCR**
  - pH, electrical conductivity
  - performance parameters  $T_c$  &  $IMC_{30°F, 60min}$

### Deicers for the FOTs

Deicer Product	Salt Concentration (by vendor)	Corrosion Inhibitor Concentration (by vendor)	Salt Concentration (by WTI)	Corrosion Inhibitor Concentration (by WTI)	Inhibitor to Chloride Ratio
NaCl+GLT	23%	5%	18.8%	4.7%	1:4.0
CCB	31+%	12%	30.3%	16.2%	1:1.9
FreezGard	29-31%	1.7%	36.2%	1.2%	1:30.2

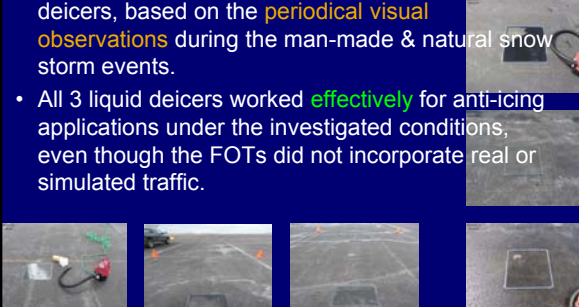
Note that the salt concentrations reported by WTI were calculated based on the elemental concentrations of cations (Na, Ca, or Mg) measured using the inductively-coupled plasma (ICP), whereas the vast majority of the salt concentrations reported in this project were calculated based on ion-selective sensor measurements of chloride concentration. The inhibitor concentrations in the three deicers were measured by WTI using the UV-vis method.

	Black Ice Event	Man Made Snow Event	Natural Snow Event
Target Precipitation	No precipitation	Minimum 1 inch of snow	1-4 inches in the first 24 hours
Actual Precipitation	Total of 0.75" of precipitation (mostly snow/ice) during day 4 to day 7.	1" of man-made snow; a total of 0.26" of natural snow during day 3 and day 4.	3.5-4" in the first 24 hours; about 0.75" of blowing snow on day 2.
Target Air Temperature	25-32 °F	15-25 °F	25-32 °F
Target Pavement Temperature	Less than 32 °F	Less than 25 °F	25-32 °F
Moisture Content in Snow (Average Density)	Not applicable	30-40% (24 lb/ft <sup>3</sup> )	20-40% (19 lb/ft <sup>3</sup> )
Target Deicer Application Rate	30 gallons/lane-mile	60 gallons/lane-mile	60 gallons/lane-mile
Actual Application Rate	33±5 gallons/l-m	53±4 gallons/l-m *	55±6 gallons/l-m *
Target Wind Speed	Not specified	Less than 6 mph	Not specified
Average Wind Speed	6 mph	9 mph	9 mph
Average Wind Direction	SSW to NNE (coming from 200°)	SW to NE (coming from 228°)	SSE to NNW (coming from 173°)

These high application rates were for improved product recovery and subsequent analysis, and they are not representative of what should be applied.

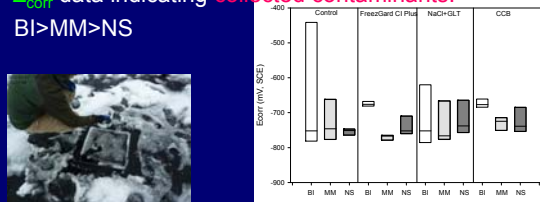
### Key Findings of FOTs (1)

- In general, **no significant difference** in anti-icing performance was observed between the 3 liquid deicers, based on the **periodical visual observations** during the man-made & natural snow storm events.
- All 3 liquid deicers worked **effectively** for anti-icing applications under the investigated conditions, even though the FOTs did not incorporate real or simulated traffic.



### Key Findings of FOTs (2)


- The samples collected from the control test lanes (with no deicer applied) seemed to contain **contaminants** that affect their UV-vis spectrum, pH, and corrosion data, yet their low [Cl<sup>-</sup>] & low conductivity suggested the **absence of salt**.
- $E_{con}$  data indicating **collected contaminants**: BI > MM > NS



Deicer Type	Storm Event	E <sub>con</sub> (mV SCE)
Control	BI	-550
	MM	-650
	NS	-600
FreezGard Cl Plus	BI	-650
	MM	-700
	NS	-650
NaCl+GLT	BI	-650
	MM	-700
	NS	-650
CCB	BI	-650
	MM	-700
	NS	-650


### Key Findings of FOTs (3)

- Passing PCR for 7 day \* 3 events: **NaCl+GLT (14/21) > CCB (13/21) > FreezGard (11/21)**.
- Possible mechanisms for the much lower chloride recovery from the pavement during the NS event, relative to the MM snow event: **warmer pavement T., more precipitation, loss of deicer to the leveling-off step, & more time waited before d-1 sampling**.




### Key Findings of FOTs (4)

- Longevity of the inhibitor and chlorides of liquid deicers after pavement application = **f(deicer type, storm type, and likely other field factors)**.
- The fate and transport of the corrosion inhibitors generally **differed** from those of the chlorides: **dilution by precipitation** and **likely wicking** of the deicer into the pavement and the top snow layer contributed to the loss of inhibitor and chlorides. **UV-degradation**, if any, might have played a minor role.




### Key Findings of FOTs (5)

- Black ice event**: total of 0.75" of precipitation (mostly snow/ice) during days 4-7.
- % chloride recovered by day 4: **~30%, 20%, & 50%** for NaCl+GLT, CCB, and FreezGard respectively.
- % CCB inhibitor recovered by day 4: **80%**.
- PCR by day 4: **40, 15 & 35** for NaCl+GLT, CCB, and FreezGard respectively.
- The relative corrosivity of deicer solutions on the field pavement differed from that of them tested in the lab** (32, 21, & 16).
- Starting on day 5, the chloride recovery for all 3 deicers significantly dropped: rain precipitation on d-3 and snow precipitation on d-3 (trace amount), d-4 (>1/2"), & d-5 (1/2").



### Key Findings of FOTs (6)

- Man-made snow event**: 1" of artificial snow and a total of 0.26" of natural snow during days 3-4.
- % chloride recovered by day 7: **~20%, 16%, & 8%** for NaCl+GLT, CCB, and FreezGard respectively.
- % GLT and CCB inhibitors recovered by day 7: **38% & 26%** respectively.
- PCR by day 7: **51, 72 & 31** for NaCl+GLT, CCB, and FreezGard respectively.
- Greatest number of non-passing PCR values: **low [inhibitor] + relatively high [Cl]**
- The PCR values showed no clear relationship with storm type, deicer type or sampling time.



### Key Findings of FOTs (7)

- **Natural snow event:** 3.5-4" of natural snow in the first 24 hrs and ~ 0.75" of blowing snow on d-2.
- % chloride recovered <0.7% by d-6 and <0.5% by d-7 for all 3 deicers.
- % GLT inhibitor recovered by d-1 & d-5: 21% & 4%.
- % FreezGard inhibitor recovered by d-7: 83%.
- PCR by d-1: 7, 10 & 18 for NaCl+GLT, CCB, and FreezGard respectively.
- The PCR values showed no clear relationship with storm type or deicer type.



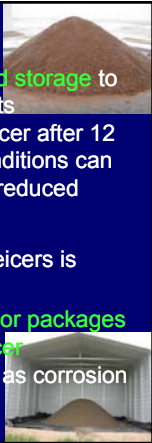
### Implementation Recommendations (1)

- The three liquid deicers (MgCl<sub>2</sub>-based FreezGard, CaCl<sub>2</sub>-based CCB, and NaCl+GLT) investigated did not lose their quality over the 14 months of field storage, regardless of the storage condition (mixed or non-mixed). As such, it is recommended **not to implement any mixing for the liquid deicer tanks.**
- It is however essential to **mix the tanks immediately prior to the use** of the liquid deicers, to ensure uniform composition and minimize stratification.



### Implementation Recommendations (2)

- Best to **cover solid deicers during field storage** to minimize leaching of active ingredients (especially inhibitor), but the solid deicer after 12 months storage under uncovered conditions can still be an effective deicer despite its reduced corrosion inhibition.
- Is inclusion of corrosion inhibitor in deicers is economical?  
Be aware that the investigated **inhibitor packages did not show any side benefits in deicer performance** and they served merely as corrosion inhibitors for the deicer products.



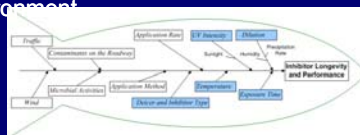
### Implementation Recommendations (3)

- The fate and transport of inhibitors **differed** from those of chlorides, once applied on the pavement.
- While such residuals could be washed away by precipitation, **their presence on the pavement could potentially be measured and taken into consideration** when re-applying chemicals for snow and ice control.



### Implementation Recommendations (4)

- This project revealed that the relative corrosivity of deicer solutions on the field pavement **differed** from that of them tested in the laboratory.
- It merits further investigation to develop **laboratory tests that can correlate better with the actual field corrosion of metals caused by deicer exposure**, considering: the fate and transport of inhibitors (vs. chlorides), R.H., T. cycles, etc. in the service environment.



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- **Kim Willoughby :** WSDOT project manager
- **Dan Williams:** liaison
- **Technical Advisory Committee and Chemical Technical Subcommittee**
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**Contact:**  
Xianming Shi, Ph.D., P.E.  
Director, Corrosion & Sustainable  
Infrastructure Lab  
PO Box 174250  
Montana State University  
Bozeman, MT 59717-4250  
Phone: 406-994-6486  
[www.coe.montana.edu/me/faculty/Shi/](http://www.coe.montana.edu/me/faculty/Shi/)

