Agricultural based products and Complex Chlorides/Minerals
We did a ton of lab testing....what does it all mean?

Laura Fay
PNS Conference
June 8, 2016
Session W5
A quick thank you...

- Clear Roads Pooled Fund and member states, and Minnesota Department of Transportation.

- Technical Advisory Committee - Ron Wright, Tom Peters, Michael Lashmet, Tim Peters, Larry J. Gangl, and Mike Mattison, and project coordinators Colleen Boss and Greg Waidley and CTC & Associates.

- Anburaj Muthumani, Dave Bergner (Monte Vista Associates, LLC), Dr. Xianming Shi (Washington State University)

- WTI Support Staff
Why did we do this?

• Agro-based products are becoming more commonly used in snow and ice control operations.
• Most commonly as additives.
• Past studies and anecdotal evidence have shown that these products improve:
  ➢ Deicing and/or anti-icing performance *(They can, but it is not as simple as yes or no across the board)*
  ➢ Reduce the corrosion *(True)*
  ➢ Reduce environmental impacts *(Did not look at this)*
• The “modes of action” by which agro-based products provide benefits is poorly understood
Here is what we did...

• Literature review
• Survey
• Systematic laboratory investigation:
  ➢ Lowering the freezing point of water
  ➢ Improving ice melting capacity
  ➢ Weakening of ice bond to pavement
  ➢ Reducing the corrosiveness to metals
  ➢ Improving the product longevity on the road surface,
  ➢ Preventing ice formation or refreeze prevention,
  ➢ and Assessing the influence of the absorbance of sunlight.
What did we learn from the Literature Review.....

- The main composition of agro-based products:
  - desugared beet molasses,
  - corn by-products,
  - cheese brewing by-products,
  - beer brewing by-products,
  - succinate salts,
  - urea,
  - and starch.

- These products are either used alone or as additives with other winter maintenance chemicals to improve performance and/or to reduce corrosion and environmental impacts.
• But...at this time limited research has been performed to examine the modes of action by which these products help in improving performance and reducing negative impacts on highway infrastructure and the environment.
What did we learn from the survey ....

– Some respondents preferred using non-chloride agro-based products at low temperatures (below 20°F).

– Longevity on the road surface (or the residual effect) was one of the observed benefits of using agro-based products.

– Improved performance at low temps and reduced material usage were common benefits observed by survey respondents when using CCM based products.

– Limited research has been conducted by survey respondents on agro-based and CCM based products.
Products Selected for Testing

- **Category A**: solid complex chlorides/minerals (CCM) based products were used as-received for testing purposes.
  - Product A1 - *Ice Slicer®*;
  - Product A2 - *Thawrox®*

- **Category B**: Liquid agro-based deicers which were prepared by mixing the vendor-provided concentrates with a 23.3 wt. % NaCl aqueous solution, at either 70:30 or 80:20 volume ratio, depending on the vendor specification.
  - Product B1 - *Beet 55®*;
  - Product B2 - *Boost™ SB*;
  - Product B3 - *Snow Melt®*;
  - Product B4 - *Geomelt® 55*

- **Category C**: Liquid agro-based deicers which were used as-received from the manufacturer for testing purposes.
  - Product C1 - *Apogee™*;
  - Product C2 - *Boost™ CCB*;
  - Product C3 - *Ice Ban® 305*;
  - Product C4 - *ThermaPoint IB 7/93*
<table>
<thead>
<tr>
<th>Product Name</th>
<th>Manufacturer</th>
<th>Major Components</th>
<th>% Added to salt brine*</th>
<th>Description</th>
<th>Reference</th>
<th>Chloride Concentration from Mohr's chemical titration method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ice Slicer®</td>
<td>Redmond Minerals, Inc</td>
<td>NaCl: 90-98%; Trace amounts of MgCl₂, KCl, CaCl₂</td>
<td>As-Received</td>
<td>Blend of complex chlorides</td>
<td>MSDS</td>
<td>58.90%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Reagent grade NaCl features a theoretical Cl content of 60.7%.</td>
</tr>
<tr>
<td>Thawrox®</td>
<td>North American Salt Company</td>
<td>NaCl: 60-100%; Thawrox Treated Salt Liquid Additive: 1-5%</td>
<td></td>
<td>Thawrox treated rock salt</td>
<td>MSDS</td>
<td>59.60%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Beet 55</td>
<td>Smith Fertilizer and Grain</td>
<td>NaCl: 17.2%</td>
<td>30 (70% salt brine)</td>
<td>Beet based product</td>
<td>PNS Qualified</td>
<td>0.25 M</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>product list:</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Category A3</td>
<td></td>
</tr>
<tr>
<td>Boost™ SB</td>
<td>America West</td>
<td>NaCl: 18.8%; CaCl₂: 2.3%</td>
<td>20 (80% salt brine)</td>
<td>organic agricultural by-product with salt brine</td>
<td>PNS Qualified</td>
<td>0.62 M</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>product list:</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Category A2</td>
<td></td>
</tr>
<tr>
<td>Snow Melt®</td>
<td>Smith Fertilizer and Grain</td>
<td>Glycerin:15 - 20%; Polyether Polymer: 10 - 20%; Sodium Lactate: 4 - 10%; Sorbitol: 2-4%; Sodium Formate: 1 - 4%; 1, 2 - Butanediol: 1 - 4%</td>
<td>30 (70% salt brine)</td>
<td>Corn based product</td>
<td>MSDS</td>
<td>0.05 M</td>
</tr>
<tr>
<td>Geomelt® 55</td>
<td>SNI Solutions</td>
<td>NaCl: 18.1%</td>
<td>30 (70% salt brine)</td>
<td>Beet based product</td>
<td>PNS Qualified</td>
<td>0.55 M</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>product list:</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Category A3</td>
<td></td>
</tr>
<tr>
<td>Apogee™</td>
<td>Envirotech Services, Inc.</td>
<td>Glycerin: % unknown (Proprietary)</td>
<td>As-Received</td>
<td>Glycerin based product</td>
<td>MSDS</td>
<td>1.05 M</td>
</tr>
<tr>
<td>Boost™ CCB</td>
<td>America West</td>
<td>organic ag by-product: % unknown CaCl₂; % unknown (Proprietary)</td>
<td></td>
<td>organic agricultural by-product with CaCl₂</td>
<td>MSDS</td>
<td>0.62 M</td>
</tr>
<tr>
<td>Ice Ban® 305</td>
<td>GMCO</td>
<td>Ice Ban Concentrate: 10 - 20%; MgCl₂ (30% Solution): 80 - 90%</td>
<td></td>
<td>Corn based product</td>
<td>MSDS</td>
<td>1.11 M</td>
</tr>
<tr>
<td>ThermaPoint IB 7/93</td>
<td>Millennium Roads, Inc</td>
<td>CaCl₂: 93%; DBFE (Organic based performance enhancer (Proprietary))*: 7%</td>
<td></td>
<td>Other (Lignin based)</td>
<td>MSDS</td>
<td>0.73 M</td>
</tr>
</tbody>
</table>

Note: For 23.3% NaCl reagent grade would feature Cl content of 3.99 M
Results – Laboratory Testing

Lowering the freezing point of water
Lowering the freezing point of water

The eutectic curve shows...

- CCM based products do not significantly reduce the freezing point of water compared to NaCl.
Lowering the freezing point of water

The eutectic curve shows..

- Liquid agro-based products blended with 23.3% salt brine **Significantly lowered** the freezing point of water compared to NaCl.
Lowering the freezing point of water

The eutectic curve shows...

- Agro-based products (as-received) significantly lowered the freezing point of water compared to NaCl.
Do these products aid in lowering the freezing point of water?

- CCM no, but this makes sense
- Agro-based products, yes they do.
Results – Laboratory Testing

Improve ice melting capacity
Ice Melting Test Results

**25°F**

CCM products did melt more ice at 15°F, but not at 25°F.

**Category A: CCM**

**15°F**
Ice Melting Test Results

Agro-based products blend with salt brine did not produce more melt than salt brine alone except for one product (B3).

Category B: Agro-based & Salt brine
Agro-based products as received did produce more ice melt than salt brine.

Category C: Agro-based as received
## Summary Table – DSC, Eutectic Curve, Ice Melting

<table>
<thead>
<tr>
<th>Product</th>
<th>Original State</th>
<th>Average (°F)</th>
<th>COV</th>
<th>Average</th>
<th>COV</th>
<th>Eutectic Temperature °F</th>
<th>Eutectic Concentration (wt.%</th>
<th>60 min @ 25°F</th>
<th>60 min @ 15°F</th>
<th>60 min @ 5°F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Product A1</td>
<td>Solid</td>
<td>28</td>
<td>20%</td>
<td>162.2</td>
<td>8%</td>
<td>-6.61</td>
<td>27%</td>
<td>7.15</td>
<td>4.46</td>
<td>1.53</td>
</tr>
<tr>
<td>Product A2</td>
<td>Solid</td>
<td>22.9</td>
<td>1%</td>
<td>89.4</td>
<td>4%</td>
<td>-6.70</td>
<td>25%</td>
<td>7.23</td>
<td>4.16</td>
<td>-</td>
</tr>
<tr>
<td>Product B1</td>
<td>Liquid</td>
<td>24.8</td>
<td>3%</td>
<td>138.7</td>
<td>3%</td>
<td>-18.64</td>
<td>27%</td>
<td>2.62</td>
<td>1.49</td>
<td>-</td>
</tr>
<tr>
<td>Product B2</td>
<td>Liquid</td>
<td>30.4</td>
<td>42%</td>
<td>156.1</td>
<td>7%</td>
<td>-17.86</td>
<td>24%</td>
<td>2.44</td>
<td>1.36</td>
<td>-</td>
</tr>
<tr>
<td>Product B3</td>
<td>Liquid</td>
<td>25.4</td>
<td>4%</td>
<td>136.1</td>
<td>6%</td>
<td>-9.52</td>
<td>26%</td>
<td>3.16</td>
<td>1.90</td>
<td>-</td>
</tr>
<tr>
<td>Product B4</td>
<td>Liquid</td>
<td>28.1</td>
<td>23%</td>
<td>176.1</td>
<td>4%</td>
<td>-15.43</td>
<td>27%</td>
<td>2.49</td>
<td>1.53</td>
<td>1.14</td>
</tr>
<tr>
<td>Product C1</td>
<td>Liquid</td>
<td>16.2</td>
<td>2%</td>
<td>120.9</td>
<td>6%</td>
<td>&lt;45</td>
<td>As-received</td>
<td>4.48</td>
<td>2.81</td>
<td>1.58</td>
</tr>
<tr>
<td>Product C2</td>
<td>Liquid</td>
<td>6.1</td>
<td>6%</td>
<td>124.6</td>
<td>4%</td>
<td>&lt;45</td>
<td>As Received</td>
<td>3.85</td>
<td>3.11</td>
<td>-</td>
</tr>
<tr>
<td>Product C3</td>
<td>Liquid</td>
<td>8.9</td>
<td>4%</td>
<td>161.1</td>
<td>10%</td>
<td>&lt;45</td>
<td>As Received</td>
<td>2.96</td>
<td>2.50</td>
<td>-</td>
</tr>
<tr>
<td>Product C4</td>
<td>Liquid</td>
<td>6.4</td>
<td>5%</td>
<td>131.5</td>
<td>6%</td>
<td>&lt;45</td>
<td>As Received</td>
<td>3.18</td>
<td>2.39</td>
<td>1.58</td>
</tr>
<tr>
<td>NaCl (reagent)</td>
<td>Solid</td>
<td>23.5</td>
<td>2%</td>
<td>197.7</td>
<td>3%</td>
<td>-6.34</td>
<td>23%</td>
<td>-</td>
<td>3.90</td>
<td>-</td>
</tr>
<tr>
<td>Rock salt</td>
<td>Solid</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>6.99</td>
<td>3.55</td>
<td>1.72</td>
</tr>
<tr>
<td>Salt Brine (Rock 23.3 wt%)</td>
<td>Liquid</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.64</td>
<td>1.55</td>
<td>1.10</td>
</tr>
</tbody>
</table>
Do these products aid in improving ice melting capacity?

- CCM, at colder temperatures
- Agro-based blended with salt brine, only one product did (B3).
- Agro-based as received, yes.
  - Additionally, as received agro-based products exhibit significantly lower characteristic temperature.
When considering the lower freezing of Agro-based products but also the small ice melting capacity...What is going on.

• Agro-based products may act as ice crystal nucleation point inhibitors, delaying the formation of ice compared to salt brine.
  – Cryoprotectants are substances that prevent ice nucleation.
  – The agro-based products significantly reduce the freezing point of water, therefore could act as cryoprotectants, delaying the freezing point of water.
Improved the ice melting capacity

- CCM based products
  - produced more ice melt than the NaCl at 15°F
- Liquid agro-based products blended with 23.3% salt brine
  - did not produce more ice melt than salt brine (NaCl, liquid) alone at 25°F, 15°F and 5°F.
- Agro-based products (as-received)
  - Produced more ice melt than salt brine.
- Agro-based products exhibit significantly lower characteristic temperature.
  - This suggests that the amount of thermal energy corresponding to the aqueous brine solution’s liquid/solid phase transition is reduced by the addition of agro-based by-products; making the agro-based by-products mixed with brine more difficult to freeze than salt brine alone.
- Agro-based products acted as freezing point depressants (or cryoprotectants).
Weakening of ice bond to pavement

250, 500, 750 passes
Video of Trafficking
For CCM products it was slightly easier to plow snow off the pavement.
For agro-based products blended with salt brine it was significantly easier to plow snow off the pavement.
For agro-based products as received it was significantly easier to plow snow off the pavement.
Do these products aid in weakening the bond between the ice and pavement more than salt?

- CCM, slightly
- Agro-based, yes
Weakening of ice bond to pavement

<table>
<thead>
<tr>
<th>Product</th>
<th>Concentration</th>
<th>Temperature</th>
<th>Viscosity (mm²/s)</th>
<th>Specific Gravity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Product B4</td>
<td>70% salt brine and 30% agro-based concentrate</td>
<td>68°F</td>
<td>2.4</td>
<td>1.20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25°F</td>
<td>5.5</td>
<td>1.21</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15°F</td>
<td>7.3</td>
<td>1.21</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5°F</td>
<td>9.2</td>
<td>1.21</td>
</tr>
<tr>
<td>Product C1</td>
<td>As-received</td>
<td>68°F</td>
<td>23.0</td>
<td>1.22</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25°F</td>
<td>102.9</td>
<td>1.23</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15°F</td>
<td>169.4</td>
<td>1.24</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5°F</td>
<td>283.1</td>
<td>1.24</td>
</tr>
<tr>
<td>Product C4</td>
<td>As-received</td>
<td>68°F</td>
<td>9.2</td>
<td>1.33</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25°F</td>
<td>16.4</td>
<td>1.33</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15°F</td>
<td>21.8</td>
<td>1.34</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5°F</td>
<td>25.5</td>
<td>1.34</td>
</tr>
<tr>
<td>Salt Brine</td>
<td>23% wt of Rock salt</td>
<td>68°F</td>
<td>1.5</td>
<td>1.17</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25°F</td>
<td>2.8</td>
<td>1.18</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15°F</td>
<td>4.1</td>
<td>1.19</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5°F</td>
<td>4.6</td>
<td>1.19</td>
</tr>
</tbody>
</table>

Agro-based products have a higher viscosity than salt brine.
Weakening of ice bond to pavement

The addition of agro-based products to salt brine increased the overall viscosity of the products.

So what does this mean...

Agro-based products with higher viscosity than salt brine may have slower grain boundary penetration than the salt brine with lower viscosity.

Products with higher viscosity may have more product remain on the pavement surface (residual effect) resulting in reduction in bond strength between ice and pavement surface.
Improving product longevity on the pavement

General trend of increased shear strength required to plow the snow off the pavement with time.
Where is the product?

1. Collected snow from the pavement surface.
2. Measured the amount of product in the snow.
3. Compared amount of product wicked up into the snow pack vs. amount remaining on the pavement surface.
45 – 90% of applied product is removed with the snow in the first plowing.
Do these products aid in improving product longevity on the pavement?

- Agro-based products tend to stay on the road surface longer than salt brine.
- Longevity of the product on the road surface depends on the amount of product dissolved into the snow before each cycle of plowing.
Prevention of ice formation/refreezing

250, 500, 750 passes
Prevention of ice formation/refreezing

General trend of decreasing friction coefficient over time => its getting more slippery overtime.
Do these products aid in prevention of ice formation/refreezing?

- Agro-based products appear to aid in reducing ice formation, or maintain friction with only a small decrease over time with trafficking.
Absorbance of sunlight
Is the performance of these products affected by UV or sunlight exposure?

• Ice melting capacity of these products significantly increased with exposure to UV light.

• At colder temperatures, darker colored agro-based products had higher ice melting capacity than lighter color agro-based products and salt brine.
Results - Corrosion
## Results - Corrosion

<table>
<thead>
<tr>
<th>Deicer</th>
<th>Original state</th>
<th>PNS Dipping Test</th>
<th>Electrochemical Test</th>
<th>Average Corrosion Rate (MPY)</th>
<th>Percentage Corrosion Rate (%)</th>
<th>( E_{\text{corr}} ) (mV, SCE)</th>
<th>( I_{\text{corr}} ) (µA/cm²)</th>
<th>Average Corrosion Rate (MPY)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3% Product A1</td>
<td>Solid</td>
<td>50.5</td>
<td>82.0</td>
<td>-683.0</td>
<td>7.2</td>
<td>32.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3% Product A2</td>
<td>Solid</td>
<td>46.2</td>
<td>74.1</td>
<td>-709.0</td>
<td>8.3</td>
<td>37.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3% Product B1</td>
<td>Liquid</td>
<td>42.8</td>
<td>80.2</td>
<td>-508.0</td>
<td>5.4</td>
<td>24.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3% Product B2</td>
<td>Liquid</td>
<td>15.1</td>
<td>30.8</td>
<td>-656.0</td>
<td>8.5</td>
<td>38.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3% Product B3</td>
<td>Liquid</td>
<td>20.3</td>
<td>34.0</td>
<td>-704.0</td>
<td>7.6</td>
<td>34.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3% Product B4</td>
<td>Liquid</td>
<td>29.5</td>
<td>52.9</td>
<td>-638.0</td>
<td>11.3</td>
<td>51.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3% Product C1</td>
<td>Liquid</td>
<td>16.8</td>
<td>31.2</td>
<td>-556.0</td>
<td>6.3</td>
<td>28.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3% Product C2</td>
<td>Liquid</td>
<td>18.1</td>
<td>38.7</td>
<td>-521.0</td>
<td>4.5</td>
<td>20.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3% Product C3</td>
<td>Liquid</td>
<td>21.2</td>
<td>45.4</td>
<td>-685.0</td>
<td>8.9</td>
<td>40.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3% Product C4</td>
<td>Liquid</td>
<td>14.3</td>
<td>30.6</td>
<td>-524.0</td>
<td>5.5</td>
<td>26.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3% NaCl</td>
<td>Solid</td>
<td>56.3</td>
<td>100</td>
<td>-751.0</td>
<td>12.8</td>
<td>58.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DI Water</td>
<td>Liquid</td>
<td>5.0</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Do these products aid in reducing corrosion?

- The PNS dipping test revealed that the CCM deicers feature slightly lower corrosivity to carbon steel than solid 3% NaCl control.
- Agro-based products (except product B1) feature much lower corrosivity to carbon steel than the controls.
Best Practices – Identified Issues with Agro-based Products

• Road slickness has been reported
  – avoid over application which may cause this.

• Clogging of spray equipment
  – Flush system with water between use of various products, agitate or stir products periodically if stored for long periods.

• Bacterial growth
  – Some products have inhibitors to prevent this, products may have a shelf life, and proper long term storage may be needed (no sun exposure, cool temperatures, periodic mixing, etc.)

• Attractant to wildlife on roadways
  – Additional research is needed to confirm this.
Available Resources/Outcomes

• Best Practices Manual
• Final Report and Webinar Presentation
• Summary Video

www.clearroads.org
Thank you!

Questions?

Laura Fay
laura.fay1@montana.edu
406.600.5777