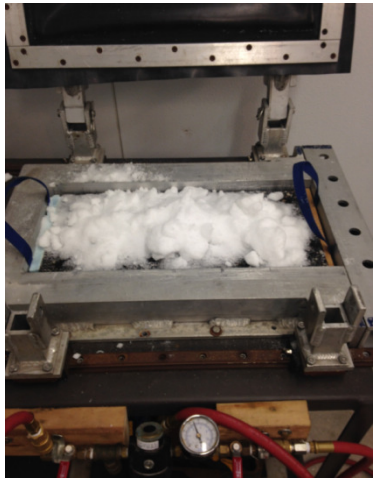
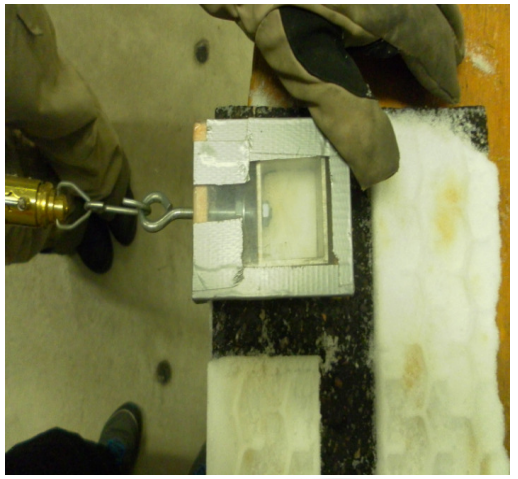
Agricultural based products and Complex Chlorides/Minerals

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.

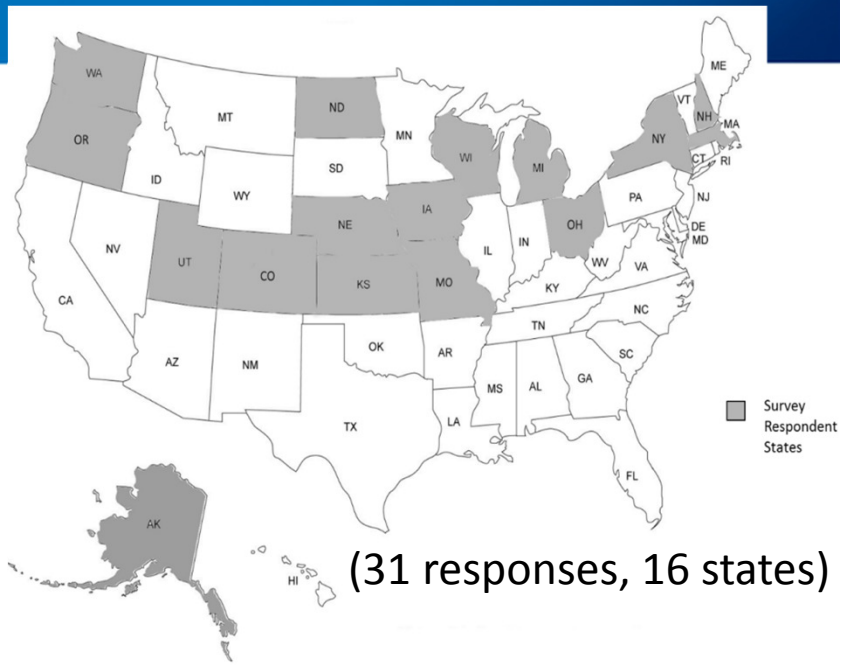
What did we learn from the Literature Review…..

- 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.

Literature Review contd

- 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 ….



(31 responses, 16 states)

- 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.

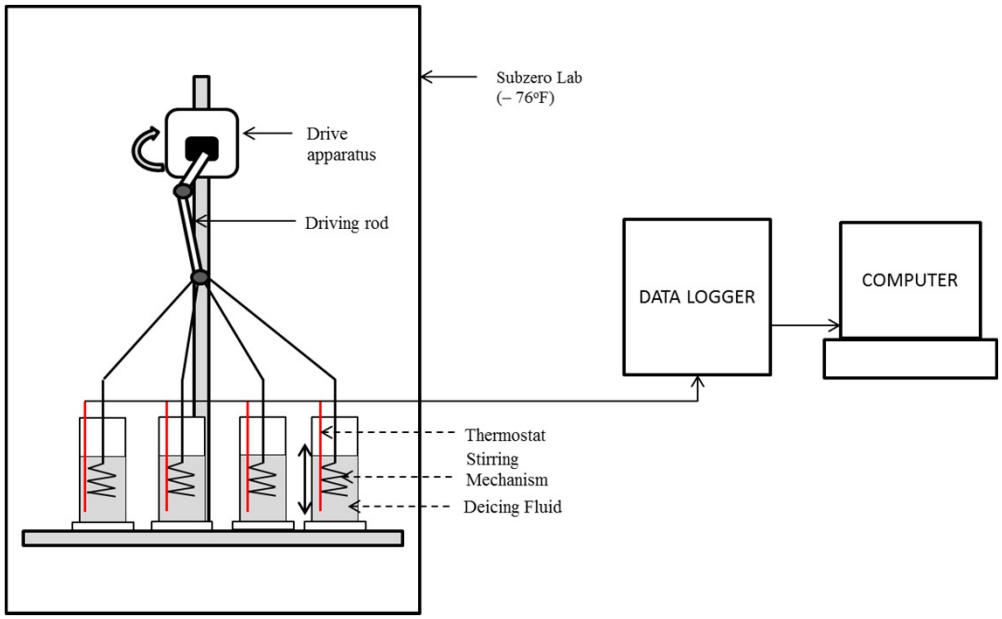
Products Selected for Testing

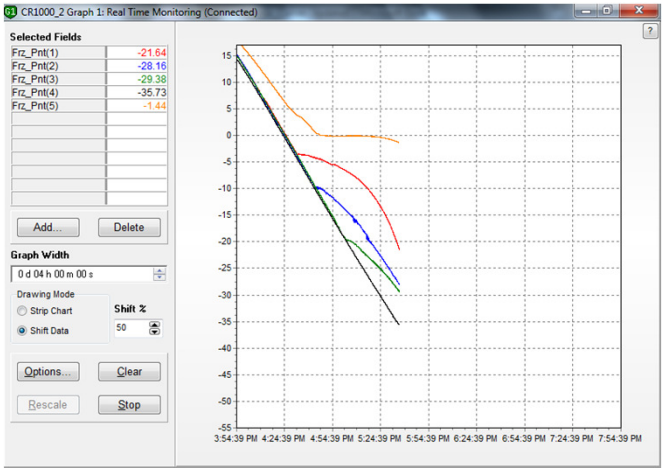
- **Category A:** solid complex chlorides/minerals (CCM) based products were used as-received for testing purposes.
  - Product A1 - *Ice Slicer®;*
  - Product A2 - *Thawrox®*
- **Category B**: Liquid agro-based deicers which were prepared by mixing the vendor-provided concentrates with a 23.3 wt. % 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*

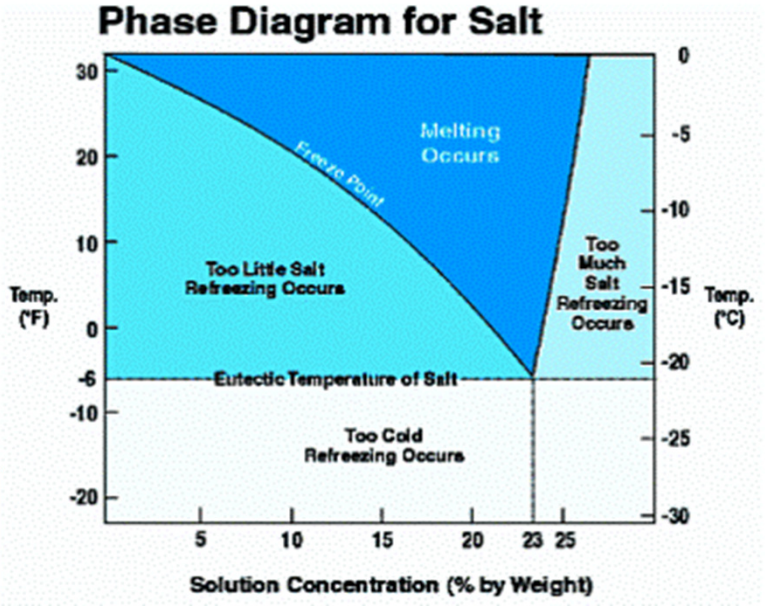
Product Name	Manufacturer	Major Components	% Added to salt brine*	Description	Reference	Chloride Concentration from Mohr's chemical titration method	
Ice Slicer®	Redmond Minerals, Inc	NaCl: 90-98%; Trace amounts of $MgCl_2$, KCl, $CaCl_2$	As-Received	Blend of complex chlorides	MSDS	58.90%	Reagent grade NaCl, features a theoretical Cl content of 60.7%.
Thawrox®	North American Salt Company	NaCl: 60-100%; Thawrox Treated Salt Liquid Additive: 1-5%		Thawrox treated rock salt	MSDS	59.60%	
Beet 55	Smith Fertilizer and Grain	NaCl: 17.2%	30 (70% salt brine)	Beet based product	PNS Qualified product list: Category A3	0.25 M	Note: For 23.3% NaCl reagent grade would feature Cl content of 3.99 M
Boost™ SB	America West	NaCl: 18.8%; $CaCl_2$: 2.3%	20 (80% salt brine)	organic agricultural by-product with salt brine	PNS Qualified product list: Category A2	0.62 M	
Snow Melt®	Smith Fertilizer and Grain	Glycerin:15 - 20%; Polyether Polymer: 10 - 20%; Sodium Lactate: 4 - 10%; Sorbitol: 2-4%; Sodium Formate: 1 - 4%; 1, 2 - Butanedoil: 1 - 4%	30 (70% salt brine)	Corn based product	MSDS	0.05 M	
Geomelt® 55	SNI Solutions	NaCl: 18.1%	30 (70% salt brine)	Beet based product	PNS Qualified product list: Category A3	0.55 M	
Apogee™	Envirotech Services, Inc.	Glycerin: % unknown (Proprietary)	As-Received	Glycerin based product	MSDS	1.05 M	
Boost™ CCB	America West	organic ag by-product: % unknown $CaCl_2$: % unknown (Proprietary)		organic agricultural by-product with $CaCl_2$	MSDS	0.62 M	
Ice Ban® 305	GMCO	Ice Ban Concentrate: 10 - 20%; $MgCl_2$ (30% Solution): 80 - 90%		Corn based product	MSDS	1.11 M	
ThermaPoint IB 7/93	Millennium Roads, Inc	$CaCl_2$: 93% ; OBFE (Organic based performance enhancer (Proprietary))": 7%		Other (Lignin based)	MSDS	0.73 M	

Results – Laboratory Testing

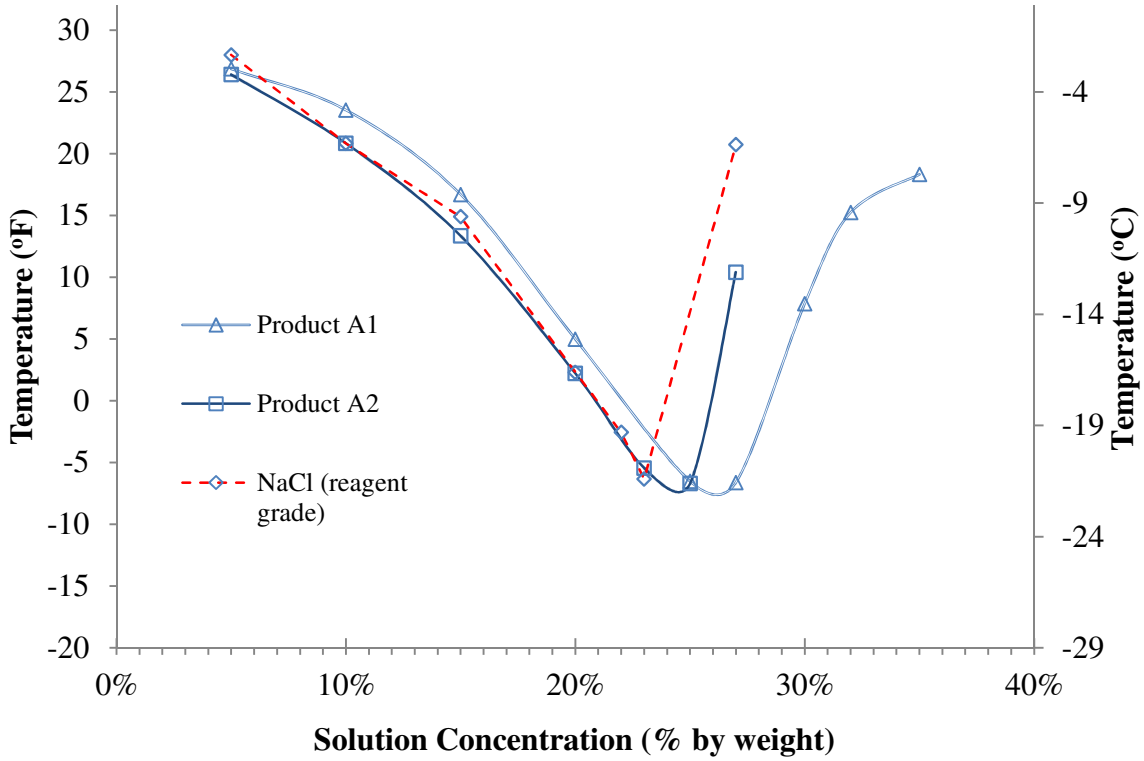
Lowering the freezing point of water







Lowering the freezing point of water

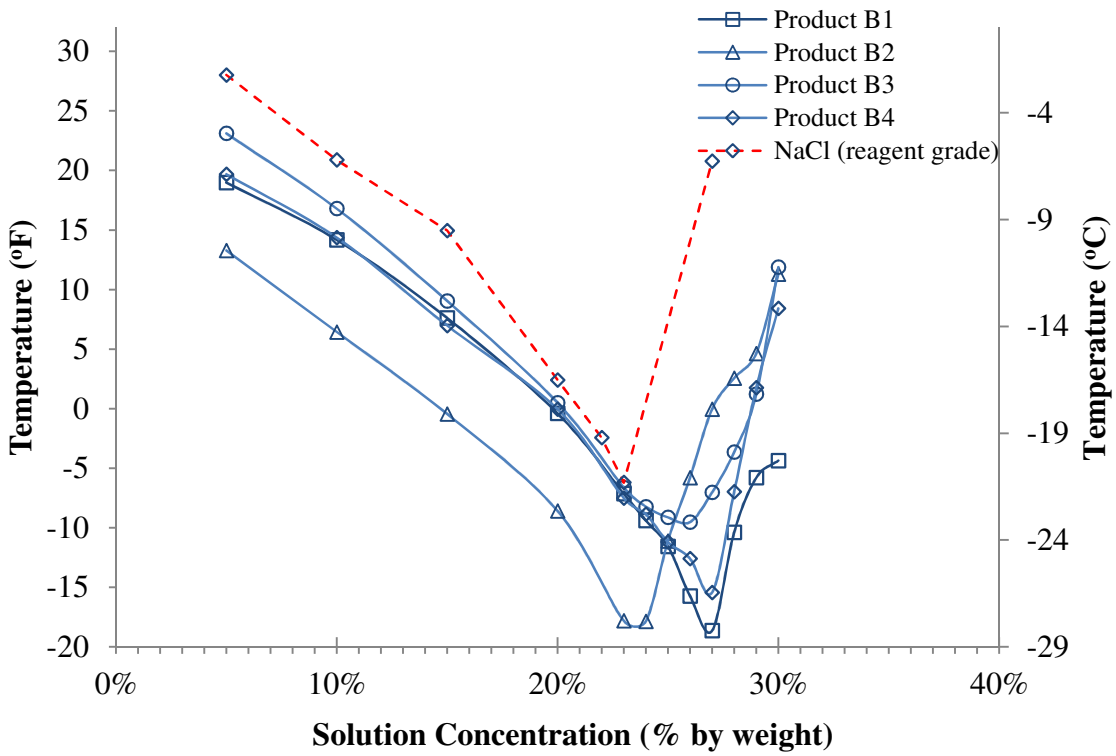


The eutectic curve shows…

- CCM based products

<u>Do not significantly</u> reduce the freezing point of water compared to NaCl.

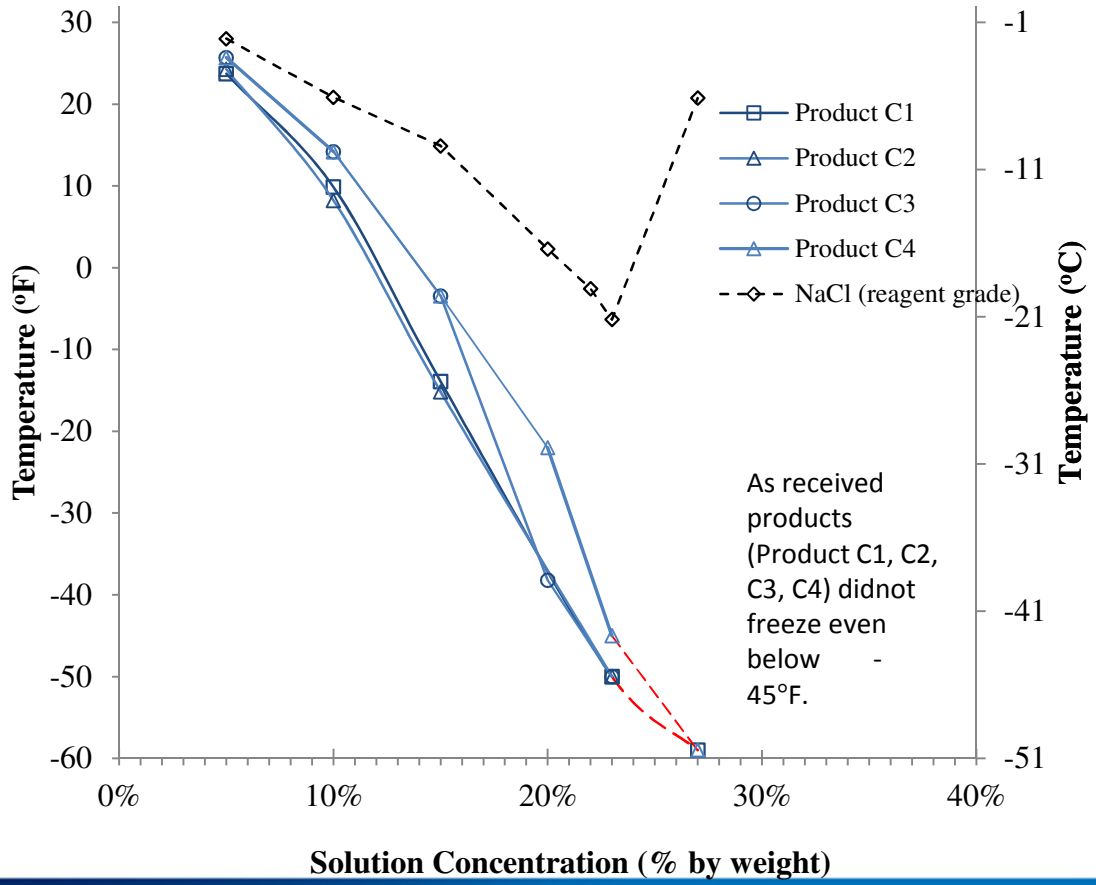
Lowering the freezing point of water



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..

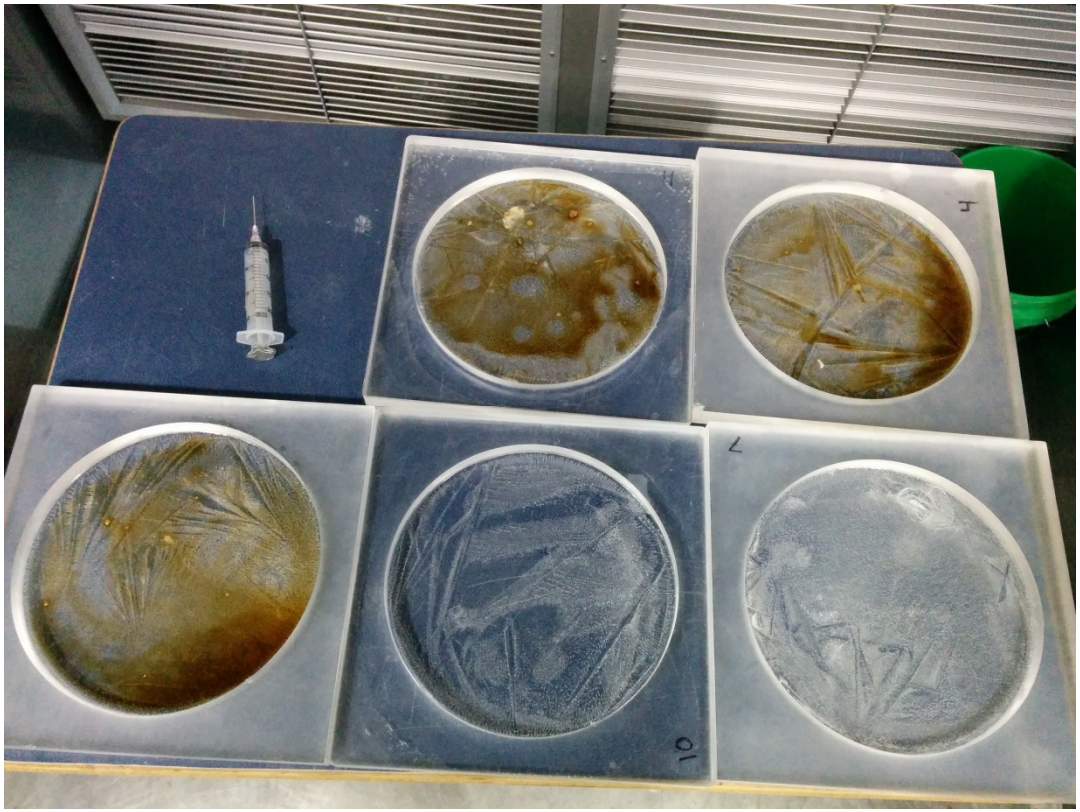
- Agro-based products (as-received) s**ignificantly lowered** the freezing point of water compared to NaCl.

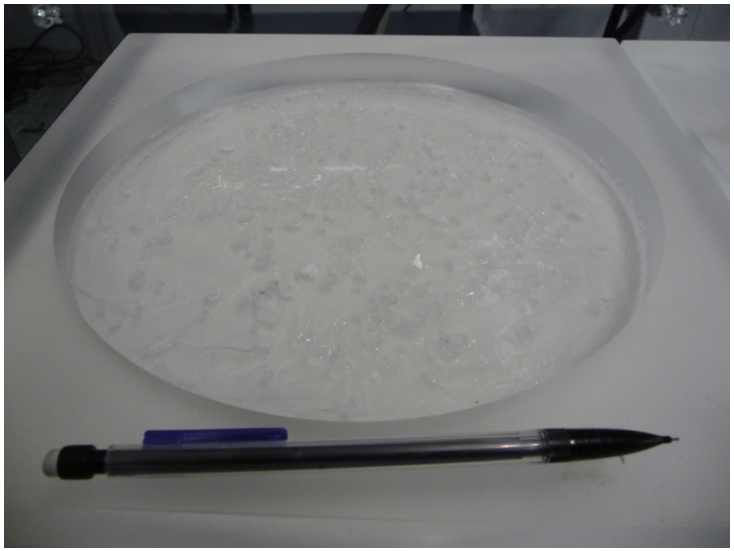
Do these products aid in lower the freezing point of water?

- CCM no, but this make sense
- Agro-based products, yes they do.

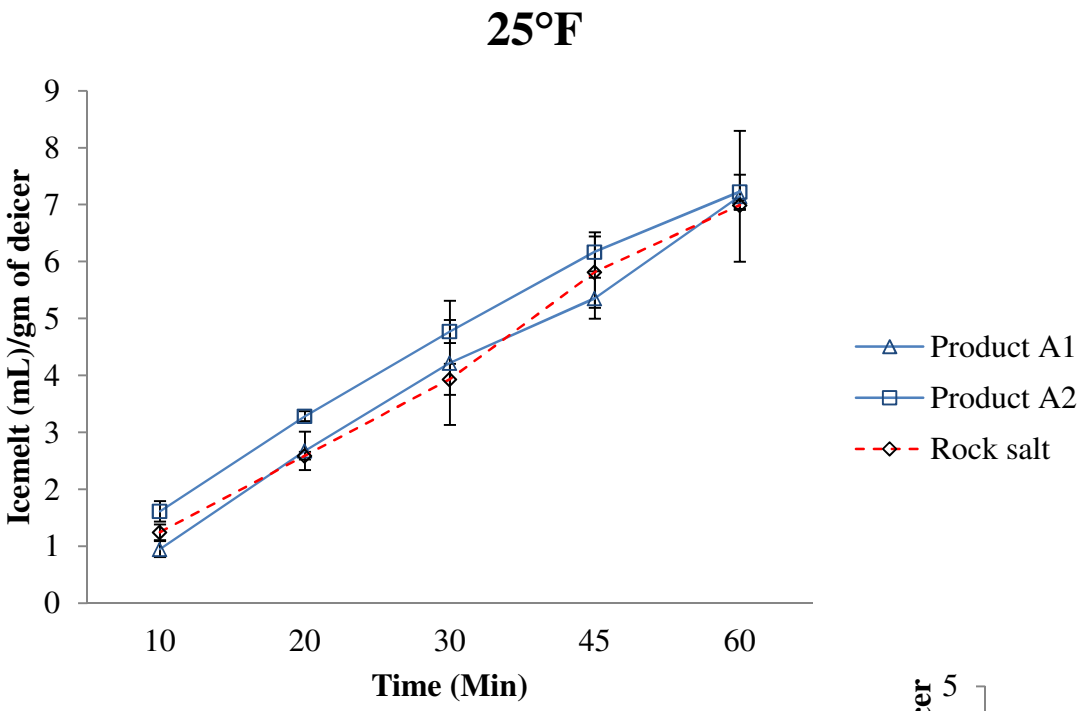
Results – Laboratory Testing

Improve ice melting capacity

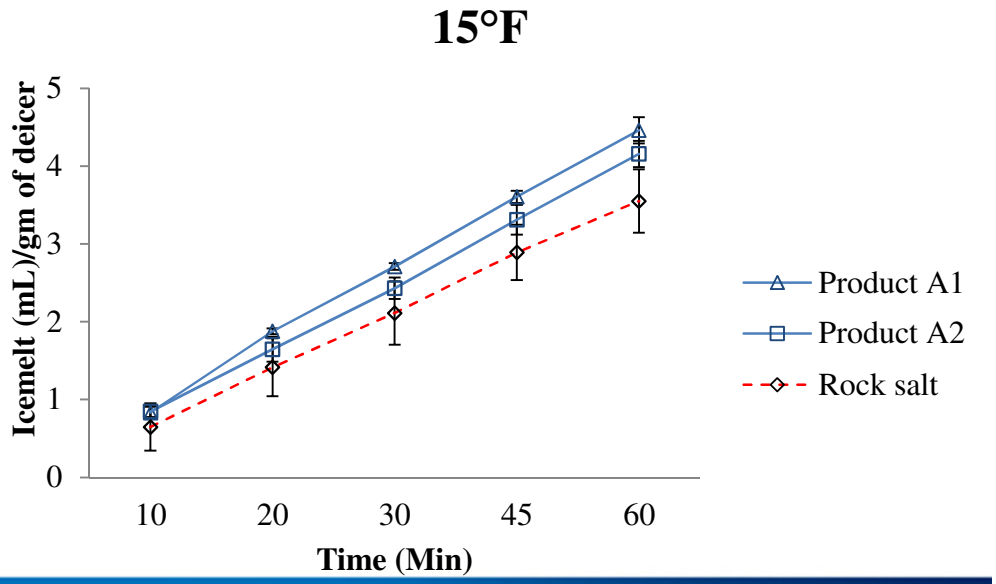




Ice Melting Test Results

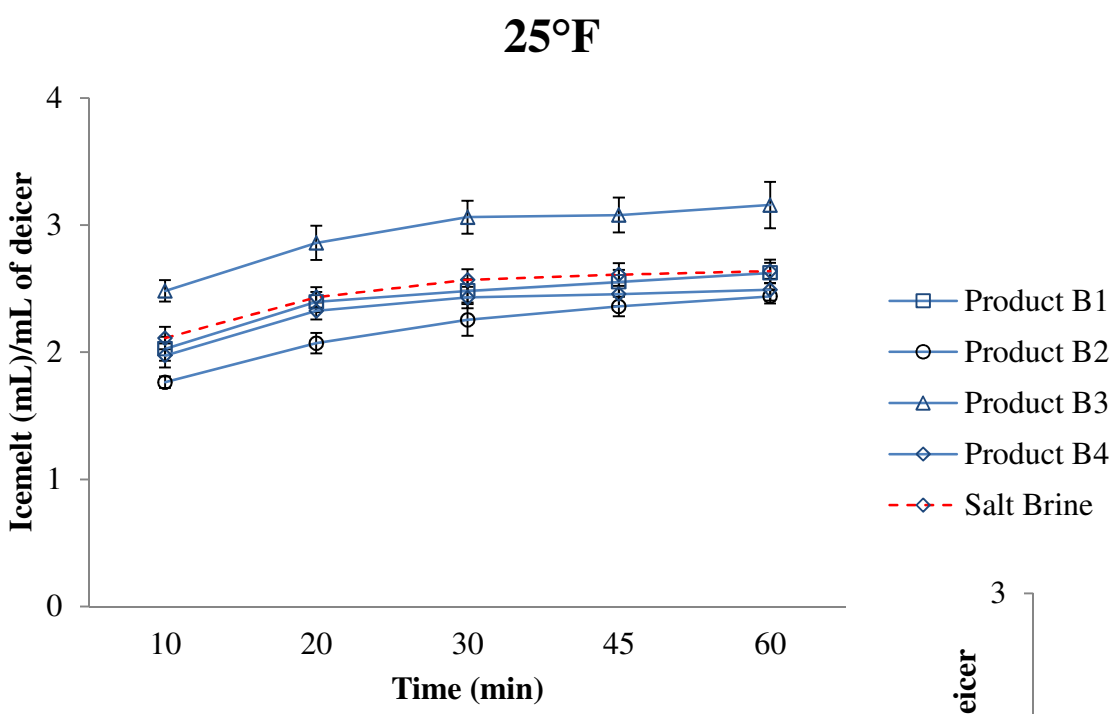


CCM products did melt more ice at 15°F, but not at 25°F.

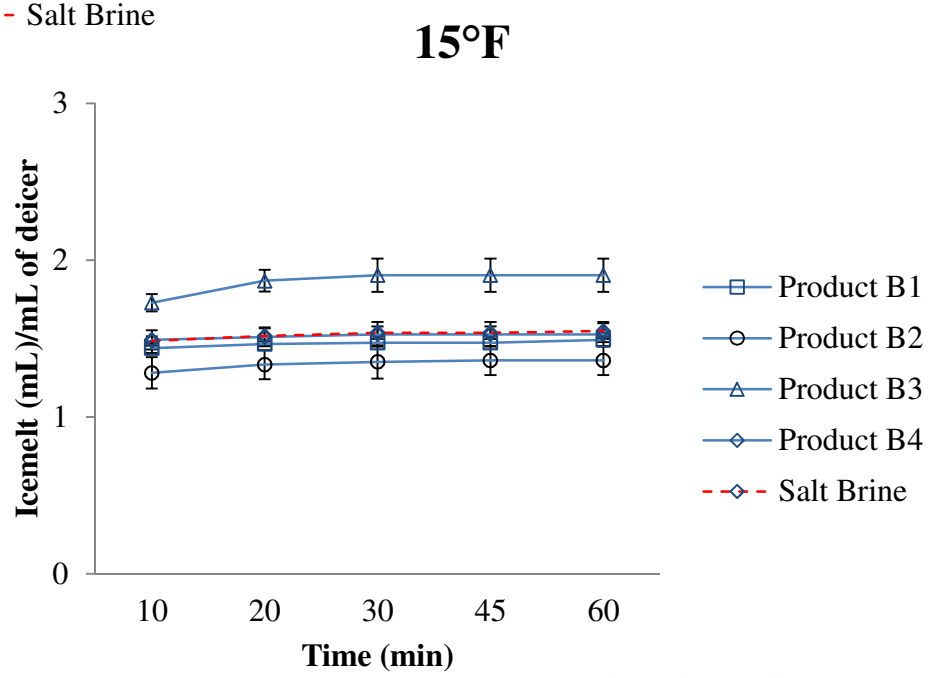


Category A: CCM

Ice Melting Test Results

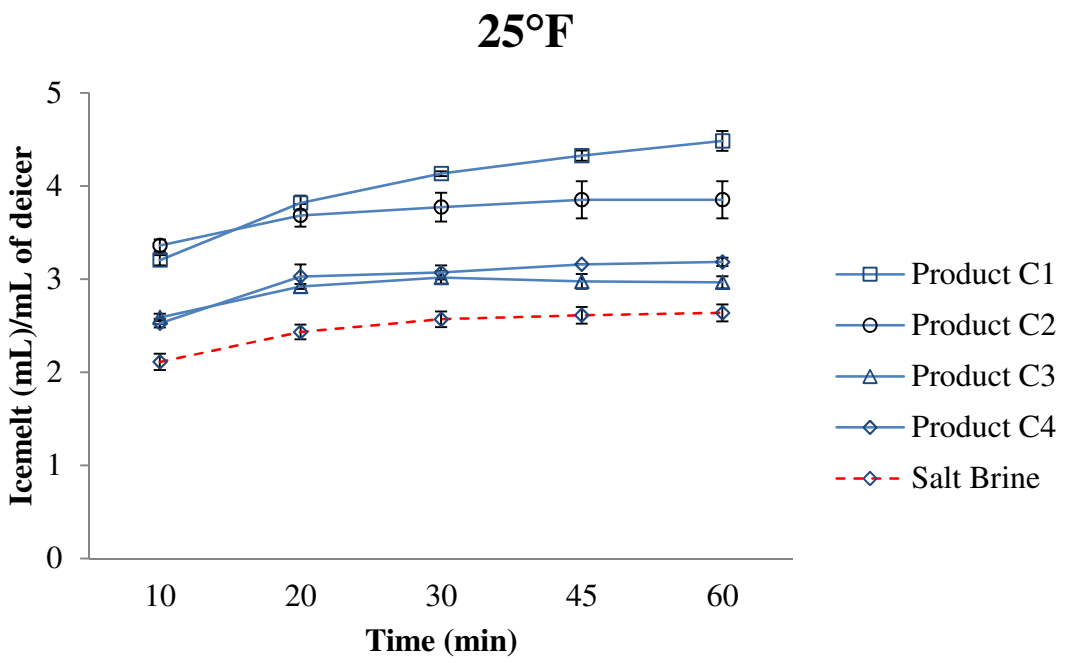


Agro-based products blend with salt brine did not produce more melt than salt brine alone except for one product (B3).



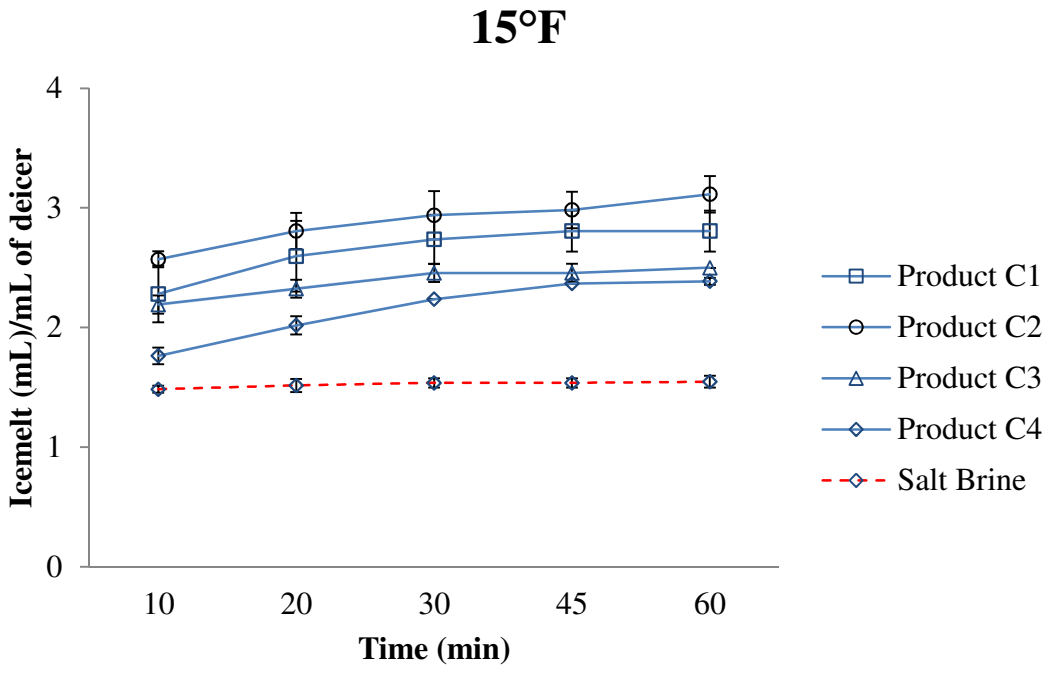
Category B: Agro-based & Salt brine

Ice Melting Test Results



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

		Characteristic Temperature Peak		Enthalpy of fusion (J/g)		Eutectic Curve		Ice Melt		
Product	Original State	Average (°F)	COV	Average	COV	Eutectic Temperature °F	Eutectic Concentration (wt.%)	60 min @ 25°F	60 min @ 15°F	60 min @ 5°F
								(ml/g for solid, ml/ml for liquid)		
Product A1	Solid	28	20%	162.2	8%	-6.61	27%	7.15	4.46	1.53
Product A2	Solid	22.9	1%	89.4	4%	-6.70	25%	7.23	4.16	-
Product B1	Liquid	24.8	3%	138.7	3%	-18.64	27%	2.62	1.49	-
Product B2	Liquid	30.4	42%	156.1	7%	-17.86	24%	2.44	1.36	-
Product B3	Liquid	25.4	4%	136.1	6%	-9.52	26%	3.16	1.90	-
Product B4	Liquid	28.1	23%	176.1	4%	-15.43	27%	2.49	1.53	1.14
Product C1	Liquid	16.2	2%	120.9	6%	< 45	as-received	4.48	2.81	1.58
Product C2	Liquid	6.1	6%	124.6	4%	< 45	As Received	3.85	3.11	-
Product C3	Liquid	8.9	4%	161.1	10%	< 45	As Received	2.96	2.50	-
Product C4	Liquid	6.4	5%	131.5	6%	< 45	As Received	3.18	2.39	1.58
NaCl (reagent)	Solid	23.5	2%	197.7	3%	-6.34	23%	-	3.90	-
Rock salt	Solid	-	-	-	-	-	-	6.99	3.55	1.72
Salt Brine (Rock 23.3 wt%)	Liquid	-	-	-	-	-	-	2.64	1.55	1.10

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.

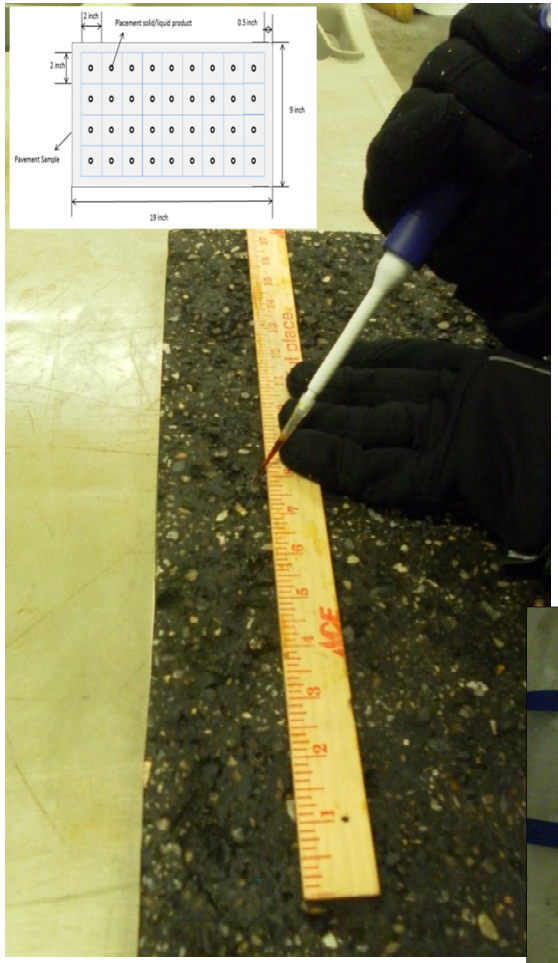
When considering the lower freezing of Agro-based products but also the small ice melting capacity…What is going on.

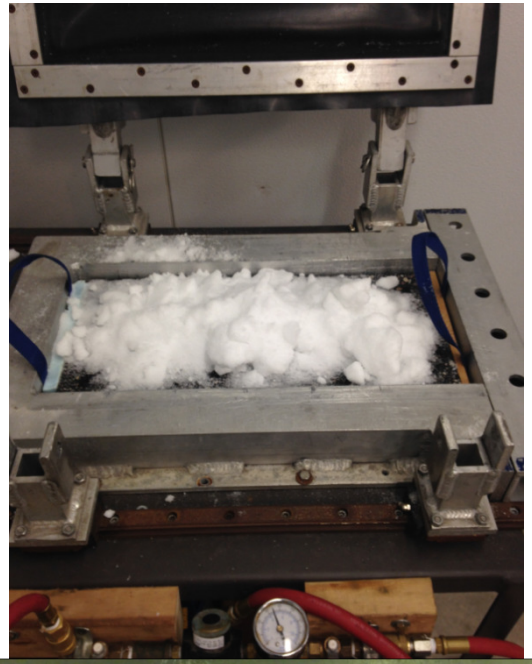
- Agro-based products may act as ice crystal nucleation point inhibitors, delaying the formation of ice compared to salt brine.
  - Cryoprotectants are substances that prevent ice nucleation.
  - The agro-based products significantly reduce the freezing point of water, therefore could act as cyroprotectants,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

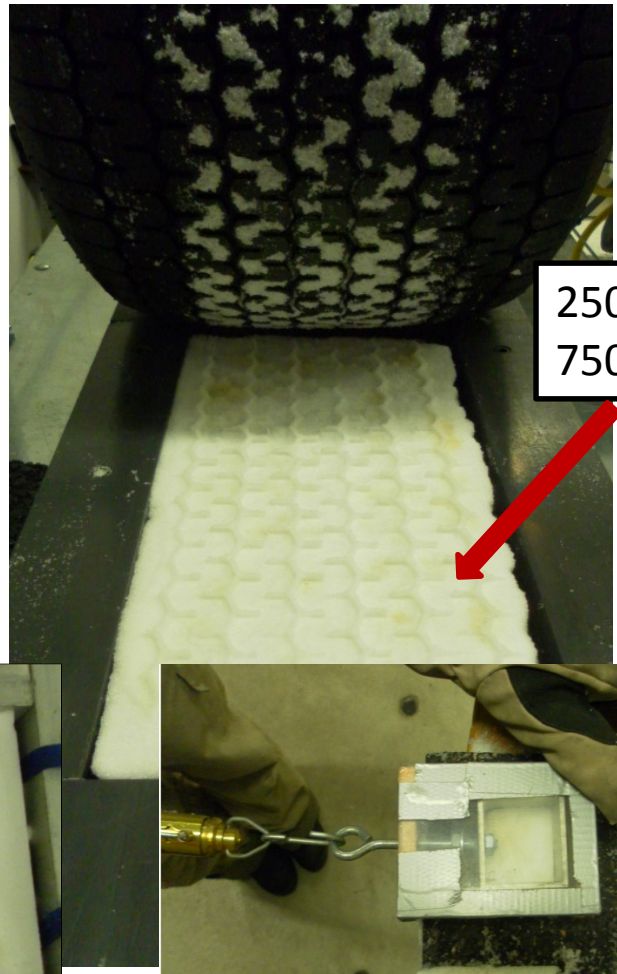
Improved the ice melting capacity

- CCM based products
  - produced more ice melt than the NaCl at 15^{o}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^{o}F, 15^{o}F and 5^{o}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).

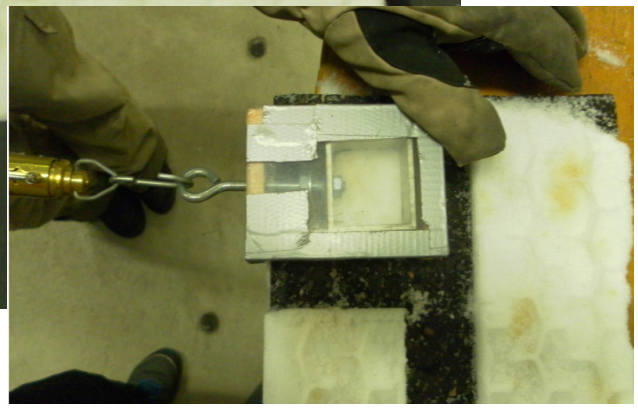
Weakening of ice bond to pavement



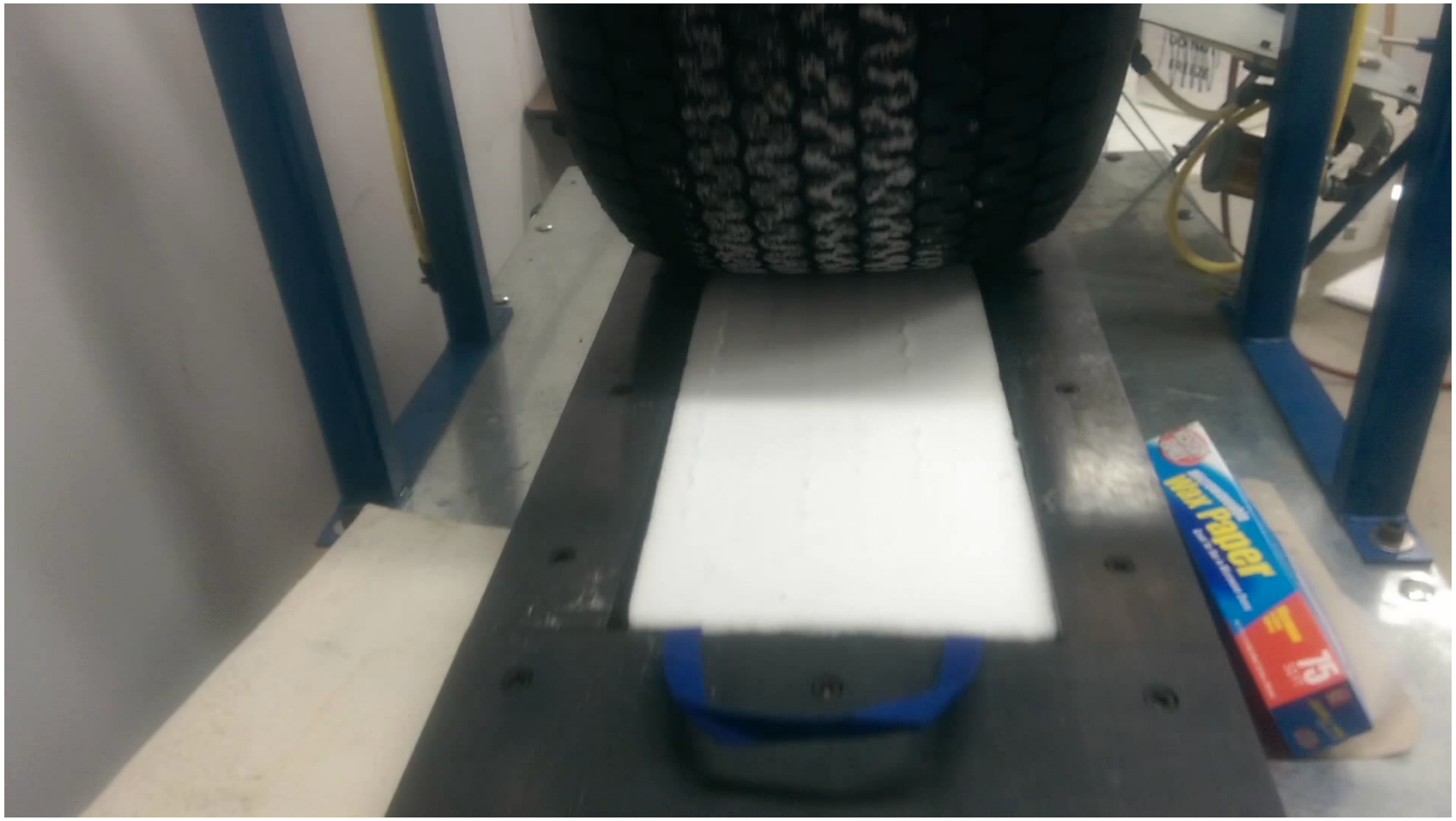


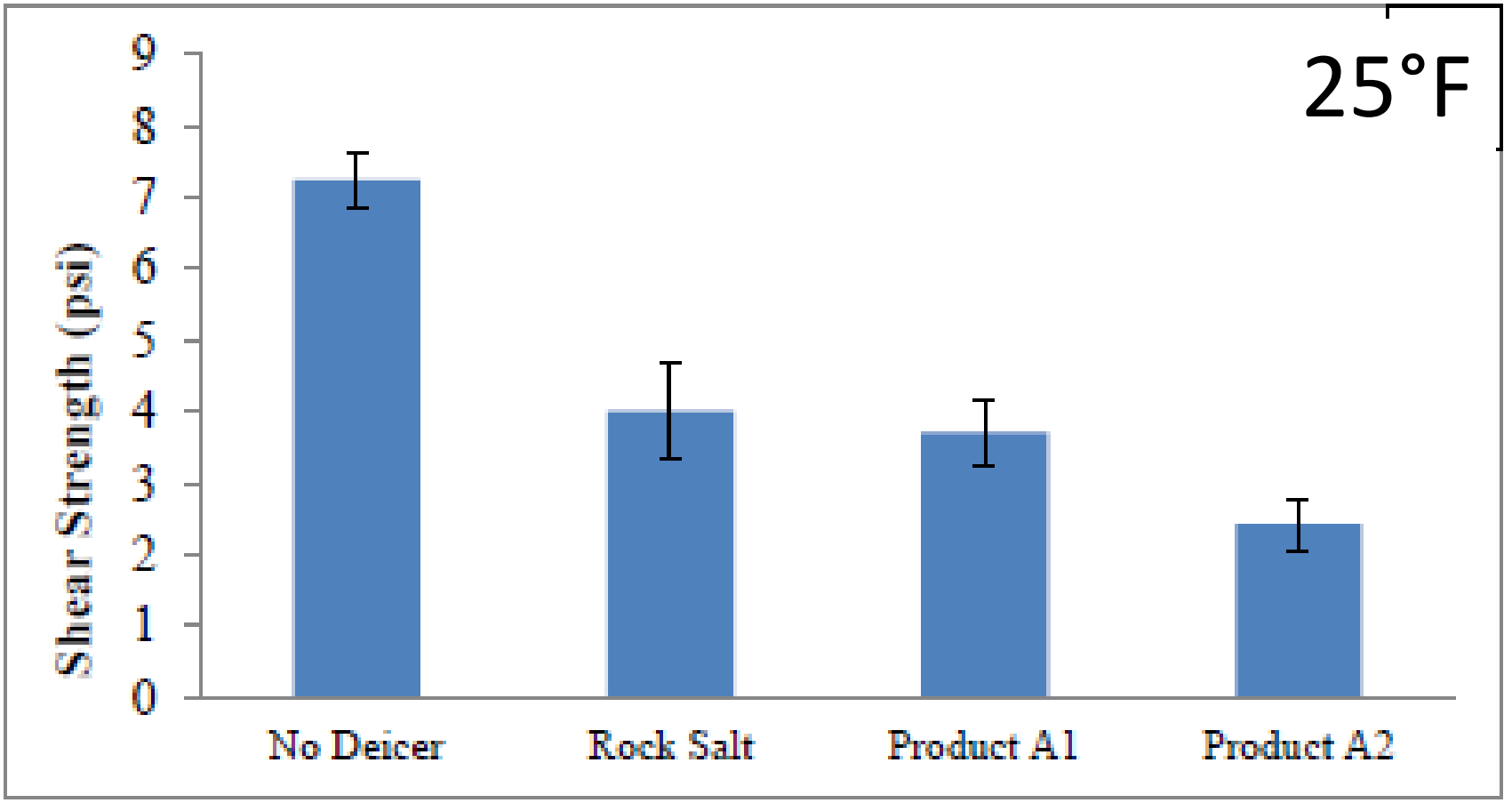


250, 500,
750 passes

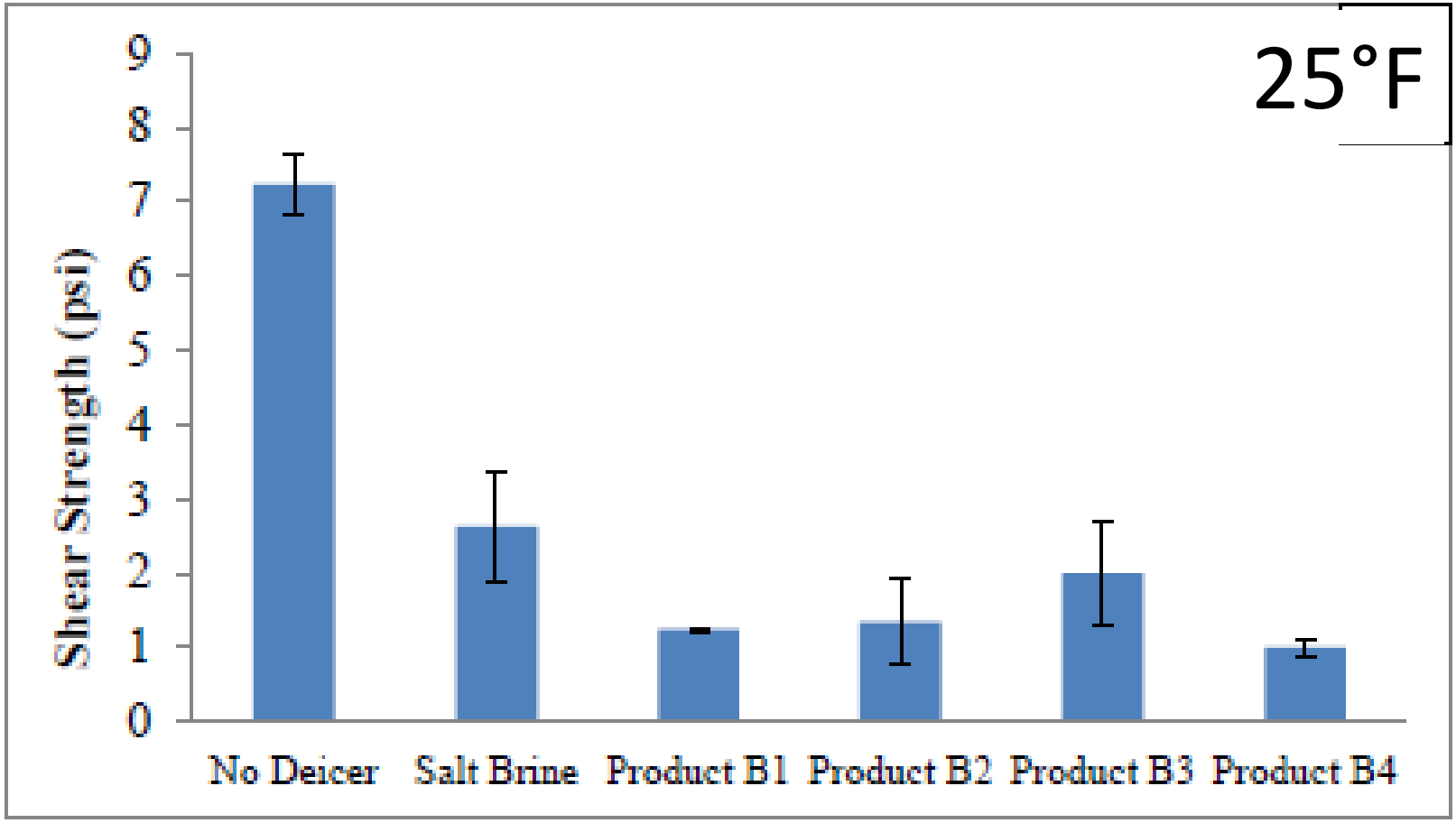


Video of Trafficking

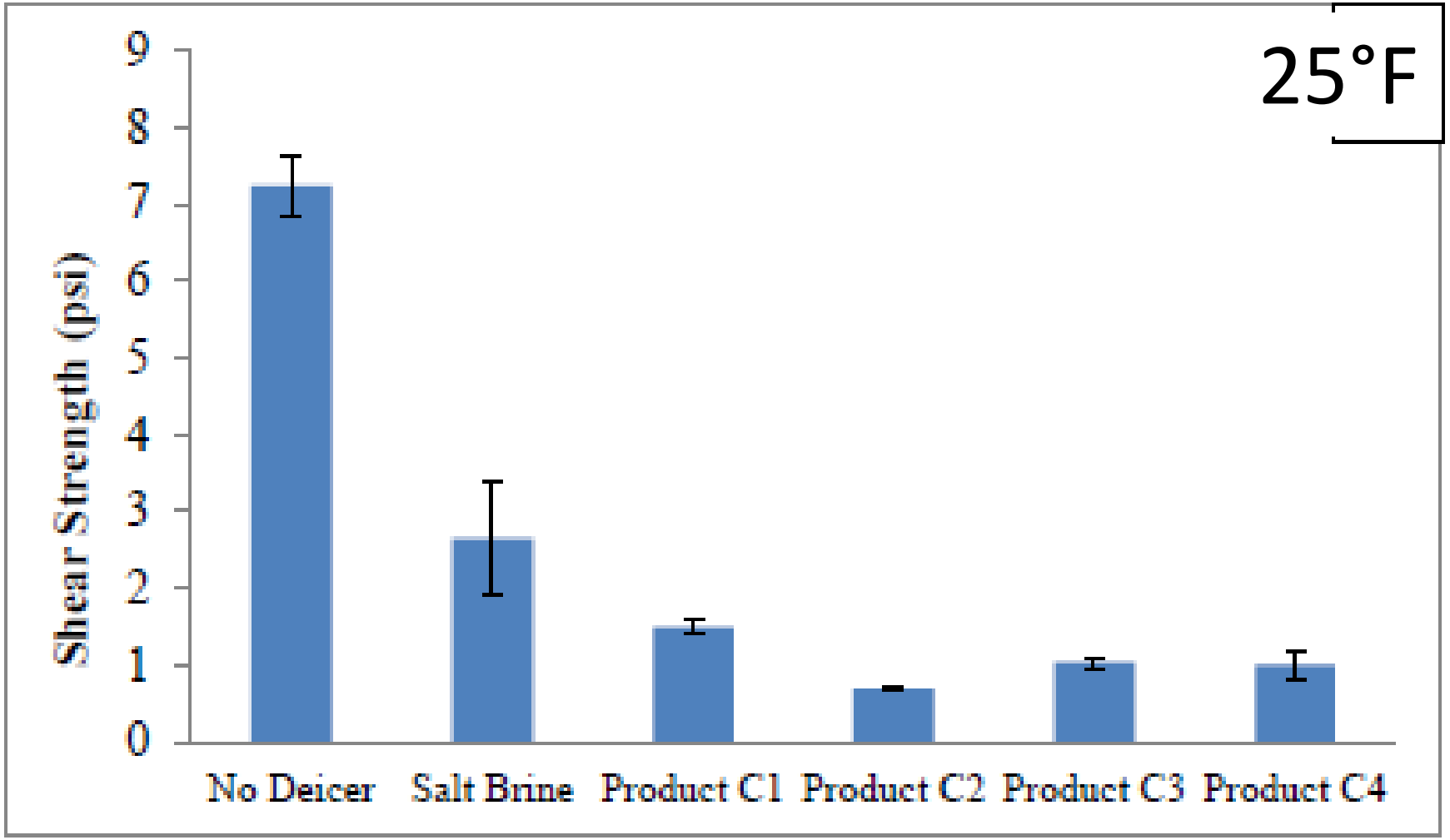




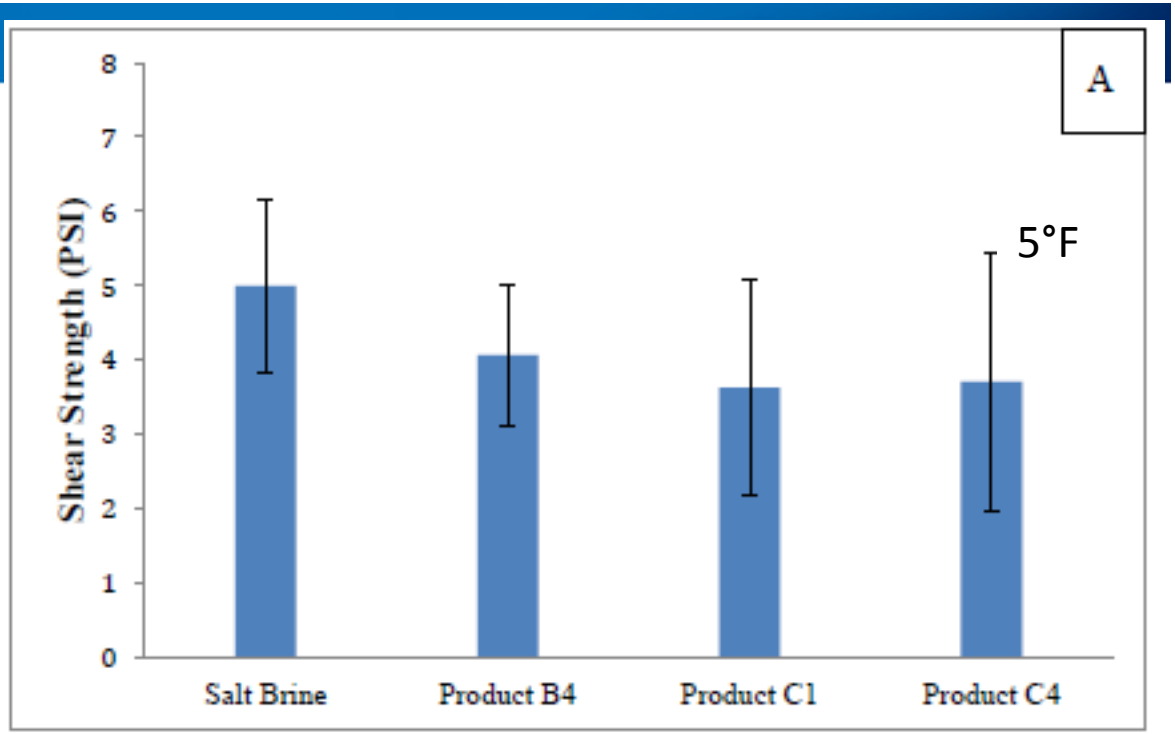
For CCM products is was slightly easier to plow snow off the pavement.

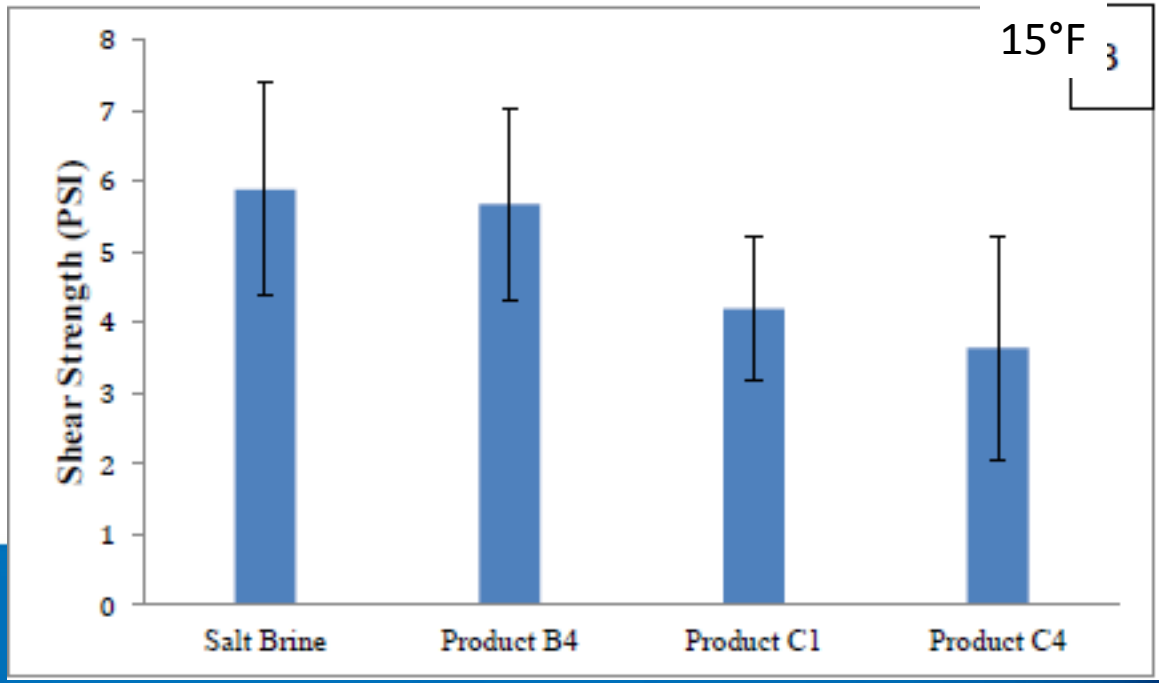


For agro-based products blended with salt brine it was significantly easier to plow snow off the pavement.



For agro-based products as recieved it was significantly easier to plow snow off the pavement.


A
5°F
Shear Strength (PSI)
0
1
2
3
4
5
6
7
8
Salt Brine
Product B4
Product C1
Product C4


15°F
Shear Strength (PSI)
0
1
2
3
4
5
6
7
8
Salt Brine
Product B4
Product C1
Product C4

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

Product	Concentration	Temperature	Viscosity (mm^2/s)	Specific Gravity
Product B4	70% salt brine and 30% agro-based concentrate	68°F	2.4	1.20
		25°F	5.5	1.21
		15°F	7.3	1.21
		5°F	9.2	1.21
Product C1	As-received	68°F	23.0	1.22
		25°F	102.9	1.23
		15°F	169.4	1.24
		5°F	283.1	1.24
Product C4	As-received	68°F	9.2	1.33
		25°F	16.4	1.33
		15°F	21.8	1.34
		5°F	25.5	1.34
Salt Brine	23%.wt of Rock salt	68°F	1.5	1.17
		25°F	2.8	1.18
		15°F	4.1	1.19
		5°F	4.6	1.19

Agro-based products have a higher viscosity than salt brine.

Weakening of ice bond to pavement

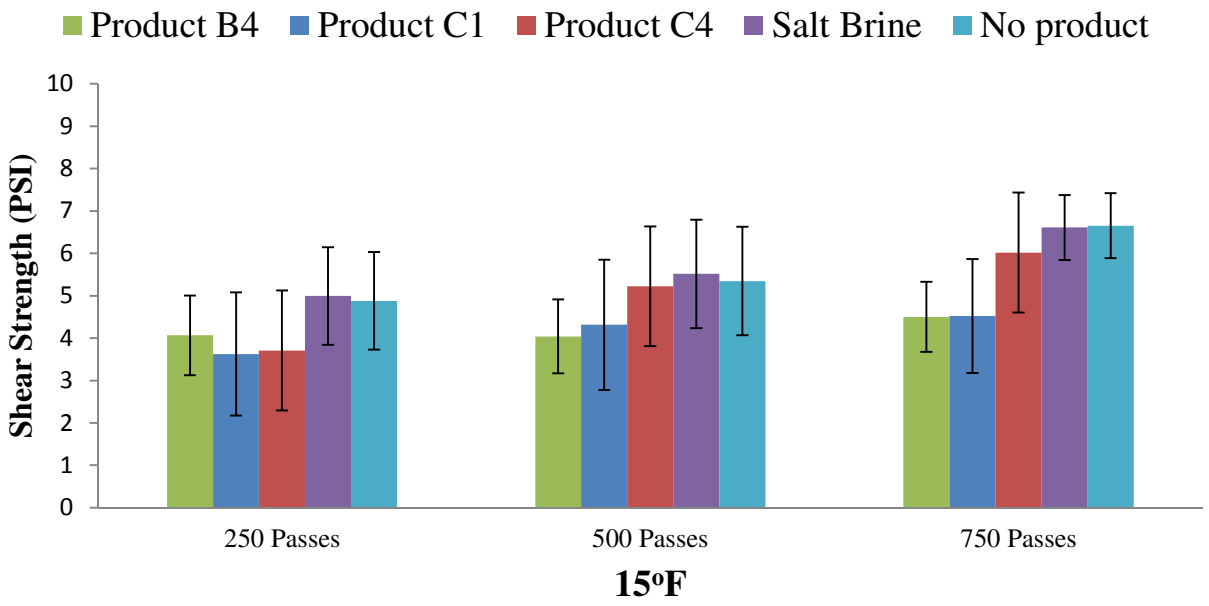
The addition of agro-based products to salt brine **increased** the overall **viscosity** of the products.

So what does this mean…

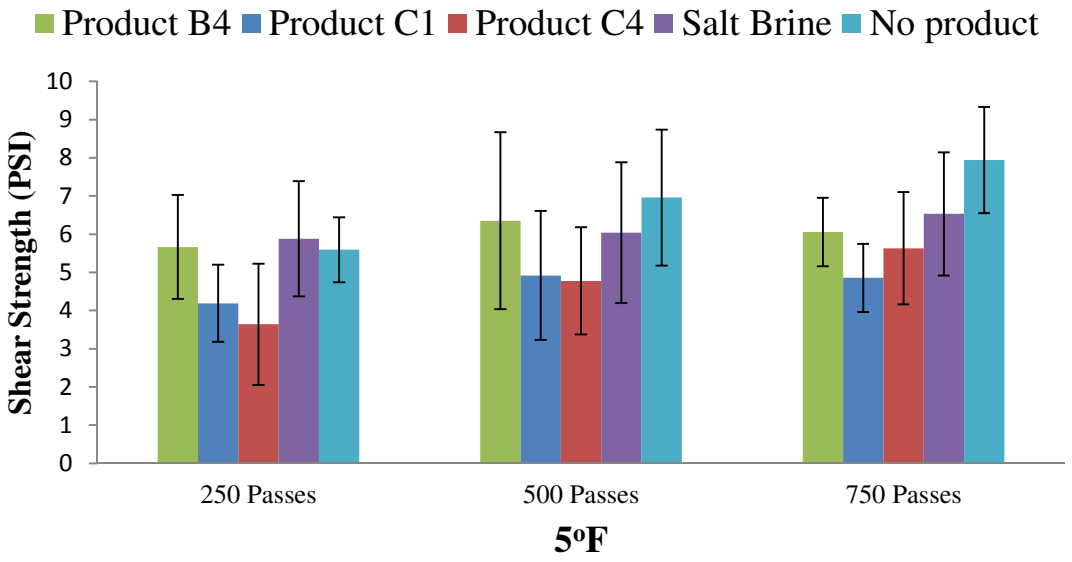
Agro-based products with higher viscosity than salt brine may have slower grain boundary penetration than the salt brine with lower viscosity.

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.

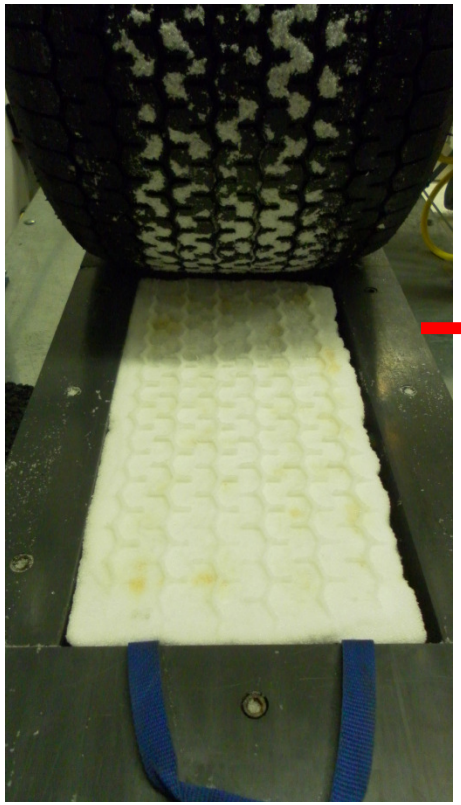
Improving product longevity on the pavement

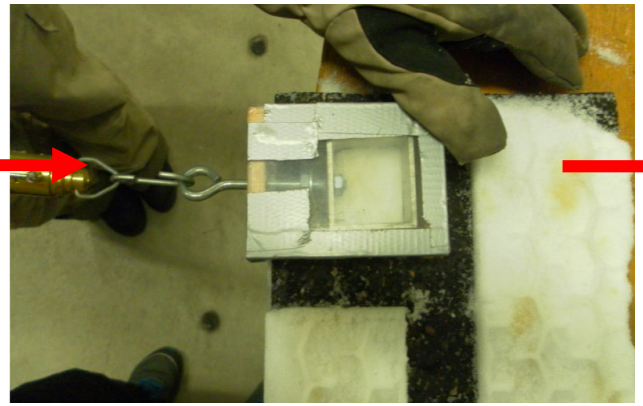


General trend of increased shear strength required to plow the snow off the pavement with time.



Where is the product?

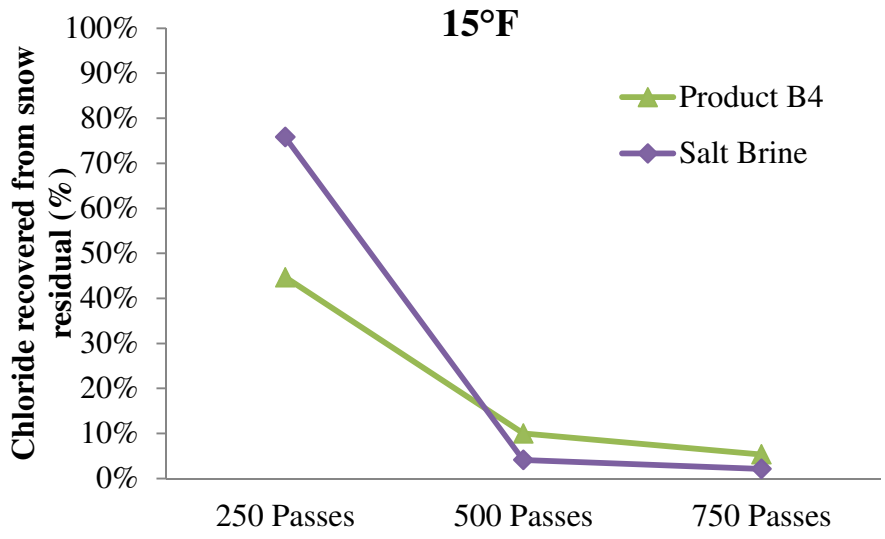




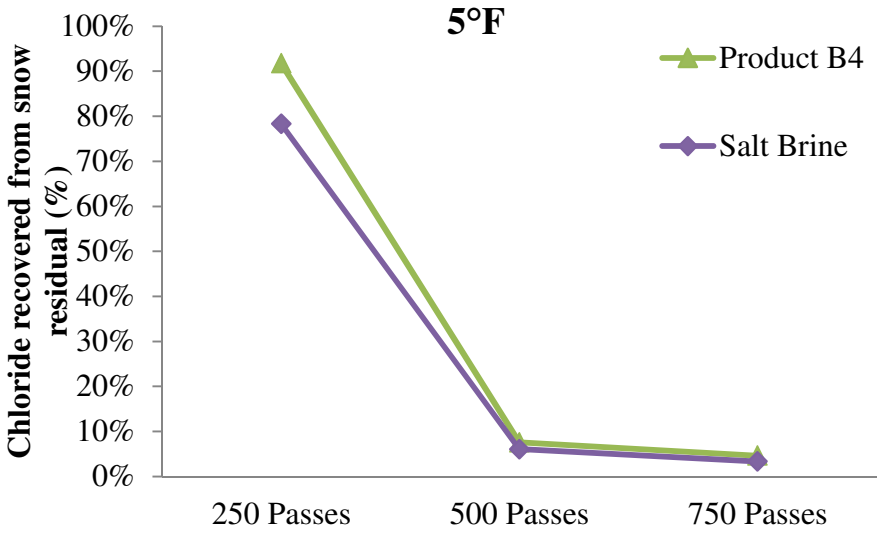
1. Collected snow from the pavement surface.

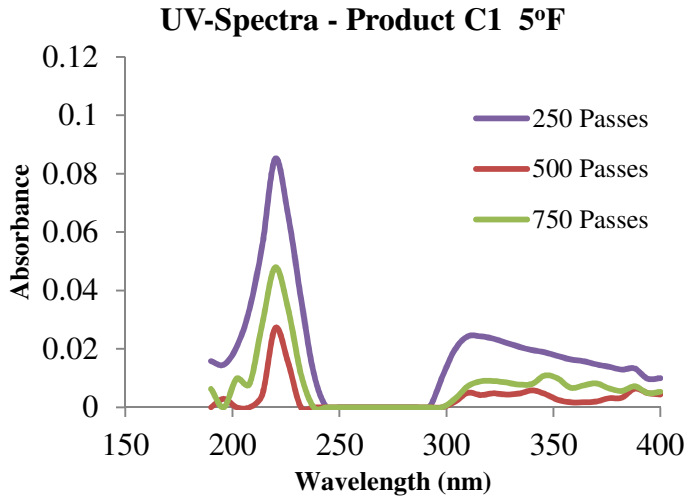
2. Measured the amount of product in the snow.

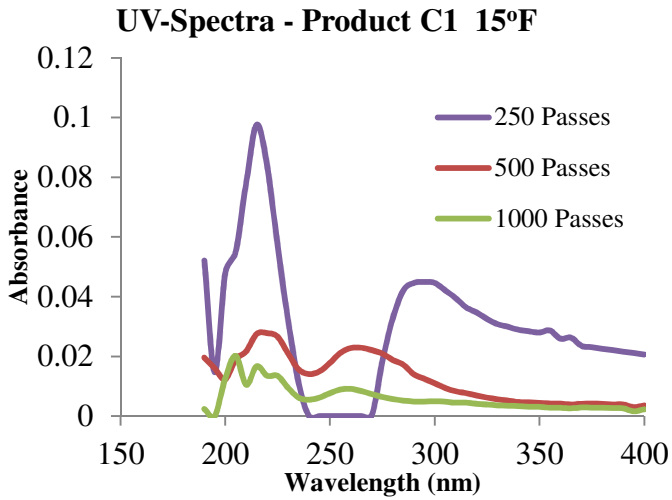
3. Compared amount of product wicked up into the snow pack vs. amount remaining on the pavement surface.

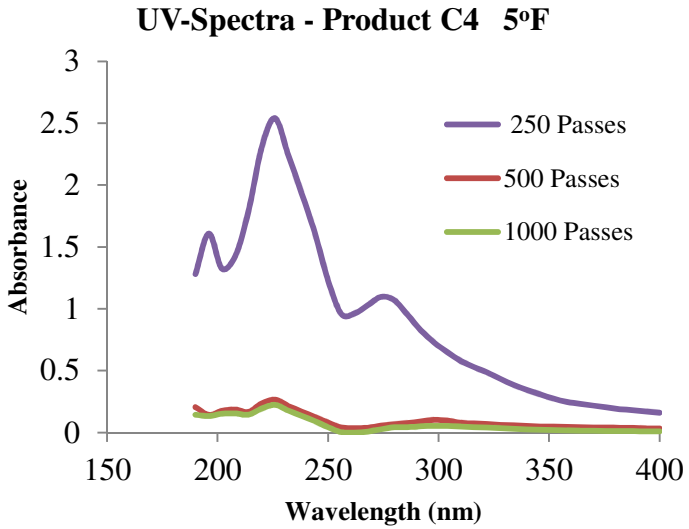


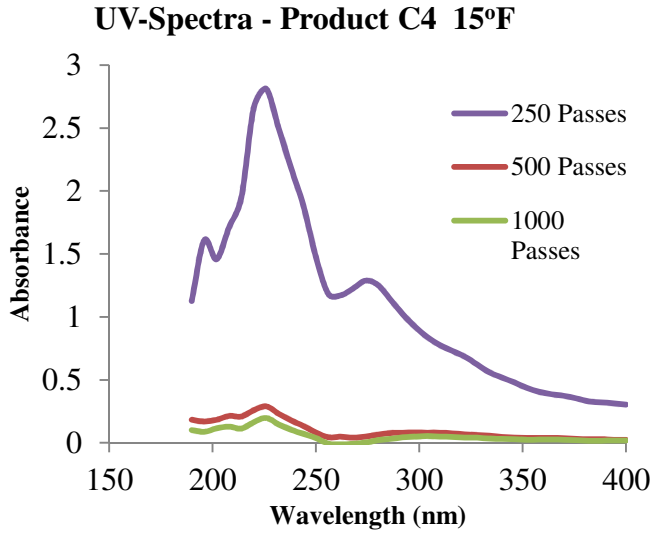
45 – 90% of applied product is removed with the snow in the first plowing.




UV-Spectra - Product C1 5ºF
Absorbance
0.12
0.1
0.08
0.06
0.04
0.02
0
150
200
250
300
350
400
Wavelength (nm)
250 Passes
500 Passes
750 Passes


UV-Spectra - Product C1 15ºF
Absorbance
0.12
0.1
0.08
0.06
0.04
0.02
0
150
200
250
300
350
400
Wavelength (nm)
250 Passes
500 Passes
1000 Passes

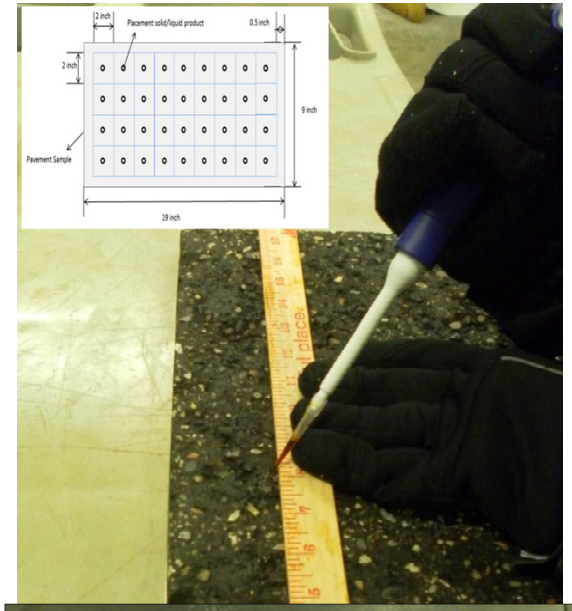

UV-Spectra - Product C4 5ºF
Absorbance
3
2.5
2
1.5
1
0.5
0
150
200
250
300
350
400
Wavelength (nm)
250 Passes
500 Passes
1000 Passes

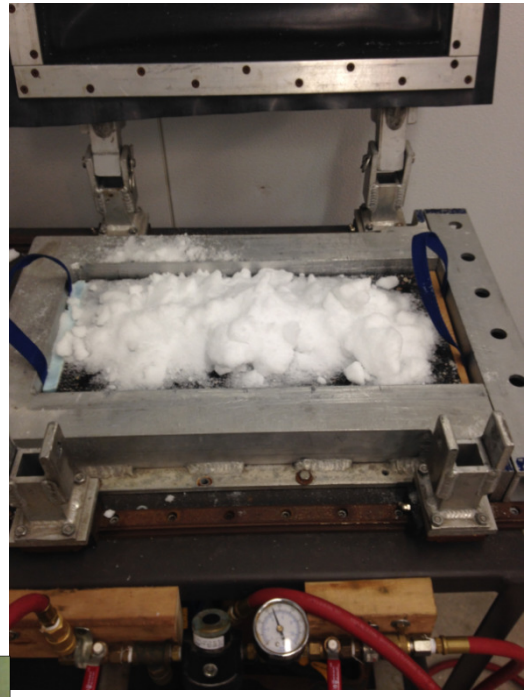

UV-Spectra - Product C4 15ºF
Absorbance
3
2.5
2
1.5
1
0.5
0
150
200
250
300
350
400
Wavelength (nm)
250 Passes
500 Passes
1000 Passes

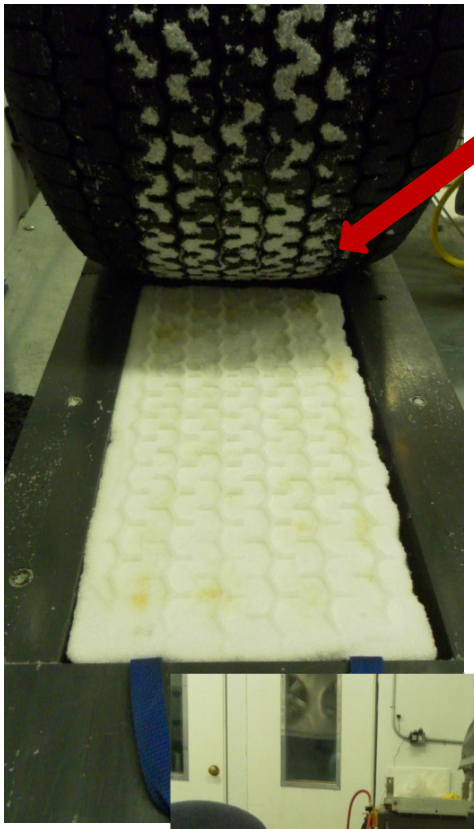
Do these products aid in improving product longevity on the pavement?

- 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.

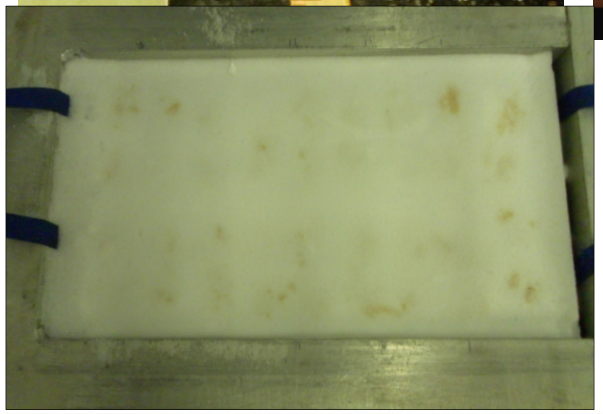
Prevention of ice formation/refreezing

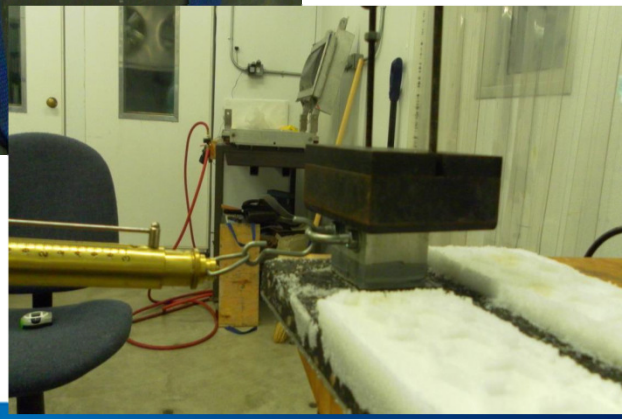




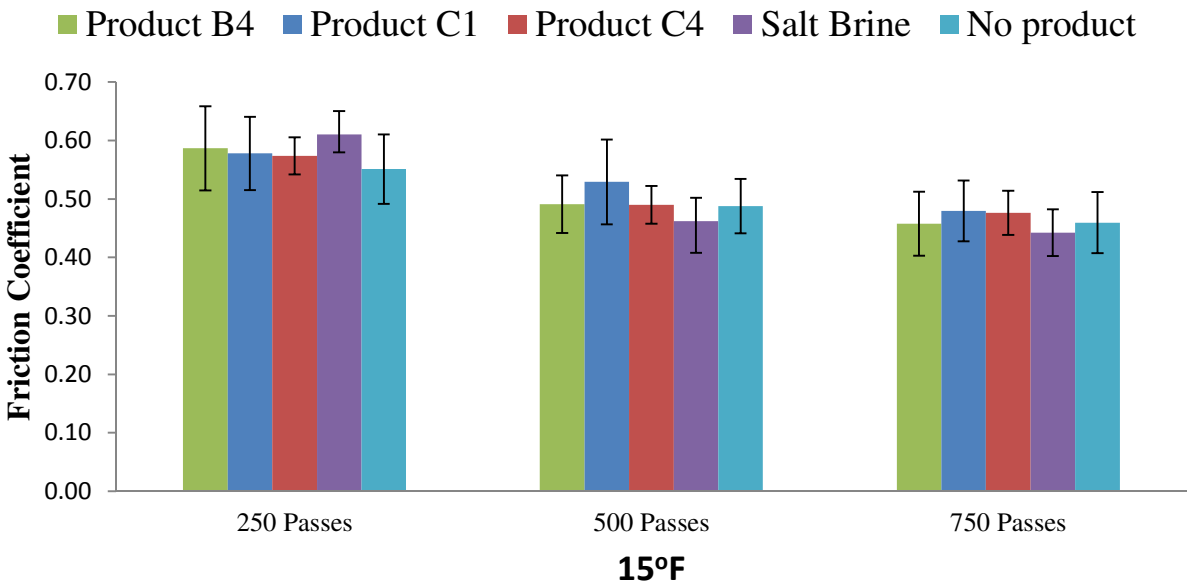


250, 500,
750 passes



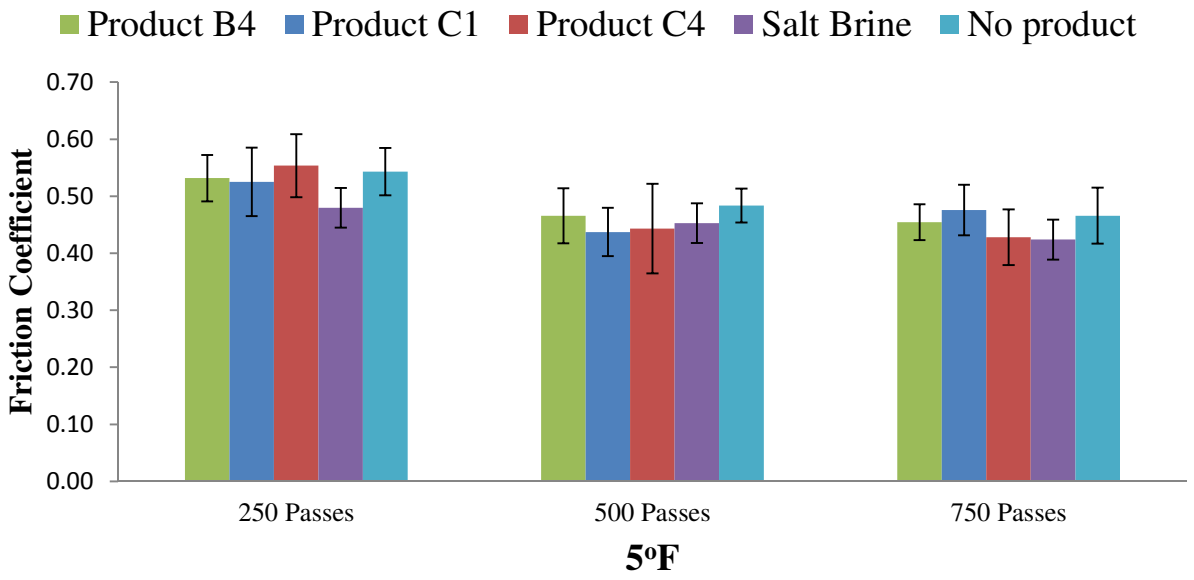


Prevention of ice formation/refreezing



15°F

General trend of decreasing friction coefficient over time => its getting more slippery overtime.



5°F

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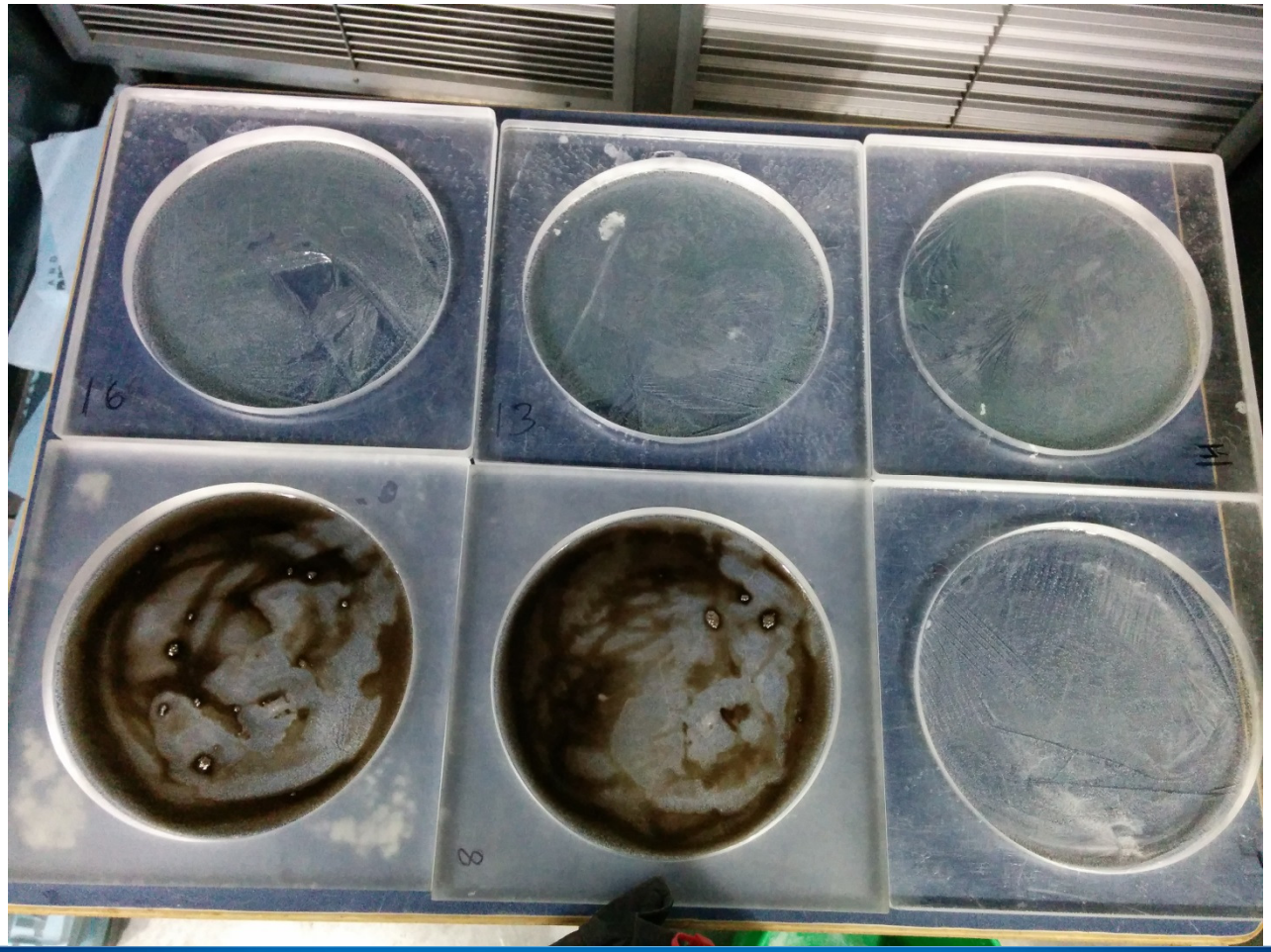
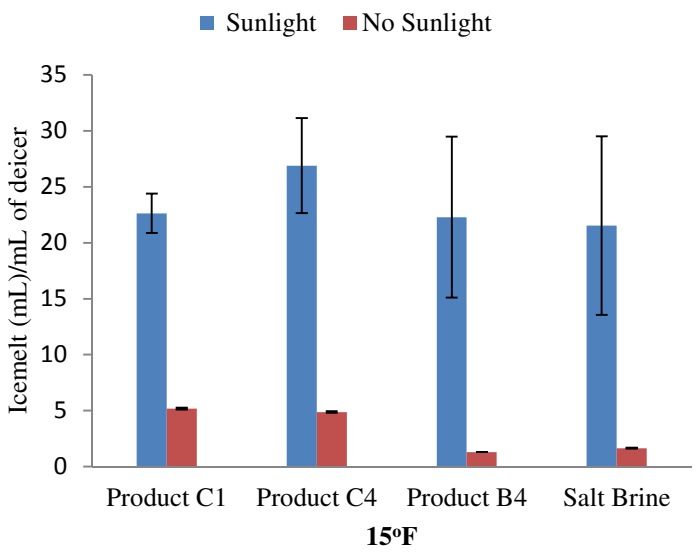
Do these products aid in prevention of ice formation/refreezing?

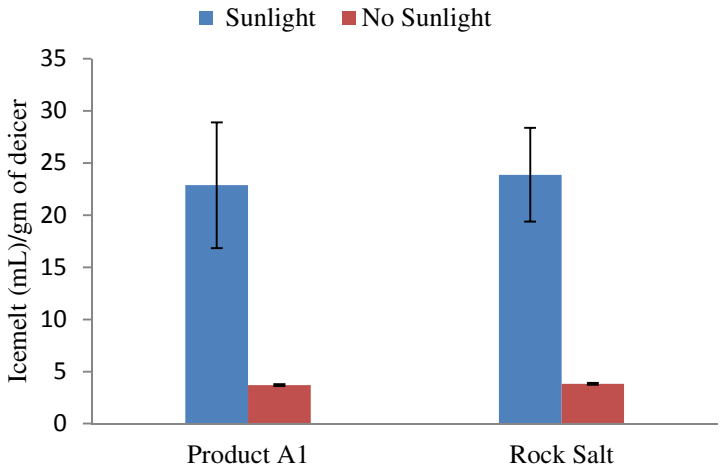
- Agro-based products appear to aid in reducing ice formation, or maintain friction with only a small decrease over time with trafficking.

Absorbance of sunlight

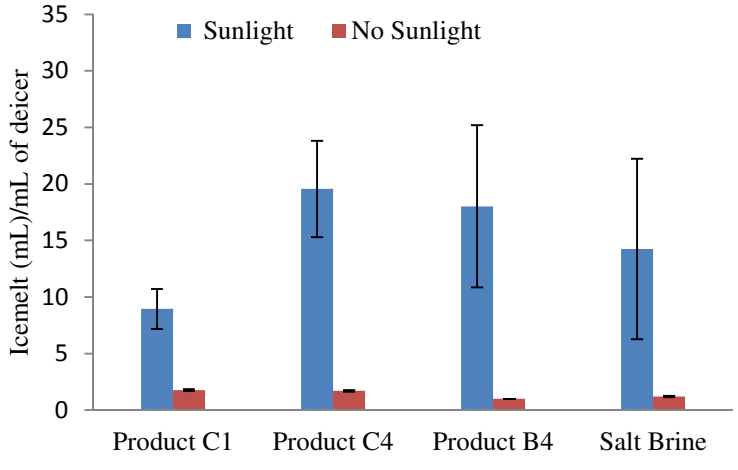



Sunlight
No Sunlight
Icemelt (mL)/mL of deicer
35
30
25
20
15
10
5
0
Product C1
Product C4
Product B4
Salt Brine

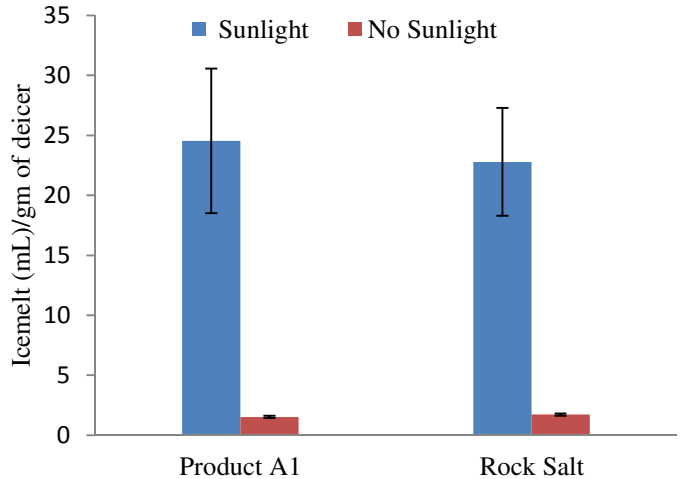
15°F


Sunlight
No Sunlight
Icemelt (mL)/gm of deicer
35
30
25
20
15
10
5
0
Product A1
Rock Salt

15°F


Sunlight
No Sunlight
Icemelt (mL)/mL of deicer
35
30
25
20
15
10
5
0
Product C1
Product C4
Product B4
Salt Brine

5°F

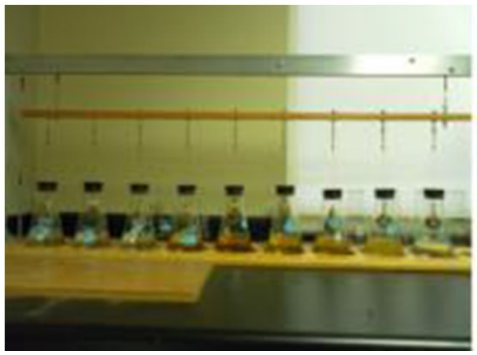

Sunlight
No Sunlight
Icemelt (mL)/gm of deicer
35
30
25
20
15
10
5
0
Product A1
Rock Salt

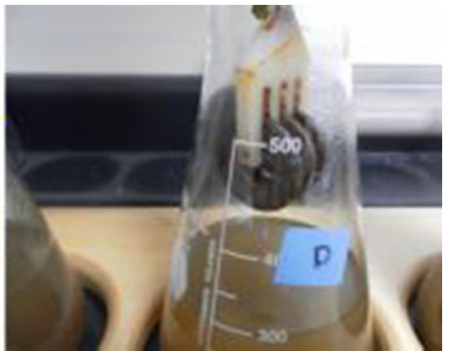
5°F

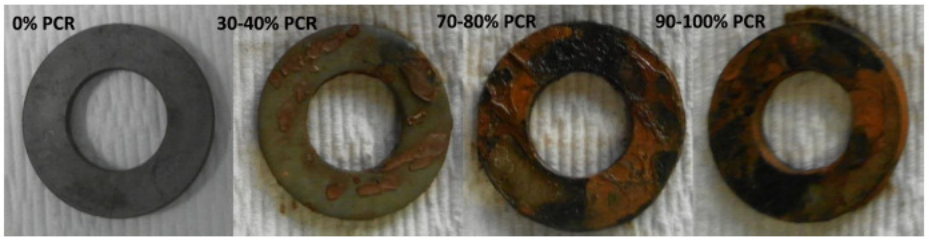
Is the performance of these products affected by UV or sunlight exposure?

- 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

Deicer	Original state	PNS Dipping Test		Electrochemical Test		
		Average Corrosion Rate (MPY)	Percentage Corrosion Rate (%)	E_{corr} (mV, SCE)	I_{corr} ($\mu A/cm^2$)	Average Corrosion Rate (MPY)
3% Product A1	Solid	50.5	82.0	-683.0	7.2	32.8
3% Product A2	Solid	46.2	74.1	-709.0	8.3	37.8
3% Product B1	Liquid	42.8	80.2	-508.0	5.4	24.6
3% Product B2	Liquid	15.1	30.8	-656.0	8.5	38.8
3% Product B3	Liquid	20.3	34.0	-704.0	7.6	34.7
3% Product B4	Liquid	29.5	52.9	-638.0	11.3	51.5
3% Product C1	Liquid	16.8	31.2	-556.0	6.3	28.7
3% Product C2	Liquid	18.1	38.7	-521.0	4.5	20.5
3% Product C3	Liquid	21.2	45.4	-685.0	8.9	40.6
3% Product C4	Liquid	14.3	30.6	-524.0	5.5	26.2
3% NaCl	Solid	56.3	100	-751.0	12.8	58.4
DI Water	Liquid	5.0	0	-	-	-

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 (http://clearroads.org/project/understanding-the-effectiveness-of-non-chlorine-liquid-agricultural-by-products-and-solid-complex-chloridemineral-products-used-in-snow-and-ice-control-operations/)

Thank you!

Questions?

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