Chemical Characteristics Workshop

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Overview

- Look at why anti-icing is valuable
- What does it take to implement anti-icing?
- Some resources for making change
- How do ice control chemicals work?
- How can you choose the RIGHT chemical for your agencies needs?

Issues Driving Change

- Anti-icing vs. de-icing
- use of liquid chemicals
- organics vs. inorganics
- changing concerns
  - corrosion
  - environmental impact

What is Anti-Icing?

"The snow and ice-control practice of preventing the formation or development of bonded snow and ice by timely applications of a chemical freezing-point depressant."

FHWA Manual of Practice for an Effective Anti-Icing Program

What does that mean?

- Pro-active
  - Do to the snow before it does to you
- Mostly uses liquid chemicals
  - Can use pre-wet solids
- Needs new equipment, new operations method, and new chemicals
- Need an understanding of how the chemicals work and how to choose them

Building Blocks to Implement

- There are four
- New equipment
- New operational methods
- New management techniques
- New chemicals/products

Equipment Toolbox

- Mostly use liquid chemicals
  - possible with pre-wet and even with dry chemicals but latter not recommended
- need to be able to deliver both liquids and pre-wet
  - pre-wet for later in storm
- need for quick change device

More Equipment

- Need to make up the liquid chemical
- need to store it
- need to transfer it
- need to keep things really clean

A Great Resource

- Iowa DOT has a guide to equipment
- Includes all the little refinements they've made
  - Doors on their brine making facilities are now clear plastic, not metal
- Available on the web

http://www.dot.state.ia.us/maintenance/manuals/equip/index.htm

Making the Liquid

- Typically done for salt brine
  - Most other chemicals come delivered as liquids
  - May need dilution, and agitation
- Need a way to mix the solid and liquid thoroughly
- Need a way to measure that you've mixed to the right mixture

Major Issue – Corrosion!

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A Word about Specification Tests

- Tests that truly replicate field conditions are:
  - Either very expensive and difficult to do
  - Or non-existent
- Some tests can produce results that don't reflect your conditions (esp. corrosion)
- The tests are good, just not representative
- Think lots about which tests to use

Corrosion Testing
from WSDOT Salt Pilot Project

2003-04 test results for corrosion inhibited solid		
sample exposure site		corrosion % compared to salt
lab (PNS test)		67% less
field	trucks	63% less
	guard rail	3% more

test results for corrosion inhibited liquid		
exposure site	lab	field
calcium chloride	81% less	65% less
mag chloride	72% less	22% less

note: field samples exposed to both liquid and solid chemicals

Brine Storage - Issues

- Must be contained to avoid spillage
- Pumps, hoses etc. need careful layout
- Most folks are using poly tanks – they seem to work well
- Ensure you have enough

Capacity Issues

- Store enough for at least two applications
- Have enough capacity to be able to make enough brine for one application in a 24 hour period
- Water supply may be a limiting factor
  - Iowa has a water tank trailer for just those locations

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Those Pumps and Hoses

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Delivering the Brine

- Many ways of getting this done
- Slide in units were initially popular
- Special trucks are great
- Trailers seem to be the current thinking
  - Easy to hitch up, do a route, then get back out with your regular load

Tank Styles

Different Spray Systems

- Many different ways of doing this
- E.g spray v stream
- Experience and personal preference generally dictate
- Streaming seems to offer less problems

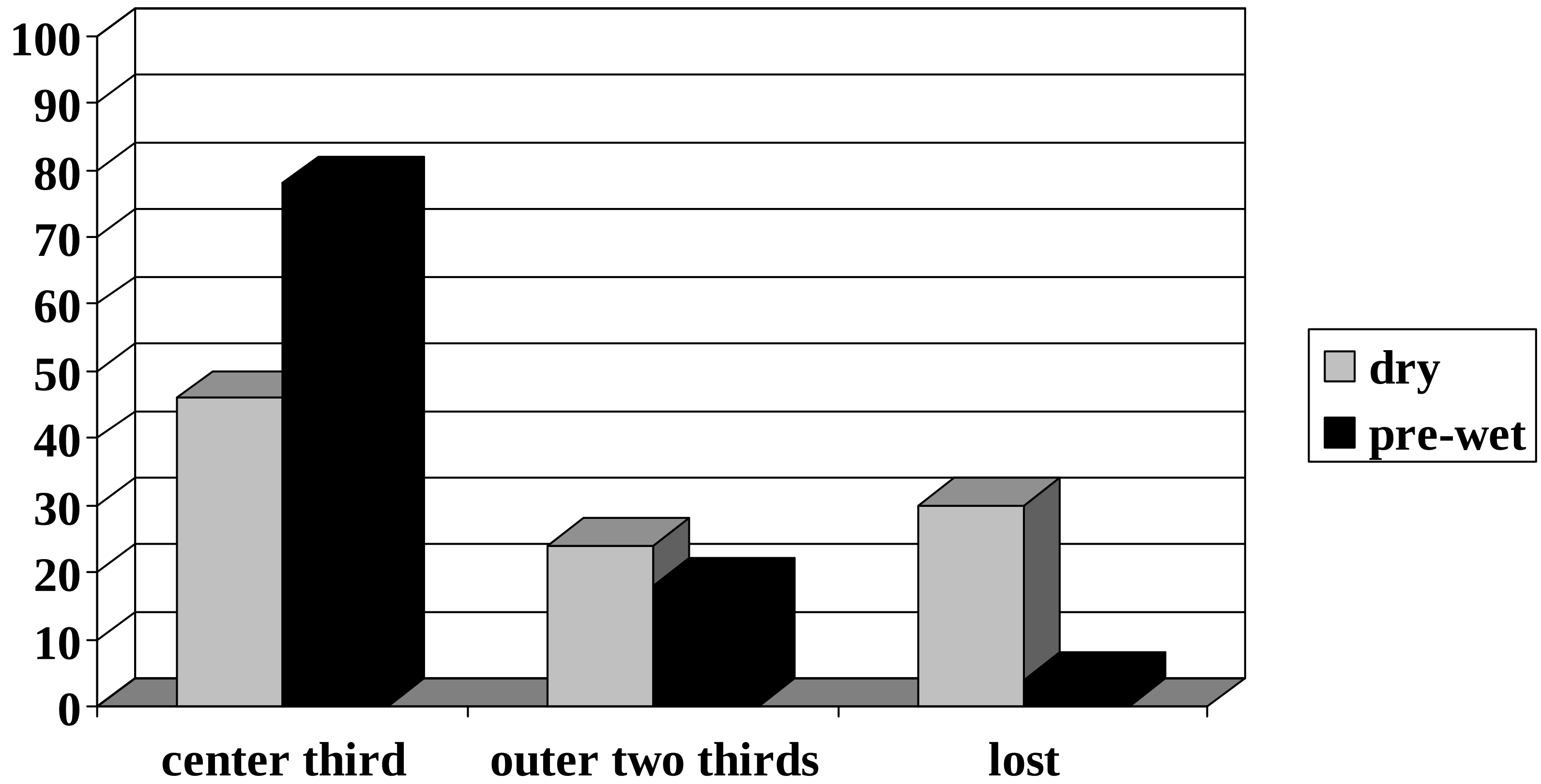
Penetration

- In de-icing activities this is a critical issue
- raises advantages of pre-wetting of solids
- also makes clear why liquid chemicals are only really useful for anti-icing activities
  - too dispersed
  - not enough volume to melt through and get to the interface

Pre-Wetting

- Typically we apply either liquid brine or liquid calcium chloride to salt (and sand)
- gets the chemical reaction going quickly
- helps the particles to stick to the road
- can reduce caking
- needs more complex equipment

Michigan Study on Salt Dispersion



Pre-wetting saves salt

- Clearly more of the salt stays on the highway
  - 96% versus 70%
- also helps jump start the melting
- measurements did not account for traffic

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Pre-wetting Equipment

- A critical part of anti-icing
- Often makes the spinner a bit complex
- Starting to get pretty well refined

Pre-wet systems

Design Factors

- Some road features create special problems for winter maintenance
- Know what they are, don't let them find their way into new designs, and try, over time, to mitigate existing ones

Examples of Problem Designs

- Roads in shade
- Snow disposal areas on the high side of super-elevations
- Any places where melt-water can flow across the road
- Roads through cuts in snow drifting areas
- And others...

New Operational Methods

- Anti-icing is pro-active, so you must be too
- Key factor is forecasting
- Road temperature more important than air
- Really need an RWIS but those are expensive
- SO...

Getting your Weather data

- State DOTs often have RWIS sites
- May make those available
- For example, Iowa DOT
  - http://www.weatherview.dot.state.ia.us/
- Ask them, they can only say no!

Where do we want to melt?

- We'll see we can't melt very much
- Try and do all our melting at the interface between the snow/ice and the pavement
- Means we need to know the pavement temperature

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Getting the pavement temperature

- Not part of the standard NWS forecast
- Need RWIS data and pavement sensors
- Need specialized pavement forecasts
- Might also use truck mounted radiometers (thermometers)

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Truck Mounted Thermometers

- Not a perfect tool
- Can give different readings depending on pavement type
- Great for tracking trends
- Focus your attention where it should be – on the road

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New Management Techniques

- Have to train your workforce in new ways of doing business
- They may be skeptical!
- Training ideas in the FHWA Manual
- Will you support them when things go wrong?
- Will you help them deal with the challenges of getting a new system operational?

What Can Chemicals Do?

- They melt snow and ice, right?
- Well, yes and no…
- They do, but as we have seen here before, they do not melt very much
- That means we should NEVER use them to "burn off" the snow or ice
- They are meant to either prevent or break the bond between snow/ice and pavement

What Chemicals Are Available?

- Lots of possibilities
- Currently either chlorides or acetates
  - Sodium, calcium, magnesium chlorides
  - Potassium, calcium magnesium acetates
- Many different additives
- Increasing use of carbohydrates and sugars (with varying levels of purity) as additives

The Guiding Principles for Chemical Usage

- The right amount, in the right form, in the right place, at the right time
- Well, OK, but let’s get a bit more specific
- We need to consider three factors when deciding how much chemical to apply
  - Temperature
  - Dilution potential
  - Cycle time

Temperature as a Guiding Principle

- Road Temperature is the key
- The lower the temperature, the more chemical we will need (for a given amount of time, and a given dilution potential)
- Whether through truck mounted thermometers, RWIS, or some other way, we need Road Temperature

Diluting Out Our Chemicals

- The more moisture is present, the quicker our chemical application will dilute
- Different types of precipitation carry different amounts of liquid
- Sleet, freezing rain have much more than a dry snow
- And so, they will need more chemicals

What About Cycle Time?

- Time between "visits" of any truck to a given point in the highway system
  - Not necessarily the same truck…
- Should be short on high priority routes, longer on lower priority
- Divide route length by average truck speed (taking refill etc. into account)

Dealing with Cycle Time

- The longer the cycle time, the more the chemical application will dilute out
- So, longer routes require higher application rates
- Avoids going too far West or South on the phase diagram

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Putting All Three Together

- Our application rates should depend on our three guiding principles
- Lower temperatures, wetter precipitation, and longer cycle times all require more chemical to avoid refreeze
- So, use your experience, and put together a chart
- Iowa DOT did this, and this is what they found…

Salt Application Rate Guidelines

Prewetted salt @ 12' wide lane (assume 2-hr route)							
Surface Temperature (º Fahrenheit)		***32-30***	***29-27***	***26-24***	***23-21***	***20-18***	***17-15***
lbs of salt to be applied per lane mile	Heavy Frost, Mist, Light Snow	50	75	95	120	140	170
	Drizzle, Medium Snow 1/2" per hour	75	100	120	145	165	200
	Light Rain, Heavy Snow 1" per hour	100	140	182	250	300	350

Prewetted salt @ 12' wide lane (assume 3-hr route)							
Surface Temperature (º Fahrenheit)		***32-30***	***29-27***	***26-24***	***23-21***	***20-18***	***17-15***
lbs of salt to be applied per lane mile	Heavy Frost, Mist, Light Snow	75	115	145	180	210	255
	Drizzle, Medium Snow 1/2" per hour	115	150	180	220	250	300
	Light Rain, Heavy Snow 1" per hour	150	210	275	375	450	525

How Could This Work for You?

- This is a simple, low level, easily applied Maintenance Decision Support System
- Select appropriate temperature ranges, storm types (dilution potential) and cycle time for your conditions
- Determine the right application rate, based upon your experiences
- And the next step?

Solids, Liquids, Both – When, When Not, How Much?

- More goes into deciding an application rate
- Progression of the storm
  - Starting with rain
  - Temperature drops and wind picks up at the end
  - Other options
- The next step considers these complexities

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When Not To Use Certain Chemicals

- Don’t use liquids with rain or on top of compact
- Don’t use liquids or pre-wet solids if this will create a wet road in a drifting situation
- Don’t put down dry chemicals on a dry road
  - Use pre-wet or slurry instead

What does it take to be a de-icer?

- Water soluble
- freezing point depressant
- whole list of possible targets

What do we mean by a freezing point depressant?

- Mixture of water and chemical must have lower freezing point than water
  - slope of phase diagram
- water would rather bond with ions in the chemical than with other water molecules
- most chemicals are salts or organic salts

What do we want in a de-icing chemical?

- Freeze point depression
- melt snow/ice in reasonable time
- penetrate to the snow/pavement interface
- non-lubricating
- Available in bulk and cheap
- easy to store, handle and apply
- not toxic to people, animals, or plants
- not damaging to infrastructure

What is a Phase Change?

- When a material goes from one phase to another
  - E.g. solid (ice) to liquid (water)
- Often, lots of energy is involved
  - Much more than just to heat things up
- Can be caused by changes in temperature AND pressure

So what's a Phase Diagram?

- A picture that shows under what conditions a system will be in a given phase
  - E.g. when is it liquid, when is it solid
- Can be for a single component system
  - E.g. water
- Or for a two (or more) component system
  - E.g. salt and water

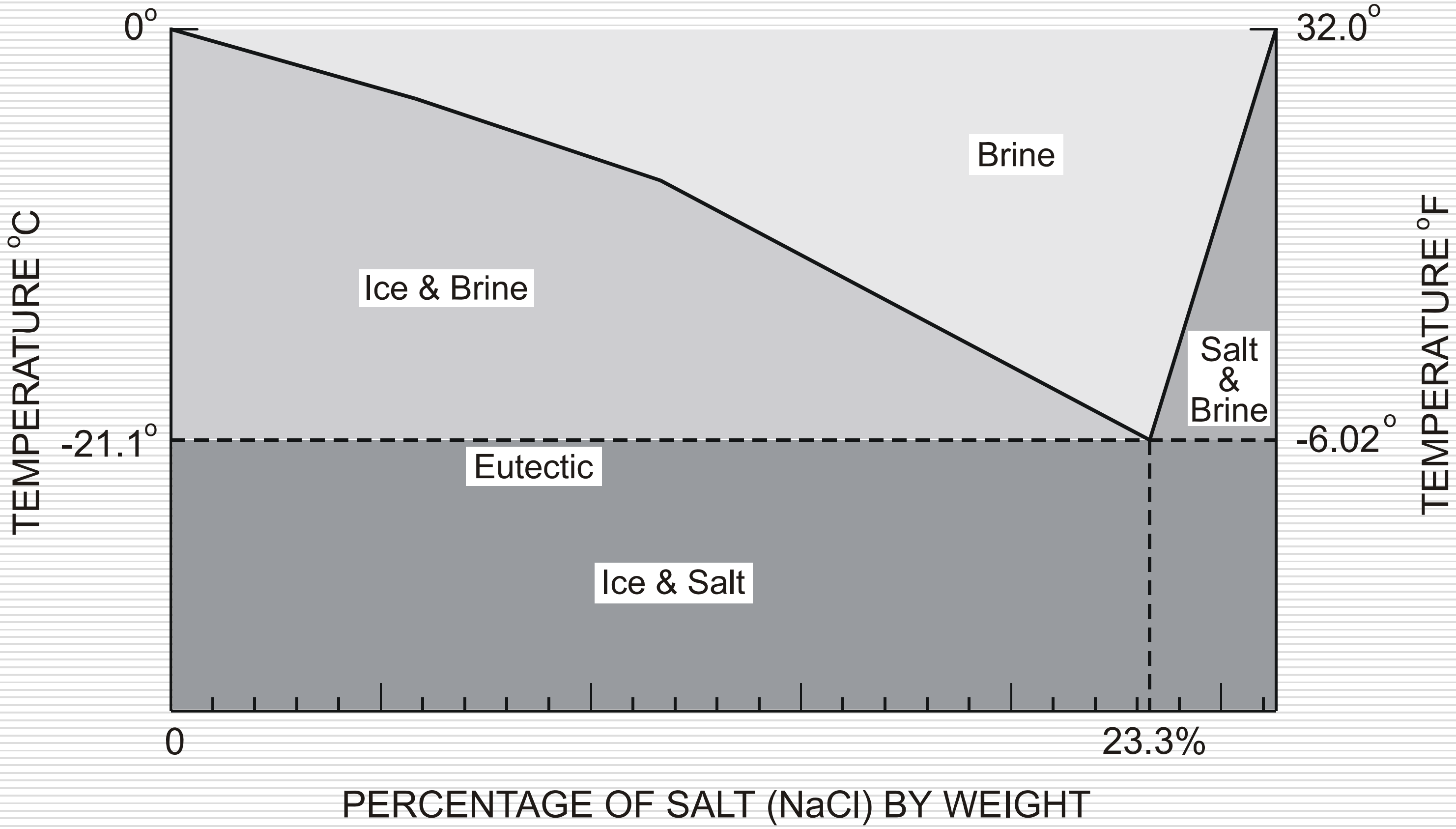
Latent Energy Helps and Hurts

- If we are frozen, and we have to melt, we must supply the latent energy
  - Takes time and heat
- BUT, if we are liquid and we are going to freeze, we must loose the latent energy
  - Takes time and cooling
- Much better to start with things liquid
- BE PROACTIVE

Two Component Phase Diagrams

- The vertical axis is temperature
- The horizontal axis is composition
- Typically percentage by weight of the added component
- The areas within the diagram may be single phase or two phase regions
- For our purposes, a two phase region typically has one phase liquid, one phase solid

Phase Diagram for Salt-Water System



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Other two phase systems we know

- Coffee and sugar
- Beer and carbon dioxide
- Water and calcium chloride, or magnesium chloride, or…
- And many, many more

What can coffee tell us?

- When we add sugar to hot coffee, it dissolves
- The coffee and sugar form a single phase
- If the coffee cools, the sugar comes out of solution and ends up as a gooey syrup at the bottom of the cup
- The coffee and sugar are now in a two phase region.

How much ice can we melt?

- Start with a salt example
- with given temperature and given salt quantity how much ice can we melt?
- straight off the phase diagram

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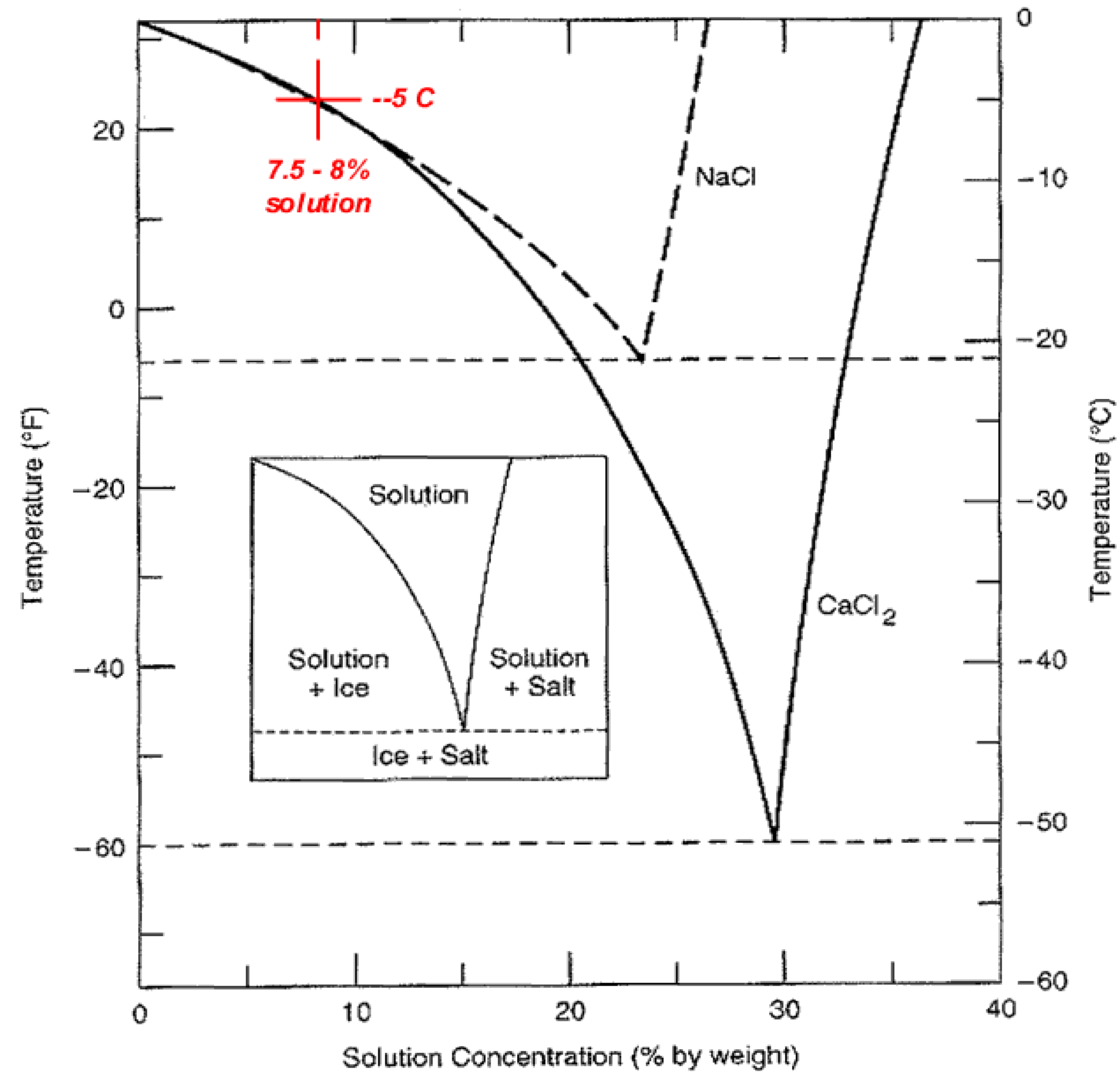
Example on Quantity of Melting

- 300 lbs/lane mile (85 kg per lane km)
- 23° F (-5° C)
- how much ice can we melt?
  - Express as inches of moisture
- first determine the percentage of salt



--5 C
7.5 - 8% solution
NaCl
CaCl2
Solution
Solution + Ice
Solution + Salt
Ice + Salt
Temperature (°F)
Temperature (°C)
Solution Concentration (% by weight)
20
0
−20
−40
−60
−10
−30
−50
10
30
40

Percentage of Salt

- All salt in solution at about 7.5%
  - read across the PD at the 23° F line
- water amount?
- water depth?

How Much Water?

Customary Units

$$W = \frac{92.5\%}{7.5\%}\left(300 lbs / mile\right) = 3700 \text{ lbs water/mile}$$

How Deep is the Water?

Diddeley Squat

$$\text{Depth of water} = \frac{mass}{density \times area}$$

$$Depth = \frac{3700 lbs / mile}{62.4 lbs / ft^3 \times (5280\, ft / mile) \times 12\, ft}$$

$$Depth = 9.358 \times 10^{-4}\ feet = 0.011\,\text{inches water}$$

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Thoughts on the example

- 300 lbs/lane mile is a standard salt amount
- not much snow is melted (maybe 0.1 inch of snow)
- no info on how long this takes
- what if we had less moisture, or were warmer?

The Refreeze Problem

- If we don’t have enough chemical, we may melt ice, and then have it refreeze
- more precipitation may dilute our solution
  - move West on the phase diagram
- lower temps may may bring us into the freezing range
  - move South on the phase diagram

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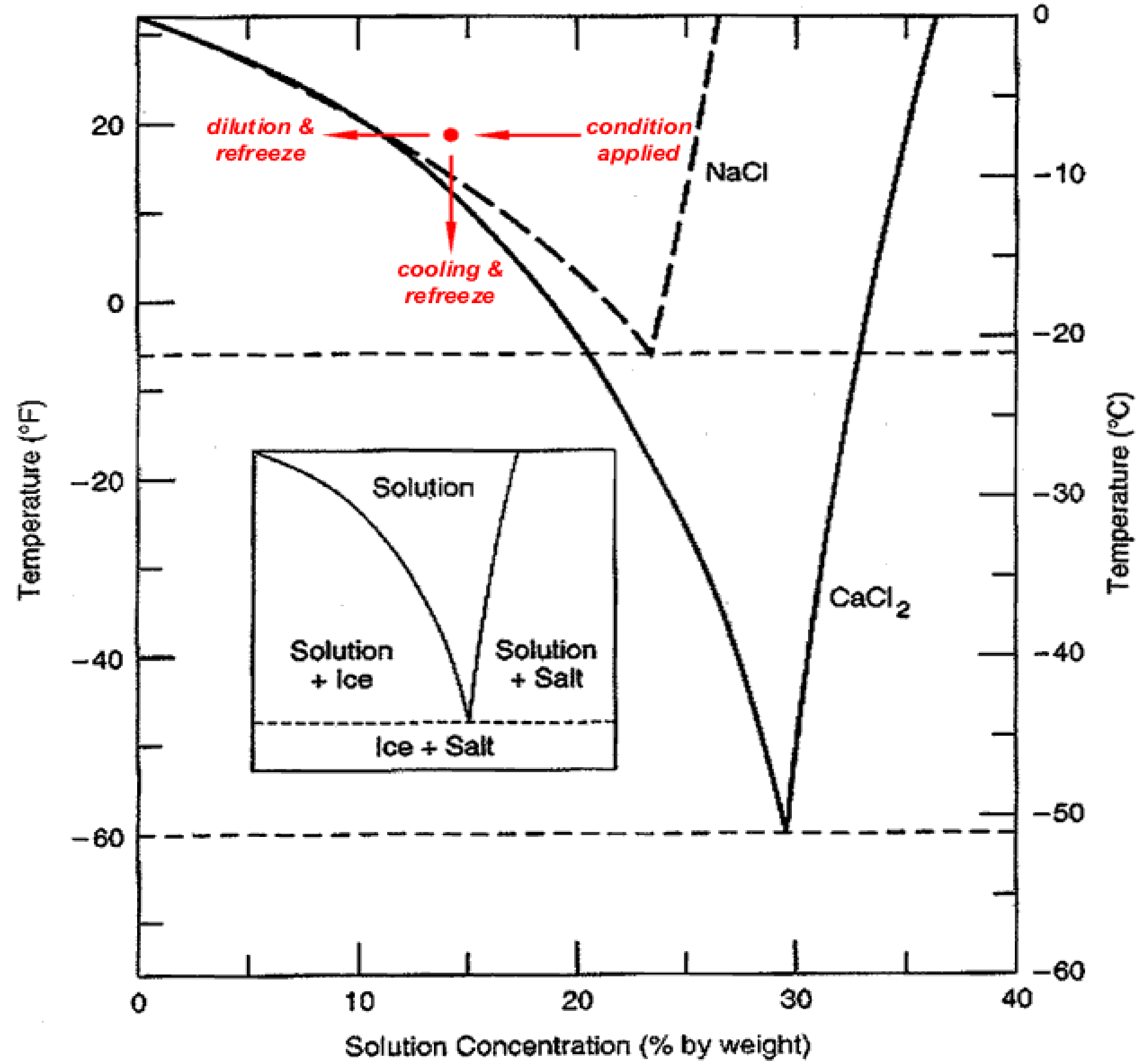

dilution &
refreeze
condition
applied
cooling &
refreeze
NaCl
CaCl2
Solution
Solution
+ Ice
Solution
+ Salt
Ice + Salt
Temperature (°F)
Temperature (°C)
Solution Concentration (% by weight)
20
0
−20
−40
−60
0
−10
−20
−30
−40
−50
−60
0
10
20
30
40

How much salt are we talking?

$$\frac{Salt}{Square\ Foot} = \frac{300 lbs / mile}{5280\ ft / mile \times 12\ ft} = 0.0047 lbs/ft^2$$

$$Salt\ in\ this\ room = 1000\ ft^2 \times 0.0047 lbs/ft^2 = 4.7 lbs$$

We do not use a lot of chemicals this way,
if we do things right

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Choosing a New Chemical

- A big opportunity (as you shift from solids to liquids)
- What do you need the chemical to do?
- What constraints do you have on how the chemical will perform?
- Approach is based on the “Guide for Selecting Anti-Icing Chemicals”
  - http://www.anti-ice-guide.com/

Purpose of the guide

- Differentiate between different chemicals
- on the basis of performance
- acknowledge that different agencies have different needs
- allow factors to be weighted

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Categories

- Properties that are important for anti-icing chemicals
- should be measurable
- data should be available
- list may develop over time
- some important factors can't be on list
  - price, availability etc.

Categories Used

- Freezing point depression
- Consistency
  - Viscosity
  - Specific gravity
- Environmental Impact
  - Heavy metals
  - BOD/COD
  - Toxicity
- Stability
- Corrosion
- Handling
- Conductivity
- Documentation
  - Unspecified content
  - Completeness
- Future categories

Most Important Ones

- Depends on your needs
  - Is corrosion a big issue for you?
  - What about the environment?
- Definitely freezing point depression
- Consistency
- Complete documentation

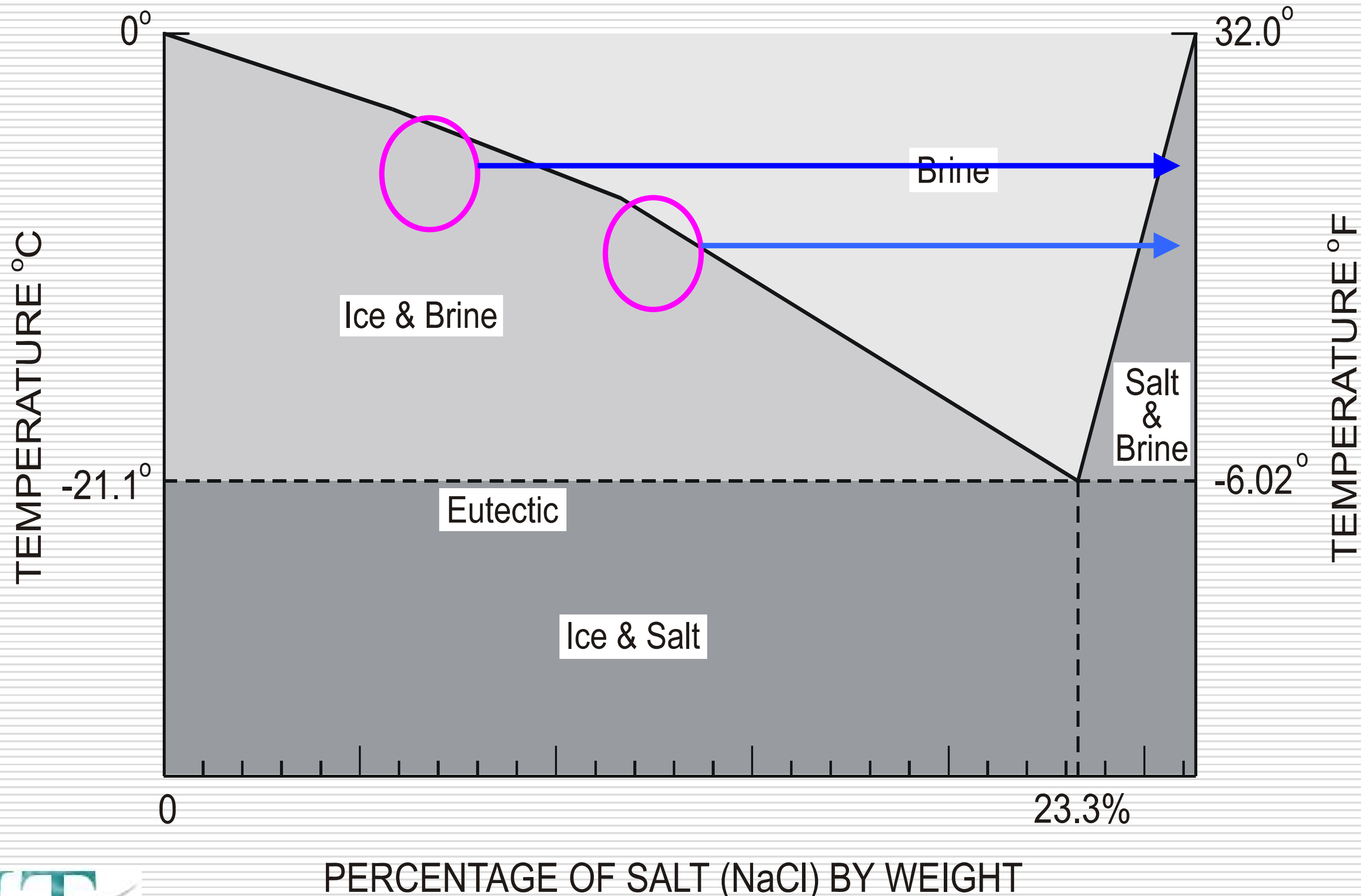
Why Freezing Point Depression?

- Tells whether it's suitable for your climate
- Tells when you should stop using it because it's too cold
- Tells how much you'll need to fight a typical storm

How Freezing Point Depression?

- Based on the eutectic curve
- BUT, not just the eutectic point
  - That's pretty useless really
- Need to know two temperatures
  - At half the concentration of the EP
  - At quarter of that concentration

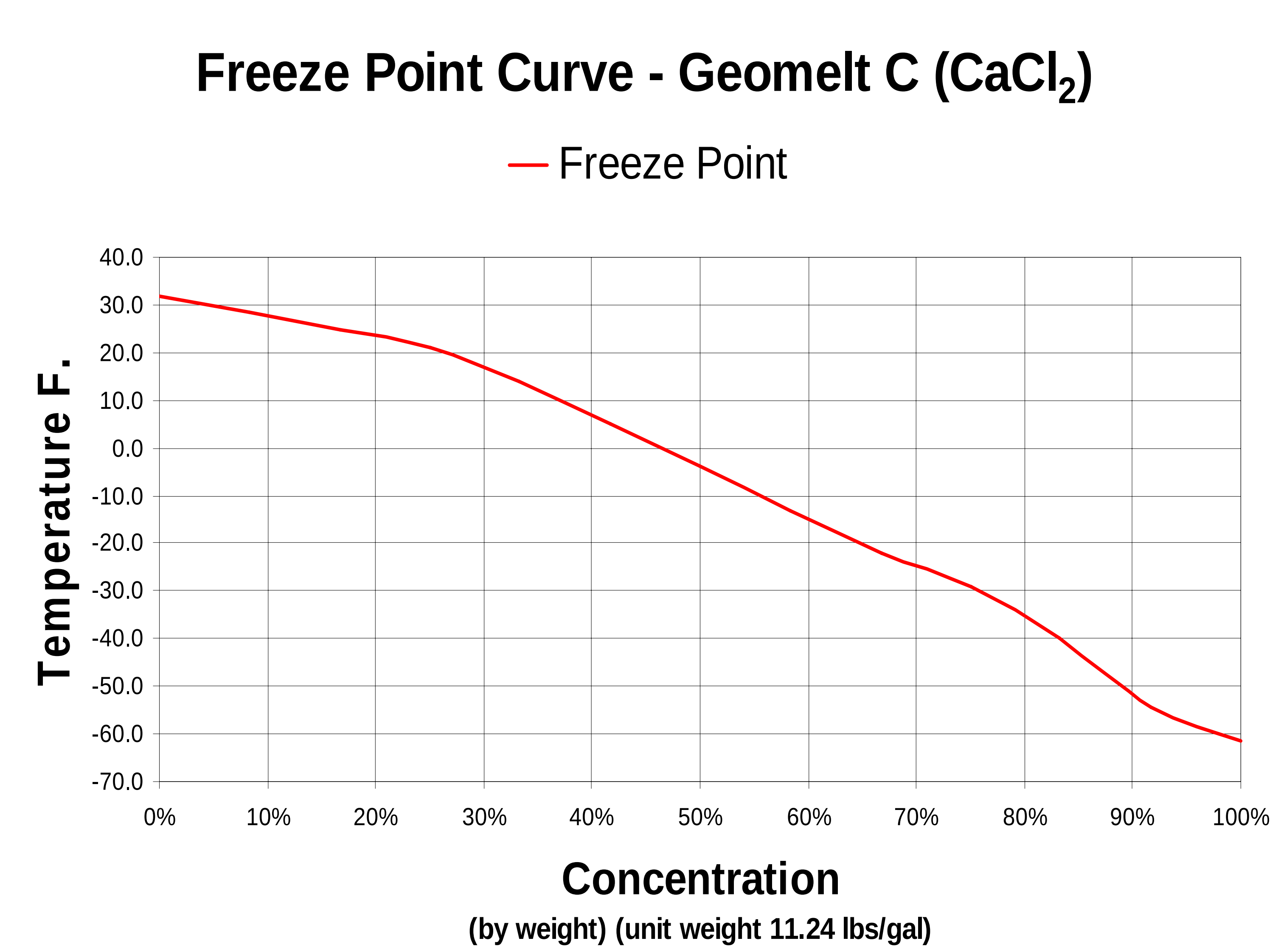
The Eutectic Diagram for NaCl



How does NaCl do?

- The half point is 18 F
  - Typically represents lower end of the useful range of salt use
- The quarter point is 26 F
  - Designed to tell us if the curve is weird in any way!

Another Product



Comparing the Geomelt product and Salt

- "half point" is -5º F for Geomelt v 18º F for salt
- "quarter point" is 20º F for Geomelt v 26º F for Salt
- So Geomelt is better, right?
- Not unless you need that better temperature performance
- By the way, which temperature do we care about?

What about Consistency?

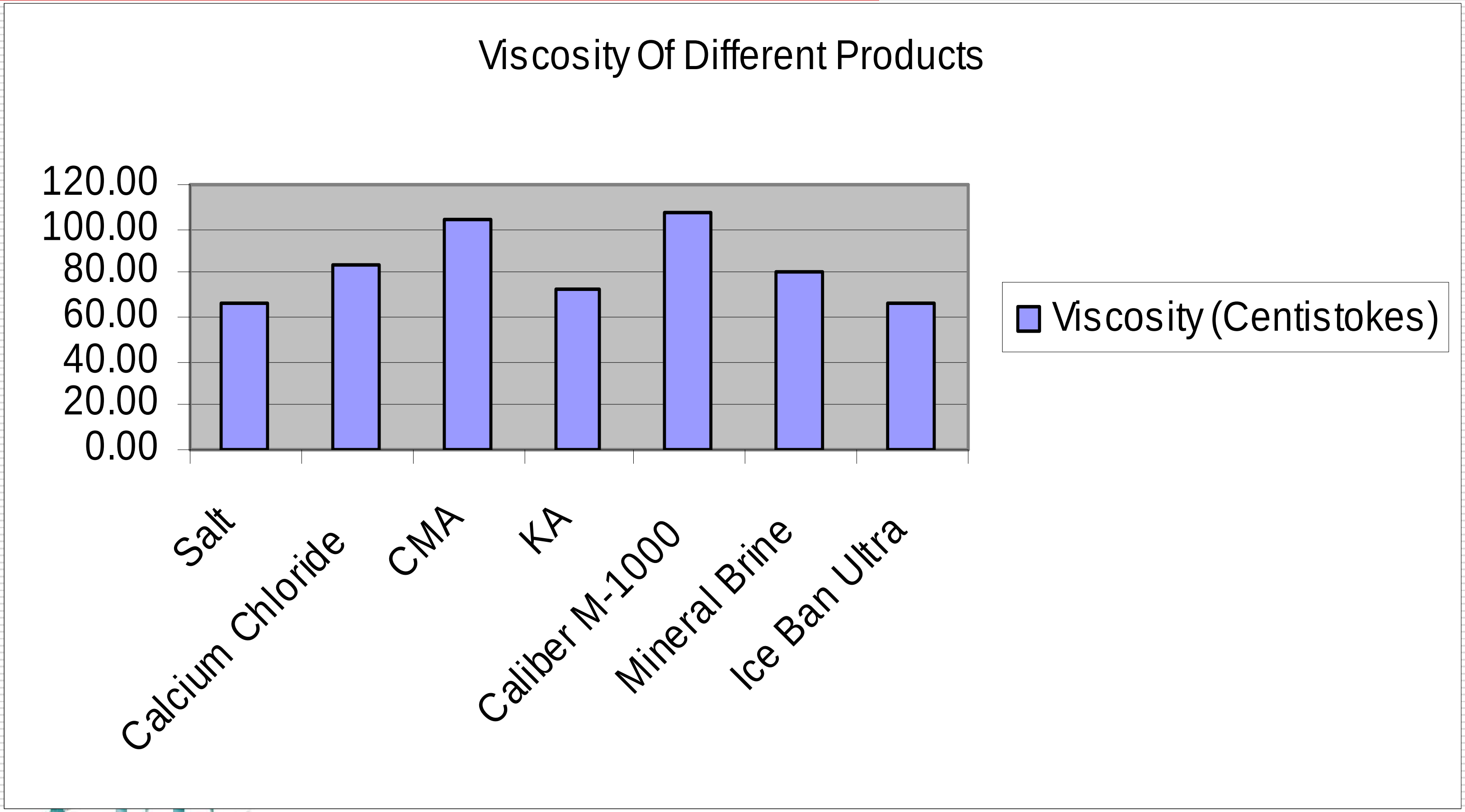
- The addition of organic chemicals and by-products makes some new liquid products much more variable than traditional chemicals
- You MUST know that the product you use this week performs the same as what you used last week

How do we Measure Consistency?

- Have to use index tests
- Viscosity and specific gravity are easy to do and will quickly tell you if something isn't right
- The only long term answer is good quality program with suppliers

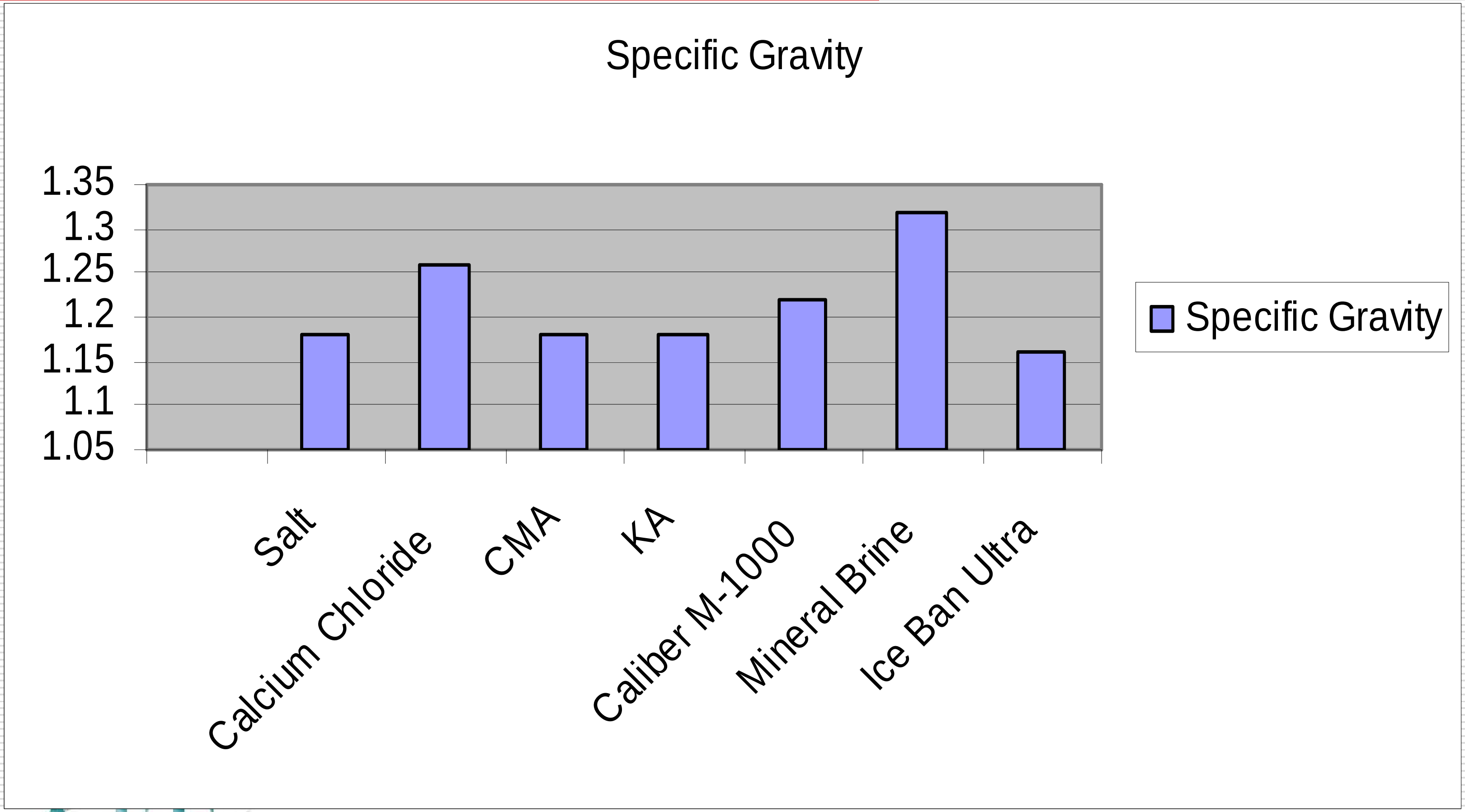

PRECISION HYDROMETER

Viscosity



Viscosity Of Different Products
120.00
100.00
80.00
60.00
40.00
20.00
0.00
Salt
Calcium Chloride
CMA
KA
Caliber M-1000
Mineral Brine
Ice Ban Ultra
Viscosity (Centistokes)

Specific Gravity



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Specific Gravity

- Is different for different chemicals
- Varies (a bit) with temperature
- Can indicate whether you have the right mixture
  - Did you order Calcium brine at 30% and they've delivered a 23% mixture
  - Specific gravity will tell you
- Crucial quality check – learn it and do it

Why Documentation?

- You can’t compare products if you don’t have enough information
- Any worthwhile product will come with documentation, test results and so forth
- Provide a critical input for your choice

How Documentation?

- Two factors
- How much of the product is termed "other" in the chemical analysis?
- Do the suppliers give you all the info you need?

Another factor for Consistency and Documentation

- Legal issues
- You HAVE to know what you've put on the road
- If you don't, you may be vulnerable during the deposition/trial process

So how do we rate different products?

- Set levels within each category
- Weight the categories according to which matter to you
- Then grade the chemicals (multiply their category level by their weight to get a grade point score)

Levels within Categories

- Mostly done with four levels (A, B, C, D)
- some only two levels
- one is a simple pass/fail condition

PROPERTIES

CATEGORY	FREEZING POINT DEPRESSION		CONSISTENCY	ENVIRONMENTAL IMPACT				STABILITY	CORROSION	HANDLING		CONDUCTIVITY	DOCUMENTATION	
	25%	50%		BOD	COD	Toxicity	Heavy Metals		PNS (MMPY)	Ease of Use	Storage		Unspecified composition	Complete-ness
A	16.5^o	0^o	< ± 1%	T.B.D.			1:1	2 years	0	A	A	T.B.D.	< 2%	PASS / FAIL DECISION
B	20^o	7^o	< ± 2%				2:1	1 year	10				< 5%	
C	24^o	10^o	< ± 5%				10:1	6 months	25	B	B		< 10%	
D	26^o	18^o	< ± 10%				100:1	1 month	50				> 10%	

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Scoring Chemicals

- First define which categories are most important by weighting
- scale 0 to 4
- weights will change depending on each agency's needs

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Table 4.1 Hypothetical Weighting of Categories

Category	Assigned Weight
Freezing Point Depression	3
Consistency	2
Environmental Impact	2
Stability	1
Corrosion	4
Handling	1
Documentation	2

Next Grade the Chemicals

- Based on performance, chemicals are given a grade
- multiply grade by weight to score
- total for all categories

Table 4.2 Scores for Hypothetical Chemicals

Category	Assigned Weight	Iceblaster		Sno-b-gone	
		Grades	Scores	Grades	Scores
Freezing Point Depression	3	A	12	B	9
Consistency	2	D	2	B	6
Environmental Impact	2	D	2	B	6
Stability	1	C	2	B	3
Corrosion	4	B	12	A	16
Handling	1	B	3	A	4
Documentation	2	D	2	B	6

Next Step

- Scores don't make the choice
- BUT they do give a ranking
- Other factors may then come into play (cost, availability etc.)
- Also possible to limit categories (e.g. require minimum grade of B in corrosion)

Final Choice

- Agency may require minimum score on ranking to be considered
- Agency may then purchase based on best price or other factors
- Goal is not to make choice for agency, but allow agency to include performance in their choice in a rational way

Conclusions

- A rational method of differentiating between and thus selecting anti-icing chemicals
- Designed to change and improve over time
- Feedback actively sought
  - Is this useful?
  - How can it be improved?