

Non-Chloride Deicing Compounds - DETAILED

Below is a summary of information from 15 different sources, mostly technical in nature. This version represents the detailed version of this summary. An accompanying document follows the same structure but only includes summarizing information. While this summary was intended to look at “emerging” deicing compounds, this review of all non-chloride deicers highlighted that many of the compounds researched through the 90s and early 2000s are not understood at the same level as Sodium Chloride (NaCl). Therefore, the focus of this summary is on non-chloride deicers

Preliminary thoughts – Things to consider and developing recommendations

- Thoughts to consider:
 - Chloride (Cl) is not the only ion of concern, Sodium (Na) is too
 - Some studies show toxicity of Potassium (K) to macroinvertebrates¹
 - In water, Calcium (Ca) and Magnesium (Mg) precipitate into carbonate and therefore have the least impact²
 - Many “alternatives” include these cations.
 - Challenges with existing research
 - Many compounds not researched well.
 - Many of the non-chloride deicers have studies showing different results.
 - There are evolving manufacturing processes that affect the purity and trace compound content.
 - All known deicers once applied, dissolve and are transported in one way or another to surface water or groundwater without significant removal in stormwater BMPs
 - Non-chloride deicers generally don’t persist long, but may have short-term impact on Biological Oxygen Demand
 - Biological Oxygen Demand (BOD)
 - BOD is the concentration of oxygen needed to breakdown a compound by X amount of days. Typical intervals include 2, 5, 10, and 20 days. These tests are done in sealed containers to eliminate reaeration.
 - BOD is a concern for many organic, non-chloride deicers.
 - However, biological activity in winter months is depressed and the re-aeration rate of water is higher at winter temperatures, possibly diminishing the impact of the high BOD.
 - A 1999 USGS study³ showed that BOD of a receiving stream was not significantly impacted by Calcium Magnesium Acetate
 - According to a 2002 study⁴, acetate-based deicers have a bigger impact on soils, but in water it takes about 3.5 times longer to deplete the oxygen. BOD of Calcium Magnesium Acetate in water at 20°C, 10°C, and 2°C take 5, 10, and 100 days deplete the oxygen in a test container (i.e., no reaeration).
 - Glycols/Glycerols have the highest BOD and can impact water quality significantly. Because it breaks down very slowly at temperatures below freezing, when temperatures warm and groundwater is flushed, it can lead to pulsed impacts.
 - Byproducts (e.g., pickle brine, cheese brine, agricultural byproducts) have variable composition and are subject to regional availability.
 - Byproduct brines need the same NaCl content to be effective, so no reduction in NaCl⁵

¹ <http://www.the-aps.org/mm/hp/Audiences/Public-Press/2018/71.html>

² <http://onlinepubs.trb.org/Onlinepubs/sr/sr185/185-043.pdf>

³ <https://pubs.er.usgs.gov/publication/wri004092>

⁴ <https://link.springer.com/content/pdf/10.1007%2Fs11270-011-1064-6.pdf>

⁵ <https://docs.lib.purdue.edu/mwg-internal/de5fs23hu73ds/progress?id=NeQ3SCEYVQ22Nosf-bA1rIZxP6BtF3-bRYm-HoAd1hA,&dl>

- Developing Recommendations:
 - Consider how easy it is to adopt product:
 - Do they work in the existing equipment?
 - What kind of training is needed?
 - What kind of personal protective equipment is needed?
 - Consider products for mid-latitudes that:
 - Stick around through traffic and rain
 - Work best at mild temperatures
 - Provide recommendations for piloting mixtures or alternative compounds for particular weather patterns/circumstances
 - The most strategic use of deicers is to use a selection of products that will meet your needs and reduce the total volume of deicer, abrasive or additives needed.
 - The benefit of each deicer seems to be maximized in mixtures. However due to the increased complexity of using mixtures, each mixture should be well studied before scaling up in operations.
 - There are many potential impacts that are hard to research in total. Where there are unknowns, prioritize monitoring when piloting its implementation.
 - Because of the various chemical reactions between deicers in blends and their surfaces and environment, there is much complexity in studying their efficacy.
- Additional information related to all deicing compounds (including chloride deicers)
 - Dyes are added for a number of reasons, but can have the added benefit of showing an area has been treated, which can alleviate pressure and possibly mitigate liability concerns. Impacts from dyes are unknown and represent an area for more research (Examples here: <https://www.organicdye.com/dyes-ice-melt/>).
 - Sodium Ferrocyanide when combined with iron to make Ferric Ferrocyanide converts from yellow to a deep blue pigment called Prussian Blue (some blue salts have this).
 - Anti-caking agents can increase toxicity, but direct evidence is limited. Common anti-caking agents include:
 - Sodium Cyanide (NaCN)
 - Sodium Ferrocyanide ($\text{Na}_4[\text{Fe}(\text{CN})_6]$) (Yellow Prussiate of Soda)
 - Less toxic than other cyanide salts because they tend not to release free cyanide
 - Toxicity due to Cyanide does not appear to be a major problem. Free CN is quickly diluted and volatile so it is lost to the atmosphere.⁶
 - Concentrations can range from 10 to 250 ppm, typically fall within 50-100ppm⁷

Products

- From Minnesota Local Road Research Board 2014 Report and summarized on **SaMS IP NonCl Deicer Minnesota Summary.xlsx**. Information provided below is in addition to what is summarized on the spreadsheet. The products in this group include Acetates, Formates, Glycerol/Glycol, Succinates, and Beet Juice⁸
 - Acetates
 - Found to significantly damage asphalt pavements, through the combination of chemical reactions, emulsifications and distillations, as well as generation of additional stress inside the asphalt concrete.⁹
 - Calcium Magnesium Acetate¹⁰

⁶https://engineering.purdue.edu/watersheds/webinars/RoadSalt/Royer%20road%20salt%20webinar_rev.pdf

⁷<http://sp.research.transportation.org/Documents/tsranticaking.pdf>

⁸<https://lrrb.org/media/reports/TRS1411.pdf>

⁹<https://www.codot.gov/programs/research/pdfs/2009/antiicing.pdf>

- Is said to take 15-30 minutes longer to induce melting than NaCl
- Effectiveness diminishes in temperatures below 23°F, freezing rain, drier snowstorms, and light traffic zones
- Residual CMA can last on roads for up to 2 weeks (much longer than NaCl)
- Improvement in manufacturing has gotten its effective application rate close to a 1.7:1 to 1:1 ratio by weight of CMA to NaCl
- When wet can clog spreading equipment/stick to truck beds
- Low toxicity
- High price (\$650-675/ton)
- Formates
 - Includes Apogee – Sodium Formate
 - \$3/gallon including transportation costs
 - Found to significantly damage asphalt pavements, through the combination of chemical reactions, emulsifications and distillations, as well as generation of additional stress inside the asphalt concrete.¹¹
- Glycerol/Glycol
 - Potential human carcinogen (may be influenced by purity, more pure is less carcinogenic)¹²
- Succinates¹³
 - Includes Potassium Succinate, Ammonium Succinate, and Sodium Succinate
 - Potassium Succinate (KSu) outperformed other succinate salts
 - Reduces corrosion to steel when blended with salt brine (best at 2%)
 - Minimal to no concrete scaling
 - Cost about \$2.50/gallon
 - Should not be used below 23°F
 - Similar performance to NaCl with regards to friction
 - A mix of water, KSu, potassium acetate, and potassium formate at a ratio of 5:3:1:1, respectively, may warrant investigation as a roadway deicer. Based on findings from the vendor, this mixture has been reported to perform down to -19°C (-2.2°F)
 - Additional testing is needed to quantify impacts on soil, water, flora, and fauna.
- Beet Juice
 - National Geographic Article¹⁴
 - Can be mixed with salt to help it stick to surfaces
 - Like molasses and corn starch
 - All can clog machinery used to spread as a brine or a treated salt
 - Has a deicing quality that can work at lower temperatures than NaCl
 - Sugar in the solution lowers the freezing point, allowing it to deice below NaCl's 15°F limit
 - 2018 American Physiological Society Press Release¹⁵
 - Contains about 12% NaCl
 - Can coat the road for up to 1 week
 - Can attract wildlife to the road (sweet taste)

¹⁰ https://www.michigan.gov/documents/ch2-deice_51438_7.pdf

¹¹ <https://www.codot.gov/programs/research/pdfs/2009/antiicing.pdf>

¹² https://www.michigan.gov/documents/ch2-deice_51438_7.pdf

¹³ <https://trid.trb.org/view/1508221>

¹⁴ <https://news.nationalgeographic.com/news/2014/02/140204-melt-snow-ice-salt-beet-juice-pickle-brine/>

¹⁵ <http://www.the-aps.org/mm/hp/Audiences/Public-Press/2018/71.html>

- Has an anti-corrosion property
- Higher cost than NaCl
- Through decomposition of organic content it exerts a high Biological Oxygen Demand (BOD) when it makes it to waterways
- This study shows additional stress on Mayflies, causing them to retain too much water with elevated blood salt levels, although more research was necessary to understand the mechanics of that effect.
- Products not from Minnesota Local Road Research Board 2014 Report (i.e., not on the SaMS_IP_NonCl_Deicer_MinnesotaSummary.xlsx)
 - Non-Chloride Agricultural Products
 - “. . . the effectiveness of these products and the mechanism by which they work are not well documented. Potential users need quantifiable research to validate performance and verify the chemical or physical processes by which the products are of value in winter maintenance.”¹⁶
 - A report titled, “Developing Locally Sourced Brine Additive for Anti-Icing” outlined a process for identifying potential deicers from waste material¹⁷
 1. Identify potential waste material or by-product (e.g., free of contaminants)
 2. Design experiment to determine concentrations
 3. Determine ice melting performance, corrosion to steel, and impacts to concrete
 - May be worth adding impacts to the environment here
 4. Field operational testing of highest performers
 5. Implementation to maintenance agencies
 - Distillery brine
 - One study showed favorable results as an anti-icer when mixed with other compounds to both reduce corrosivity and function at temperatures below those where NaCl and MgCl₂ brines work.¹⁸
 - Another study from here in Virginia evaluated the effect of a pre-wetting agent that is derived from byproducts of the agricultural industry (e.g., whey, brewers’ condensed solubles, and other byproducts commonly used as animal food). That study concluded that the composition of this agent varies from batch to batch and over time, and overall did not perform in a beneficial way as a pre-wetting agent.¹⁹
 - Pickle Brine & Cheese Brine
 - Pickle Brine
 - Similar in concept to any Chloride-based brine. Therefore with regards to sodium and chloride is not functionally different, but instead may offer cost savings if available at a discount.²⁰
 - Still need 23.3% NaCl²¹
 - Some testing has shown that the salinity can vary and pH levels could damage equipment²²

¹⁶ <http://clearroads.org/project/13-02/>

¹⁷ <https://pdfs.semanticscholar.org/dc7d/b590bba5eec847a379a71dc670bc0a9152ce.pdf>

¹⁸ <https://pdfs.semanticscholar.org/dc7d/b590bba5eec847a379a71dc670bc0a9152ce.pdf>

¹⁹ http://www.virginiadot.org/vtrc/main/online_reports/pdf/00-r12%20.pdf

²⁰ <https://pdfs.semanticscholar.org/dc7d/b590bba5eec847a379a71dc670bc0a9152ce.pdf>

²¹ <https://docs.lib.purdue.edu/mwg-internal/de5fs23hu73ds/progress?id=NeQ3SCEYVQ22Nosf-bA1riZxP6BtF3-bRYm-HoAd1hA,&d>

²² <https://mntransportationresearch.org/2018/08/01/carver-county-evaluates-pickle-brine-for-ice-control/>

- Cheese Brine
 - Similar in concept to any chloride-based brine. Therefore with regards to sodium and chloride is not functionally different, but instead may offer cost savings if available at a discount.
 - Still need 23.3% NaCl²³
 - National Geographic Article²⁴
 - Most available where lots of cheese making is occurring (e.g., Wisconsin)
 - “stinky” odor
 - Cheese brine freezes at -21°F not -6°F like NaCl brine
- Organics (from Transportation Research Board’s: 1980 Alternative Highway Deicing Chemicals)²⁵
 - Methanol:
 - Works well below temperatures experienced in the mid-Atlantic. Water with 83% methanol freezes at -125°C
 - It has a neutral pH and is noncorrosive
 - At snow and ice temperatures volatility is reduced, however the volatility serves to minimize the concentration of methanol in runoff and therefore its contribution to BOD.
 - Also facilitates housecleaning since spills are self-removing
 - Flash point (combustion with a flame) of methanol is 60°F, well above the freezing point, while gasoline is fifty degrees below 0°F.
 - When in water it is higher than 60 degrees F
 - This 1980 paper states no ill effects from long-term exposure to low concentrations or to short intermittent exposures to high concentrations of its vapors (reference 1930).
 - MSDS state at >99% methanol it is toxic and may cause blindness or death. Handling can be a challenge
 - Vapor density slightly greater than air. It is slow, but faster than ethanol and isopropanol to rise
 - Cost is generally low
 - Methanol has been ruled out of use in Michigan because²⁶:
 - Volatizes and turns into a gas quickly and must be reapplied more often than salt
 - When evaporating, the breakdown products of methanol can affect ambient air quality and can contribute to ozone pollution in the lower atmosphere
 - Protective gloves, impervious clothing, and a self-contained breathing apparatus are necessary when handling methanol
 - Specialized application equipment is required
 - Cost is 5.5 times that of NaCl
 - Ethanol and Isopropanol
 - Like methanol the ethanol and isopropanol freeze at very low temperatures, have a neutral pH, are noncorrosive, contain no nitrogen or phosphorus, and are volatile and flammable above freezing temperatures.
 - Ethanol is the least toxic of all 3 alcohols, however it’s reaction with chlorine in water supplies can produce chloroform (implication for runoff into source waters)

²³ <https://docs.lib.purdue.edu/mwg-internal/de5fs23hu73ds/progress?id=NeQ3SCEYVQ22Nosf-bA1rIZxP6BtF3-bRYm-HoAd1hA,&dl>

²⁴ <https://news.nationalgeographic.com/news/2014/02/140204-melt-snow-ice-salt-beet-juice-pickle-brine/>

²⁵ <http://onlinepubs.trb.org/Onlinepubs/sr/sr185/185-043.pdf>

²⁶ https://www.michigan.gov/documents/ch2-deice_51438_7.pdf

- Vapor density much greater than air (will stick around a while)
 - Each is 3 times the cost of methanol
- Acetone
 - Similar to the 3 alcohols, but more flammable and more expensive.
- Formamide
 - Favorable in many ways but cost and formic acid creation
 - Contains nitrogen, so it is not allowed to be used in Virginia
- Dimethyl Sulfoxide (DMSO)
 - Favorable in some senses
 - No nitrogen or phosphorus
 - Relatively low toxicity
 - Very high solubilization and penetration properties leading to its ability to pick up and mobilize other pollutants
- Verglimit²⁷
 - Patented bituminous concrete pavement that contains calcium chloride pellets encapsulated in linseed oil and caustic soda. The pellets remain inactive until the roadway surface wears under traffic. As the pavement wears, the exposed particles dissolve by attracting and absorbing moisture from the air, creating minute pores in the pavement. When a pore becomes full, the spillover dampens surrounding pavement. These many damp spots create a surface on which it is very difficult for ice or packed snow to adhere.
 - Because it absorbs water problems with effectiveness occur below 24-27°F
 - Does not melt much snow after snowfall but prevents ice and snow from binding to the road surface, enabling traffic to break up the ice. When traffic is lighter, it is less effective. At least 5000 ADT (annual average daily traffic) is necessary to maximize full deicing potential.
- Sodium propionate²⁸
 - “SP was found to conform to the standard for toxic substances of deicer in Japan, to achieve more rapid deicing than sodium chloride (NaCl), and to cause almost no corrosion of metal. To reduce costs while taking advantage of SP, the mixing of NaCl and SP, which exhibits performances intermediate between those of NaCl and SP, is considered to be a solution. A mixture of 80% NaCl and 20% SP shows freezing point and ice melting performance equivalent to those of NaCl, mitigates the concentration of chloride ions and the inhibitory effects of NaCl on plants, and is still 80% less corrosive to metal than NaCl is. Considering SP’s high solubility in water and the field test results, it is recommended that SP be used as a pre-wetting material.”
 - This is the only identified deicing use of this food preservative that is toxic to mold and some species of bacteria.

²⁷ https://www.michigan.gov/documents/ch2-deice_51438_7.pdf

²⁸ <https://trid.trb.org/view/1437472>