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Comparison of Ag-Based Deicing Additives

APPLIED RESEARCH & INNOVATION BRANCH

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16. Abstract

The objective of this project is to assist Colorado Department of Transportation (CDOT) in the identification of regionally sourced agricultural co- or by-product deicer additives that will enhance corrosion protection and provide added deicing performance and longevity to road surfaces. A literature review provides a summary of agriculturally derived additives (ag-based) that have been used in deicing products, the benefits of incorporating these ag-based additives into deicing products, and potential sources local to Colorado for these products. Based on information gained from literature reviewed, the agricultural products with the greatest potential to serve as locally sourced additives for deicing are sugar beets, corn, and apples. Colorado based industries with the most promising co-products or by-products include the dairy industry, and beer, wine, and distilled alcohol production.

Products investigated for further testing included waste cheese brine, apple pomace, and by-products from regional beer and cider production. Cheese brine was the only ag-based product in which further testing was performed. Laboratory analysis of the Leprino cheese brine (LCB) determined it functions as a deicer, because it is a sodium chloride based product, that provides some corrosion protection.

A beneficial use permit was granted by CDPHE to Leprino Foods for the use of LCB by CDOT as a pre-wetting agent for field trial applications. LCB must only be applied at 8 gal/ton to pre-wet salt or salt sand and can only be applied in the defined field trail locations in Fort Morgan and Greeley, CO.

Initial field trail results suggest training before the 2022-2023 winter season is needed to support use of LCB in winter operations. Future work will consider improvements to LCB to reduce the phosphorus concentration, support data collection and analysis from field trials, and investigate other regionally sourced ag-based additives that could be used by CDOT in deicing operations.

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Introduction

The objective of this project is to assist Colorado Department of Transportation (CDOT) in the identification of regionally sourced agricultural co- or by-product deicer additives that will enhance corrosion protection and provide added deicing performance and longevity to road surfaces.

The following sections present work completed thus far and include a summary of key literature on agriculturally derived deicing additives (ag-based), the benefits of incorporating those ag-based additives into deicing products, and potential Colorado sources for the additives. This report also summarizes laboratory results for a selection of ag-based products and presents the steps required to set up the laboratory process, acquire a beneficial use permit from the Colorado Department of Public Health and Environment (CDPHE), and assist CDOT as they conduct field trials with the selected ag-based products.

Background

Muthumani et al. (2015) investigated the mechanism by which ag-based deicers improve deicer function. This project was able to quantitatively validate qualitative observations from the field. The results show that the addition of ag-based products improve deicer performance by suppressing ice nucleation (formation) at the lower limits of the deicer's working temperature, decreasing that lower limit and allowing the base deicing material to be used at even colder temperatures. Additionally, ag-based additives provide a residual effect; allowing more deicing material to remain on the pavement after plowing and for a longer period than additive-free deicers. Practically, this could mean an automatic reduction in black ice due to the residual material on the road as well as a reduction in deicer application rates. The addition of ag-based products was found to exert a lower corrosion rate than additive-free deicers (Fay and Akin, 2019; Fay and Akin, 2018; Muthumani, Fay and Shi, 2016; Muthumani et al., 2015; Nazari et al., 2019) and work by Fu et al. (2012) found that the application of organics (read: ag-based) to pre-wet solids and liquid anti-icers provided improved pavement friction. Additionally, Cuelho et al. (2010) concluded that the ag-based product Ice Clear RDF caused lower bond strength between snow, ice, and pavement, making plowing easier.

Ag-based products that provide benefits to deicers can be derived from a variety of organics, including beets, apple pulp, pulp/paper plants, potatoes (vodka co-products), tomato juice, corn steepwater or millings, wheat, rice, peonies, distillery and brewery by-products, vintner's condensed solubles, cheese brines, and many other co- or by-products of various industries (Jungwirth et al., 2014; Hansen 2016; Nazari et al., 2017; Nazari et al., 2019; Nazari and Shi, 2019).

While investigating potential sources of deicing additives from within the state, it was revealed that Colorado's agricultural production is dominated by livestock and livestock products (75%) (Purdue University, 2022). In terms of revenue generated, Colorado's top five agricultural commodities are cattle and calves, dairy products, corn for grain, greenhouse and nursery products, and hogs. Colorado crops include wheat, corn, hay, beans, grain sorghum, potatoes, and sugar beets. Apples are the leading fruit crop and carnations are the most valuable of the greenhouse and nursery products. The agricultural products with the greatest potential to serve as Colorado-sourced deicing additives are sugar beets, corn, and apples, while the industries with the most promising co-products or by-products include the dairy industry, beer, wine, and distilled alcohol production.

Products Investigated

Following the initial research identifying regionally sourced ag-based additives, CDOT staff connected the research team with Leprino Foods, a Colorado-based cheese company. While making mozzarella, Leprino Foods produces a waste brine that they offered to CDOT to use as a deicer. A detailed summary of laboratory analysis of the Leprino Cheese Brine (LCB) is provided below.

Another ag-based additive, apple pomace, was identified as a potential regionally sourced option for deicer additives. While currently under development by east coast based Fusione CORP, apple pomace has great potential in Colorado due to the local production of cider and other apple products. Details on Apple/Fruit Pomace are provided below.

To fully explore potential regionally sourced ag-based products, the research team contacted Colorado breweries and cider companies and invited them to participate in this project. The contacted companies decided that they were not interested in participating at this time; however, this effort could be pursued again in the future.

Leprino Cheese Brine

Leprino Foods has mozzarella cheese making facilities in Greeley and Fort Morgan, Colorado and is headquartered in Denver. Staff from Leprino Foods reached out the CDOT after learning about the use of F&A Dairy cheese brine for winter maintenance operations in Polk County, Wisconsin. Leprino Foods hoped to replicate the process with CDOT and use their own mozzarella-curing cheese brine as a liquid deicing product and pre-wetting agent. Additional information the use of F&A Dairy cheese brine by Polk County, WI is provided below.

Historical use of Cheese Brine in Winter Maintenance Operations

The following information was provided by Emil "Moe" Norby, Director of Recycling and Solid Waste in Polk Co, WI on the use of F&A Dairy cheese brine in winter maintenance operations.

- Polk County, WI is no longer using the cheese brine because the factory moved locations and they no longer have access to it.
- Moe found the cheese brine worked in the field and remained in storage at temps down to -21°F.
- Because of the colder working temperatures, he was able to use the product as a pre-wetting agent (applied at 8-15 gal/ton) on all routes except one.
    - Moe recommends a higher pre-wetting rate (15-40 gal/ton) but his equipment at the time did not allow for this.
    - They pre-wet at the auger and spinner.
- Moe worked with the Department of Natural Resources (DNR) to get a permit to use the product. Due to high BOD (Biological Oxygen Demand) they were only approved to use the product to pre-wet.
- They received the cheese brine after filtration and had no issues with clogging or mold even when stored outside through summer. It did have a cheesy smell, but not bad.
- The cheese brine arrived with a salt concentration of 21.8 - 24%.
- Challenges: When the cheese brine was blended with $MgCl_2$ (Moe attempted to make a cold temperature blend) the solids would drop out of suspension. This could cause clogging during liquid application.

Contact: Emil "Moe" Norby, emil.norby@co.polk.wi.us, (715) 485-8723

Supplemental material on this effort is provided below.

Norby, E.M. F&A Dairy Salt Brine Report. 2008-2009 Winter Season. Polk County Highway Department. April 2009. (Submitted to CDOT project along with this Task Report)

Chappell, B. "Cheese to the rescue: Surprising Spray Melt Road Ice." National Public Radio, January 21, 2014. https://www.npr.org/sections/thetwo-way/2014/01/21/264562529/cheese-to-the-rescue-surprising-spray-melts-road-ice

Laboratory Testing Results

This section presents laboratory testing results for LCB. Note that a summary of the lab results used in the CDPHE beneficial use permit (Appendix A. Beneficial Use Permit & Letter of Approval) are provided in Appendix C. Summary of WTI & Analytical Lab Testing Results (Appendix C. Summary of WTI & Analytical Lab Testing Results).

The following table summarizes the salt brine and LCB samples and blends used in all testing for this project (Table 1). Note that Leprino Foods filters the cheese brine to remove solids and fats.

Table 1. Sample ID and description for all salt brine, LCB, and blended samples.

Sample ID	Description
NaCl1	23.3% salt brine made from reagent grade NaCl and deionized water
NaCl2	23.3% salt brine made by Colorado DOT
LCB-W	14% salt brine, Leprino cheese brine sample provided to Weld Laboratory by Leprino Foods
LCB1	14% salt brine, Leprino cheese brine sample provided to WTI by Leprino Foods
LCB2	14% salt brine, Leprino cheese brine sample with phosphorus removal provided to WTI by Leprino Foods
LCB4	19% salt brine, Leprino cheese brine sample with phosphorus removal provided to WTI by Leprino Foods
Prewet blend (LCB2 + NaCl2)	23.7% salt brine, CDOT salt brine blended with 1.5% by volume LCB2 (equivalent to prewet rates of 8 gals LCB to 1 ton of rock salt). Blend made by WTI.
50:50 blend	50:50 blend of LCB1 with NaCl1. Blend made by WTI.

Elemental Analysis

Preliminary testing of LCB was conducted by two labs: Weld Laboratory in Greeley, Colorado; and Bridger Analytical in Bozeman, Montana. Test results indicated that LCB is a complex chloride comprised of approximately 14% NaCl (sodium chloride or salt) and lesser to trace amount of potassium chloride (KCl), calcium chloride ($CaCl_2$), and magnesium chloride ($MgCl_2$) (Table 2).

Table 2. Summary of elemental analysis of Leprino cheese brine sample #1 (LCB1). Reported results are from Bridger Analytical.

Element	Concentration (mg/L)	Percent concentration (%)
Calcium (Ca)	42.5	0.00425
Chloride (Cl)	142000	14.2
Potassium (K)	2490	0.249
Magnesium (Mg)	5.8	0.00058
Sodium (Na)	91300	9.13

Elemental analysis showed phosphorus concentrations were of potential concern in LCB (Table 3). The LCB has a higher amount of phosphorus than is allowed by CDOT and the state of Colorado, which has strict water quality guidelines and requires that total phosphorus be equal to or less than 25 mg/L. The LCB1 sample had a total phosphorus concentration of 344 mg/L. To address this, Leprino Foods used an iron-based flocculation method to remove phosphorus from the cheese brine. After an initial flocculation, the LCB2 sample had a much lower total phosphorus concentration of 40.7 mg/L. LCB2 still exceeded the Colorado State water quality limit of 25 mg/L but the flocculation process clearly succeeded. Additional work by Leprino Foods paired evaporation and flocculation to produce a high salt, low phosphorus concentration sample (LCB4). With a low total phosphorus concentration of 9 mg/L, LCB4 easily passed the Colorado State water quality limit of 25 mg/L. This shows that the flocculation method could remove enough phosphorus from a large volume (200,000 plus gallons) of LCB for it to pass Colorado State water quality regulations and be used by CDOT as a liquid deicing product in the future.

Table 3. Summary of phosphorus values for various LCB samples and blends.

Sample ID	Total Phosphorus (mg/L)
LCB – W	300
LCB1	344
LCB2	40.7
Prewet blend (LCB2 + NaCl)	58
LCB4	9

Biological Oxygen Demand

Biological, or biochemical oxygen demand (BOD) is the amount of oxygen used by bacteria and microorganisms while they decompose organic matter (USGS, 2018). BOD is relevant to all ag-based deicing additive products because BOD represents the largest potential impacts of the product on the environment. Results for a prewet blend of LCB2 and CDOT salt brine, and the LCB4 sample, are presented in Table 4.

Table 4. Summary of BOD values for various LCB samples and blends.

Sample ID	BOD (mg/L)
Prewet blend (LCB2 + NaCl)	800
LCB4	3600

The BOD values measured for LCB2 and LCB4 are typical for agriculturally derived deicing additives. From a water quality perspective these values are high, with very poor-quality water having a BOD of 100 mg/L or more and sewage having a BOD of approximately 200 mg/L. Therefore, the BOD of LCB should be monitored and considered, and testing for BOD should occur at least once per year.

Ice Melting Performance or Ice Melt Capacity

The ice melting performance of LCB was assessed using two methods: the Strategic Highway Research Program (SHRP) H 205.1/205.2 (Chappelow et al., 1992), and the Mechanical Rocker Test (MRT) method (Hansen and Halsey, 2019). Table 5 summarizes the results of both methods, which are reported as average and standard deviation of mL of ice melted per gram of deicer. Overall, the results of the ice melting capacity tests provided inconsistent results. Note that ice melting capacity test results can vary greatly for an individual deicer between test methods and labs (Nilssen et al., 2016). For this reason, additional testing should only be pursued after the validity of the data set provided by these test methods is discussed with CDOT.

Table 5. Summary of ice melting capacity results for salt brine, LCB, and blended samples.

Test Method	Sample ID					
	NaCl1	NaCl2	LCB2	LCB4	Prewet Blend	50:50 Blend
SHRP Ice Melting Capacity (mg/L)	0.48 ± 0.03		0.52 ± 0.02			0.46 ± 0.04
MRT (mg/L)		0.37 ± 0.08	0.09 ± 0.04	0.22 ± 0.07	0.29 ± 0.10	

Improved Performance – Corrosion Protection

Corrosion testing was performed using the National Association of Corrosion Engineers Pacific Northwest Snowfighters (NACE PNS) testing method specified in the Clear Roads Qualified Product List test method guide. The following results are reported for LCB2, a prewet blend of LCB2 and CDOT salt brine, and LCB4 (Table 6). Note that, when using the NACE PNS corrosion test method, an effective value of 70% or better than the salt brine baseline is considered passing for corrosion inhibiting products. The results of corrosion testing show that LCB provides corrosion protection.

Table 6. Corrosion rates for LCB samples.

Sample ID	Corrosion Rate (%)
LCB 2	60.2
Prewet blend (LCB2 + NaCl)	67.2
LCB4	74.6

Blending LCB with $MgCl_2$-Based Products

When cheese brine was originally used as a deicer in Wisconsin, one of the concerns was that, if blended with magnesium chloride ($MgCl_2$)-based liquids, the mixture would clog equipment and lines. This is a valid concern for CDOT as well because they use $MgCl_2$-based liquid deicers routinely. To test for potential clogging using LCB, CDOT provided a sample of two $MgCl_2$-based liquids used for deicing in Colorado – Apex and Torch. The experiment consisted of two 300 mL beakers filled with 200 mL of LCB1. Each beaker then had 1% by volume of Apex or Torch added to the respective beaker, mixed for 5 minutes, then allowed sit on the benchtop for up to five days. For each 1% by volume addition of either Apex or Torch no observed changes were identified up to 5%. Precipitate was observed when 6% by volume of either Apex or Torch was added to the respective beaker of LCB1, mixed for 5 minutes, and allowed to sit for up to 5 days (**Error! Reference source not found.** and **Error! Reference source not found.**).

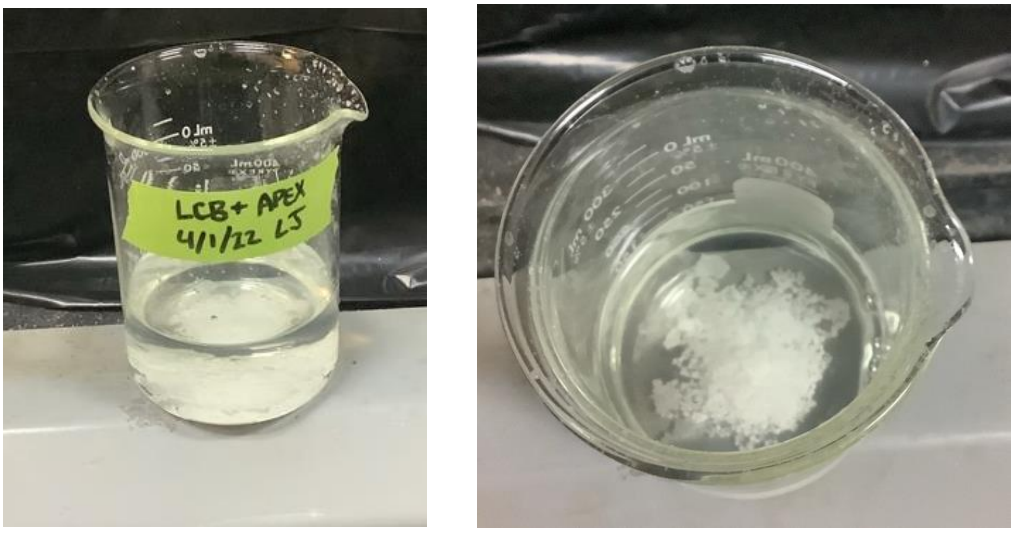

Figure 1. Photographs of 6% Apex by volume added to LCB1 showing precipitate present at the bottom of the beaker.

Figure 2. Photographs of 6% Torch by volume added to LCB1 showing precipitate present at the bottom of the beaker.

Note that blending either Apex or Torch, both $MgCl_2$-based deicing liquids, with LCB should be avoided, especially at volumes great than 5% because the presence of precipitate may clog lines in the liquid application systems. To avoid precipitate from forming and to prevent clogging LCB should be stored and transported in new or well-cleaned tanks. Additionally, all lines and equipment that will be used to apply LCB should be flushed or cleaned.

Addressing Concerns

Key concerns when using a waste stream product, such as the leftover salt brine from cheese manufacturing, include addressing any water quality standards in the state where it will be used and determining if the product performs as intended. Laboratory testing showed that LCB is a complex chloride that ranges in concentration from 13-19% chlorides (Na, K, Ca, Mg), that functions to melt ice and provides corrosion protection. For Leprino cheese brine both total phosphorus and BOD were noted as potential areas for concern for LCB, though testing confirmed that BOD values were not a primary concern. However, LCB phosphorus values failed to meet Colorado State requirements. For the research team to recommend the use of LCB as a liquid deicing product, additional work will need to be done by Leprino Foods to consistently reduce total phosphorus concentrations to 25 mg/L or less. Additionally, to make the LCB product easy to use it is recommended that salt brine concentration be increased to 22-24%, closer to the 23.3% target concentration for salt brine.

Given the high phosphorus concentrations, the research team recommended that CDOT not apply LCB directly to the road surface in its unflocculated state. Instead, based on previous use in Wisconsin, the research team recommended that LCB be used as a pre-wetting agent. CDOT currently prewets rock salt or salt-sand blends at 8 gallons per ton (gal/ton) of solid material and applies 150 pounds of material per lane mile (lb/l-m). Based on this application rate the research team found that 662 mg of Phosphorous

would be added to road over the course of one lane mile (or 63,360 ft^2) per treatment. This information was shared with CDPHE and used in the beneficial use permit application.

Beneficial Use Permit for Leprino Cheese Brine

Based on LCB's promising test results as a pre-wetting agent, Leprino Foods applied for a CDPHE beneficial use permit for the use of LBC as a pre-wetting agent, which was granted by CDPHE on February 17, 2022 (Appendix A. Beneficial Use Permit & Letter of Approval). The permit stipulates that the LCB be used as pre-wetting agent only and be applied at no more than 8 gal/ton (typical CDOT prewetting rate). Additionally, the LCB may only be applied in the approved field trial locations: Fort Morgan, Colorado - US 34 from mile marker (MM) 159-180.7, Hwy 71 MM 175.5-181.4, and Hwy 6 MM 371-380.5 (Figure 3); and Greeley, Colorado - I-76 frontage road from MM 25-31 (**Error! Reference source not found.**).

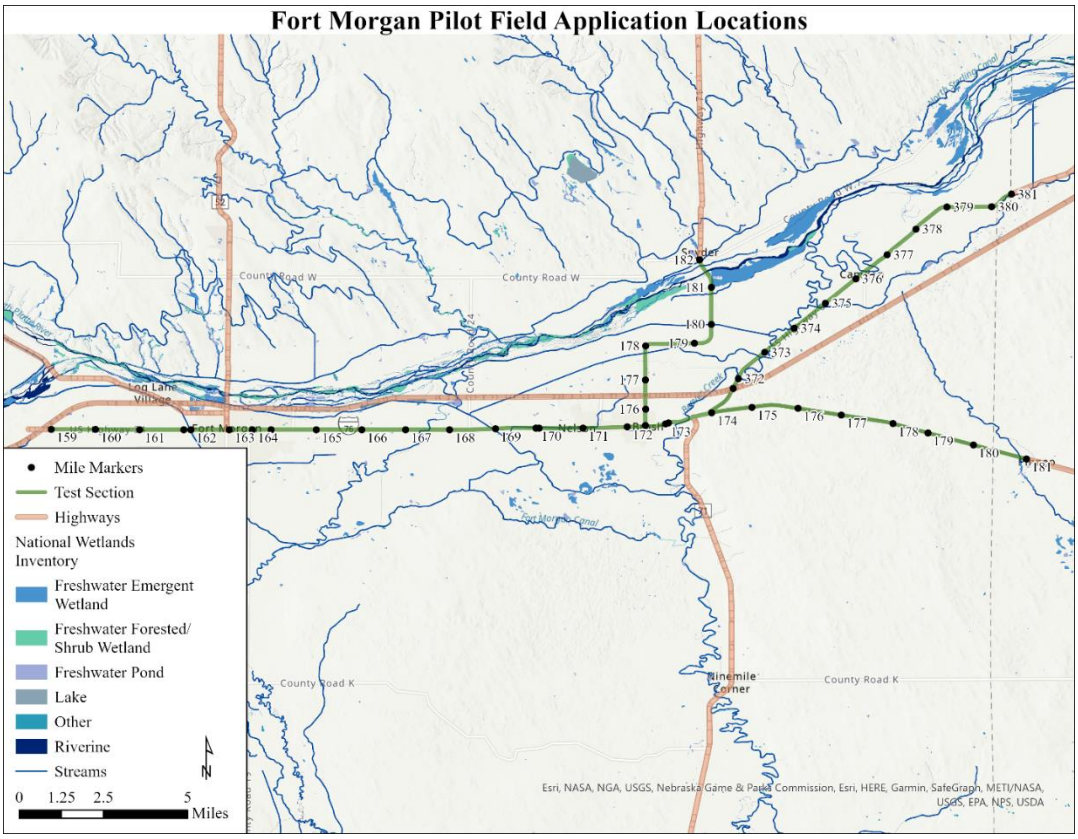

Figure 3. Map of Fort Morgan, Colorado field trial locations.

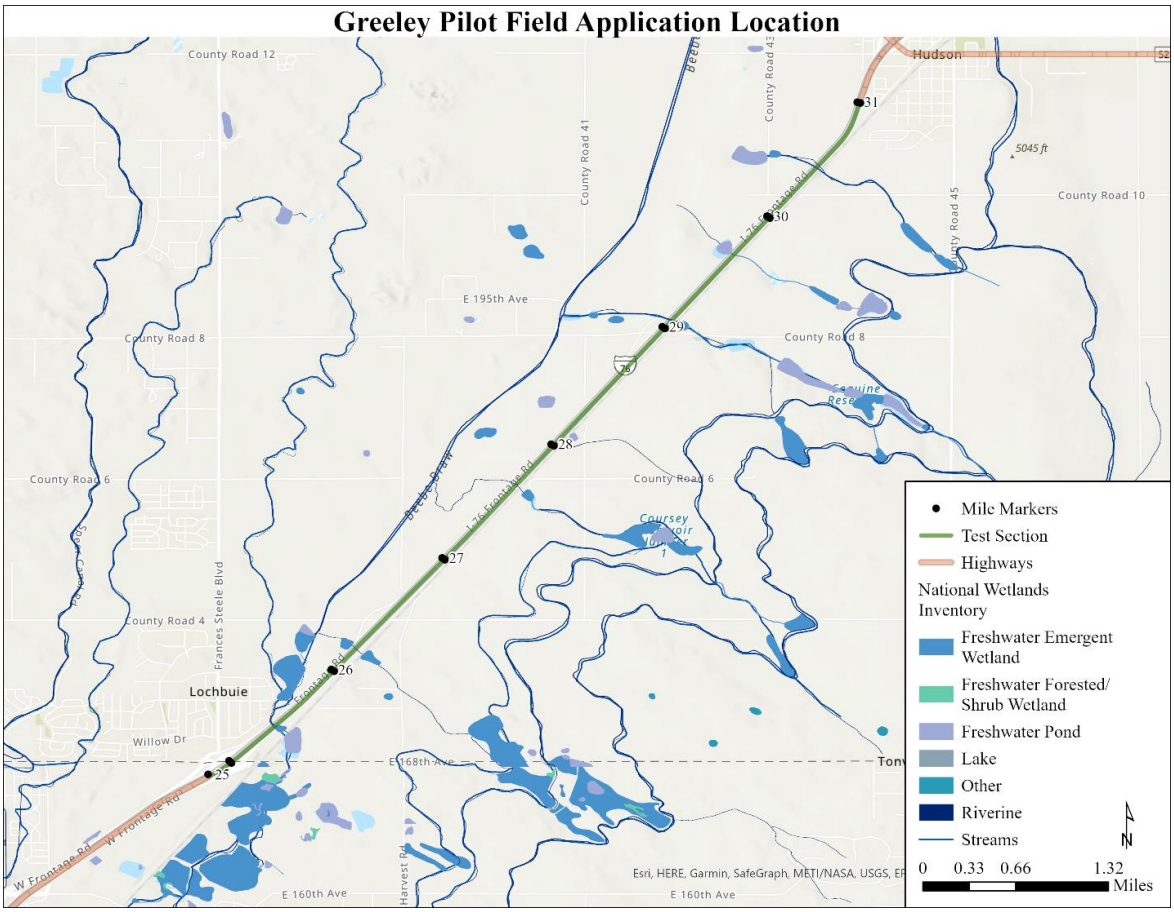

Figure 4. Map of Greeley, Colorado field trail locations.

Field Trials – Pre-wetting with Leprino Cheese Brine

A kick-off meeting in March with the CDOT research project team, CDOT maintenance staff from Fort Morgan and Greeley, the WTI research team, and Leprino Foods was held to discuss the logistics of the field trial: the application method approved (pre-wetting salt or sand with LCB at 8 gal/ton), the locations where the product could be applied, the data that would be collected, and LCB pick-up protocol from the Fort Morgan Leprino Foods facility. A field trail plan was developed for CDOT in and is provided Appendix B. CDOT Field Testing Plan. The limited time remaining in the winter season prevented both the Fort Morgan and Greeley CDOT facilities from picking up more than one load of LCB each.

Fort Morgan

Fort Morgan CDOT staff picked up 800 gallons of LCB from the Fort Morgan Leprino Foods facility and no challenges or issues were reported. CDOT then attempted to apply the LCB along Hwy US 34 from MM 159 to 181 on 3/16/2022 at 16:00 and at an air temperature of 45°F. However, despite using freshly rinsed tanks and a clean spray bar, the system clogged with a thick, chunky material (**Error! Reference source not found.**). Due to the clogging, the LCB was NOT applied on the road and was instead used to treat the sand pile on site at the CDOT Fort Morgan facility.

Figure 5. Photograph of "thick chunky material" that formed during application. D. Walker, CDOT

Greeley

Greeley CDOT staff picked up 900 gallons of LCB from the Fort Morgan Leprino Foods facility and no challenges or issues were reported. CDOT then applied the LCB on the I-76 frontage road from MM 25 to 38 at a rate of 30 gal/l-m. "The day before the storm we sprayed the product and let it break (read: sit and dry) to leave behind a residue to create (read: prevent) a bond [sic: from forming] between the pavement and ice/snow to save time" [sic: in winter maintenance operations] (Personal communication, CDOT staff from Greeley, May 18, 2022).

Greeley CDOT applied the LCB at 14:00 on 3/16/2022 and an air temperature of 57°F with full sun exposure. A mixture of rain and snow fell at approximately 04:00 on 3/17/2022. By 05:30 the air temperature was 32°F. Note that rain occurred as the storm arrived and a slight difference in road conditions occurred between the I-76 frontage road (field trail location) and Hwy 52 (untreated road in close proximity to the field trial location). It is possible that the rain diluted and/or remove some or all of the pretreatment that was applied.

The challenges faced during Fort Morgan and Greeley CDOTs initial effort to use LCB in winter operations highlights the importance of training on both the application method and applicate rate

approved in the permit. Additionally, the research team and CDOT will need to address the clogging issue in the late summer/early fall of 2022, prior to LCB use in the 2022-2023 winter season.

Apple/Fruit Pomace

Agriculturally derived pomace, the pulp that remains after pressing fruits for juice, can be sourced from local waste streams and converted into deicer additives. Washington State University has conducted extensive testing on the use of apple pomace as a deicer additive (Nazari et al., 2020; Nazari et al., 2017; Nazari et al., 2018) and found it improves the performance of salt brine; the product remains on the road longer, increases roadway friction, improves function at colder temperatures, and reduces corrosion to metal and impacts on concrete and asphalt.

The conversion of pomace to a deicer additive uses a unique, and currently patent-pending process that degrades biowaste and biowaste extracts the rights to which are held by Fusione Corp (WSU, 2020). Fusione Corp is currently working to scale up this process and have plans to conduct field trials across the United States during the 2022-2023 winter season.

Non-fruit biowaste sources may also be used and include leaves of flowers, vegetation, vegetables, shrubs or combinations of these. Specific examples of biowaste sources:

- Flower leaves – peony, tulip, rose, daffodil, etc.
- Vegetation – Kentucky blue grass, sugarcane bagasse, crop residues, corn stover, wheat straw, barley, oats, rice straw, millet, sorghum extracts, etc.
- Vegetables – potato, squash, etc.
- Fruit rind or skin – grape, apple, pear, tomato, cherries, citrus fruits, melons, pineapple, etc.

In patent No. 63/972, the degradation of biowaste refers to the chemical and biological processes that break down biowaste into smaller molecules using urea (CH_4N_2O), sodium hydroxide (NaOH), potassium hydroxide (KOH), lithium hydroxide (LiOH), bacteria (*Bacillus Megaterium*), or fungus as a degradant. The two-step process first uses chemical degradation with CH_4N_2O, followed by biological degradation using *Bacillus Megaterium*. The degradation process occurs at 15±5°C (approximately 59°F) or colder temperatures. The process was designed to occur at room temperature.

The degradation product will have a molecular structure of $C_{4\text{-}42}H_{5\text{-}63}O_{2\text{-}15}P_{0\text{-}1}N_{0\text{-}8}$, which can be confirmed with Fourier transformed infrared Spectrometer and Liquid chromatography-mass spectrometry (FTIR LC-MS). For example, the apple degradation product is $C_{26}H_{50}NO_7P$, or 1-Linoleoyl-sn-glycero-3-phosphocholine, and sugar beet leaf, apple and pomace also contain $C_{42}H_{63}O_4P$.

The degraded biowaste products can be added to a variety of deicers and work as effective corrosion inhibitors by adsorbing onto steel surfaces and forming a barrier layer that blocks active anodic sites. Patent No. 63/972 suggests that these products be added to deicers at 0-6%, by weight, depending on the biowaste source material. Additional materials may be added to these deicer blends to further improve performance.

The benefits of using agriculturally degraded deicer additives include a lower than typical additive rate for corrosion protection, potential reduction in NaCl application rates of 29-37%, and a low COD and BOD compared to all other agriculturally derived products. Given the product benefits, large number of apple cider producers, and significant number of apple orchards in Colorado, degraded apple pomace is

a viable locally sourced ag-based deicer additive option for use by CDOT. As this project progresses, any updates on the use of apple pomace will be provided.

Future Work

The research team has proposed that CDOT continue field trials of the LCB as a prewetting agent to salt or sand in the same Fort Morgan and Greeley field trail locations during the 2022-2023 winter season. This would allow for information to be captured on the logistics, functionality, costs, and benefits of using LCB. It would also allow for the exploration of a flocculated (low phosphorus concentration) version of LCB that could be directly applied roads as an anti-icing treatment. The research team will work with Leprino Foods on the development and testing of the product, and if deemed feasible, will pursue a CDPHE beneficial use permit so this it may be tested in similar field trials.

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WSU, (Biologically-derived Deicer, Provisional Patent No. 62/972, 142, filed Feb. 10, 2020)

Appendix A. Beneficial Use Permit & Letter of Approval

COLORADO
Hazardous Materials & Waste Management Division
Department of Public Health & Environment

Application for a solid waste beneficial use determination

This form should be used to request a Beneficial Use Determination (BUD) in compliance with Section 8.6 of the Regulations Pertaining to Solid Waste Sites and Facilities, 6 CCR 1007-2. Please consult with the division at (303) 692-3320 prior to beginning the beneficial use process outlined below.

A. Applicant information

Applicant name: Leprino Foods Company
Business name (if different than applicant name): _____
Mailing address: 1830 West 38th Avenue
City: Denver State: CO Zip code: 80211
Billing address: 1830 West 38th Avenue
City: Denver State: CO Zip code: 80211

Consultant name (if applicable): Laura Fay
Mailing address: 2327 University Way
City: Bozeman State: MT Zip code: 59715

B. Type of beneficial use requested

Application type: New ☒ Re-characterization ☐ Modify existing determination ☐

Does the beneficial use proposal involve the land application of any material? Yes ☐ No ☐

Application category: Category 1 ☒ Category 2 ☐ Category 3 ☐ Case-by-case ☐

Category 1: Wastes that have been characterized according to the methods established in Section 8.6.5 and test results indicate the material contains the constituents in Tables 1A and 1B at or below the specified standards or at or below the levels contained in the raw materials being replaced. Category 1 beneficial use materials may be used for those uses identified under Waste Category column 1 on Table 2.

Category 2: Wastes that have been characterized according to the methods established in Section 8.6.5 and test results indicate the material or *final product containing the material* contains the constituents in Table 1B at or below the specified standards or at or below the levels contained in the raw materials being replaced. Category 2 beneficial use materials may be used for those uses identified under Waste Category column 2 on Table 2.

Category 3: Wastes that have been determined to not be a hazardous waste may be used in solid and hazardous waste disposal areas that are approved to accept the beneficial use material for those uses identified under Waste Category 3 on Table 2.

Case-by-Case determinations apply to those solid wastes to be beneficially used, but not identified at the top of Tables 1 and 2.

C. Signature

This document must be signed by the applicant or a legally authorized representative of the applicant.

I certify under penalty of law that this document and all attachments contained in this application are true and correct to the best of my knowledge and belief.

Signature: James Frazier Printed name: James Frazier Date: 01 Feb 2022

D. Required attachments to the application

For an application to be complete, you must provide the required information for each listed item as it applies to the application category.

- ☒ A description of the material and the generation process, including initial characterization or re-characterization test results, if applicable.
- ☒ A description of the proposed beneficial use and methods for storing the materials.
- ☒ A comparison of the chemical and physical characteristics of the material proposed for beneficial use and the material it will replace.
- ☒ An estimate of the quantity of material to be beneficially used.
- ☒ Documentation that the proposed use is acceptable by the local governing authority, if applicable.
- ☒ Any other information that may be required to evaluate the proposal.

E. Performance criteria

For all categories - an application for beneficial use determination must demonstrate satisfactory compliance with the following performance criteria.

The use is beneficial, including:

- There is an identified or reasonably likely use for the material that is not speculative;
- The use is a valuable part of a manufacturing process, an effective substitute for a valuable raw material or commercial product, or it is authorized by the Department and does not constitute disposal;
- The use is in accordance with applicable engineering standards, commercial standards, and agricultural or horticultural practices.

The use will not create an adverse impact on public health and the environment, including:

- The material is not hazardous waste under the rules developed by the Solid and Hazardous Waste Commission in compliance with § 25-15-302 C.R.S.;
- The material will be managed to prevent nuisance odors or ground water contamination;
- Contaminants in the material do not exceed the unrestricted use levels, naturally occurring background concentrations, acceptable risk levels, or those levels present in a comparable raw material or commercial product.

The use shall comply with all applicable federal, state and local regulations.

F. Fees

Fees will be invoiced the calendar quarter following the issuance of the beneficial use determination.

A review fee of $125 per hour will be assessed to beneficial use applicants regardless of the approval status. The fee covers professional staff time spent reviewing, evaluating and responding to documents submitted. Complete and well-organized attachments to this application can help minimize your costs.

Instructions

Complete all sections of the form, make a copy for your files and send the completed form and all attachments to:

cdphe.hmrecycling@state.co.us or

Colorado Department of Public Health and Environment
c/o Beneficial Use Determination
HMWMD-SW-B2
4300 Cherry Creek Drive South
Denver, CO 80246-1530

Executive Summary

Leprino Foods Company (LFC) is the world's largest mozzarella cheese manufacturer and is headquartered in Denver, Colorado with manufacturing sites in Fort Morgan and Greeley Colorado. These 2 sites support almost 90% of the dairy production in the State with dairy being the 3rd largest agricultural category in Colorado. The production of mozzarella cheese uses a NaCl "brine" solution to cool the cheese. Periodically, the cheese brine must be discarded. Typically, the spent cheese brine is blended with the other wastewater generated at the cheese manufacturing facilities during their daily cleaning, processed on sight through the biological wastewater treatment plants, and then is discharged into receiving streams as is allowed by their permit. Note that the biological wastewater treatment plants do not remove the NaCl, it is only diluted in this process, therefore the discharged brine is still loading the receiving waters with same quantity of chlorides. The other cheese brine disposal option involves disposal of the spent brine through stabilization/solidification followed by landfilling the material. To be able to landfill a liquid waste, you must mix it with a solid material to render it as a solid that can pass a paint filter test. And the landfill must be approved to accept salt wastes. The cost to haul, solidify, and landfill the material is $0.87 per gallon for Leprino.

Leprino foods has established aggressive targets for water use reduction at each of their manufacturing facilities. With a goal of a 2% reduction each year through 2030. This can be realized by more water either being conserved or recycled within the manufacturing facility. The more we conserve water, the higher the concentration of salt in our wastewater discharge. Collecting the brine for use in the de-icing process facilitates water conservation practices in the manufacturing facility because it removes salt from the wastewater effluent into the receiving stream.

In looking for more environmentally responsible ways to handle the spent cheese brine, Leprino Foods became aware of the use of spent cheese brine by Polk County, Wisconsin road authority as a pre-wetting material in winter maintenance operations. This led Leprino to reach out to Colorado Department of Transportation (DOT) to determine if beneficial use of the cheese brine could be achieved in partnership with the state of Colorado. Such that, by utilizing the spent brine as a prewetting agent, Leprino Foods can decrease their potable water usage in its operations.

Colorado DOT has been working with Montana State University (WTI-MSU) over the last 2-3 years to identify locally sourced agricultural byproducts that can be used as additives and alternatives in winter maintenance operations. As a part of this effort CDOT allowed WTI-MSU to work with Leprino to run preliminary testing on the spent cheese brine to determine if the product could function as a pre-wetting agent. Note that pre-wetting refers to the addition of a liquid to a solid, typically salt brine applied to rock salt or salt-sand. By using pre-wetting methods, research has found that the greatest amount of deicing material will remain on the roadway where it can function, instead of being cast of roadway into the near road environment (Michigan DOT, 2012).Preliminary laboratory findings and discussions with Polk County, Wisconsin determined that the Leprino cheese brine could perform as pre-wetting agent. Polk County and the State of Wisconsin have received a lot of positive press for their creativity on a successful sustainability effort.

The beneficial use of the Leprino cheese brine by CDOT is support by the following environmental benefits. Both Leprino and CDOT add chlorides to the environment in Colorado. Leprino cheese brine is currently permitted to discharge directly into receiving waters. This means that the chlorides, and other constituents will be added to the surface water system in Colorado as a point source. If the cheese brine was utilized by CDOT, the salt that CDOT would have bought and brought in via train from out of state can be reduced. Reducing the overall quantity of chlorides put into Colorado's environment and the

greenhouse gas emissions from shipping the material from out of state. A third potential benefit is the shift from Leprino cheese brine being discharged as a point source into receiving waters, to a diffuse discharge in the near road environment. Research has found that standard storm water measures such as detention ponds, wetlands, etc., and soils in the near road environment work effectively to remove most pollutants (Murakami et al., 2008; Scholz and Yazdi, 2009).

To support the potential beneficial use of spent cheese brine, the Fort Morgan Leprino cheese factory is storing its waste brine in tanks.

In summary, the use of the spent cheese brine has many benefits to both Leprino Foods Company and the state of the Colorado and Colorado DOT, which include;

- Free salt brine for the CDOT displacing the material cost of $1.00 per gallon
- A pre-wetting agent that can replace the one currently used by CDOT
- Agriculturally derived products have the potential to provide additional benefits of reduced corrosion, suppressing ice formation, and keeping the product on the roadway longer leading to reduced overall applications of winter maintenance products (Muthumani et al., 2016)
- Greater level of corrosion inhibition due to the components of cheese brine
- A cost-effective alternative for manufacturing operations to dispose of their spent brine
- Lowering the mass amount of NaCl that enters the state of Colorado and local watersheds along with reduced shipping impacts
- Change in the loading to the environment from a point source to a non-point source that can potentially be bound or treated in the soil.
- Allows Leprino Foods to recycle/reuse more water in its manufacturing facility resulting in the reduced use of potable water

COLORADO
Hazardous Materials
& Waste Management Division
Department of Public Health & Environment

February 18, 2022

Mr. James Frazier
Leprino Foods Company
1830 West 38th Ave.
Denver, CO 80211

RE: Beneficial Use Determination - Leprino Food Company's Spent Cheese Brine for Use as a Pre-Wetting Agent in Colorado DOT Winter Roadway Maintenance Operations - Pilot Approval

Mr. Frazier,

The Hazardous Materials and Waste Management Division ("the Division") of the Colorado Department of Public Health and Environment has reviewed the request for beneficial use of spent cheese brine generated by the Leprino Food Company's facilities in Fort Morgan, CO and Greeley, CO. The initial application package proposing a pilot project in coordination with the Colorado Department of Transportation ("CDOT") was received by the Division on January 12, 2022. Upon initial review, the Division requested further information and this supplemental information was provided by Leprino on February 1, 2022. Based on the information provided, the Division has determined that the proposed beneficial use of the spent cheese brine meets the Division's criteria for Beneficial Use as defined in Section 8.6 of the Regulations Pertaining to Solid Waste Sites and Facilities, 6 CCR 1007-2, Part 1 ("the Solid Waste Regulations").

The proposal seeks to reuse Leprino's spent cheese brine in a pilot project as a pre-wetting agent for use by CDOT during winter roadway maintenance operations. Specifically, the spent cheese brine is to be added to rock salt or sand-salt mixtures at a standard rate of approximately 8 gallons liquid cheese brine per ton of rock salt or sand-salt mixtures for use in deicing operations. The proposal has identified one area of roadway near Fort Morgan, CO and another near Greeley, CO that will serve as testing grounds to use the cheese brine in deicing operations. These areas are identified by maps supplied in the beneficial use plan. The initial beneficial use proposal along with the supporting supplemental information has been combined and now forms the approved beneficial use plan for the pilot project.

The Division's approval is contingent upon the following conditions:

- All aspects of the approved beneficial use plan must be followed;
- Use of the spent cheese brine may only occur in the areas as shown in the maps in the approved beneficial use plan;
- The spent cheese brine is only to be stored in tanks or trucks. Any storage in ponds or impoundments could render the receiving pond or impoundment as a solid waste impoundment and would then be subject to the regulations for solid waste impoundments. Any unapproved release from a failed storage tank or truck may be considered a release of solid waste;
- The duration of the pilot project is not to exceed the end of the 2022-2023 winter season.
- The proposed beneficial use pilot project must get approval from the local governing body; and
- The proposed beneficial use must meet all other local, state and federal requirements.

Leprino Foods Company must register as an Industrial Recycling Facility with the Division in order to document the volume of spent cheese brine recycled annually. Annual recycling reporting is due March 1 of every year to document the amount recycled in the year prior. The first report will be due on March 1, 2023. Please find the registration and reporting information at the link below:

https://cdphe.colorado.gov/sw-recycling-forms-apps

Upon completion of the pilot project, please submit a summary report within 90 days of the last roadway application documenting how the use of the spent cheese brine was performed within the parameters described by the beneficial use plan as well as any additional supporting information to determine whether the pilot project was successful.

In closing, the Division is authorized to bill for its review of technical submittals at $125 per hour, pursuant to section 1.7 of the Solid Waste Regulations. An invoice for the Division's review of the above referenced document will be sent under separate cover.

If you have any questions regarding this letter, you may contact Michael Bankoff at (303) 692-3438.

Sincerely,

Michael Bankoff
Environmental Protection Specialist
Materials Management Unit
Hazardous Materials and Waste Management Division

Enclosures: Leprino Cheese Brine - Pilot Beneficial Use Plan

EC: Wolfgang Kray, Colorado Department of Public Health and Environment
Joe Herrud, P.E., Leprino Foods Company

Appendix B. CDOT Field Testing Plan

CDOT Leprino Cheese Brine Field Trial

Product: Leprino Cheese Brine (LCB)
Testing Locations: Fort Morgan, Greeley, and Colorado Springs, Colorado
Date: January – April 2022

Introduction

As a part of the active research project with Colorado DOT titled *Side-by-side comparison of agriculturally-based deicing additives*, Leprino cheese brine was identified as a potential source of salt brine for use in winter maintenance operations. Preliminary testing has determined that the LCB is a complex brine made primarily of sodium chloride (NaCl) and functions similarly to traditional salt brines used in winter maintenance operations. The LCB was found to provide mild corrosion protection, compared to salt brine alone, due to additives gained in the cheese brining process.

The Leprino Fort Morgan facility produces 6000-8000 gallons of cheese brine each month. Once Leprino is done with the brine, they blend it with their influent raw wastewater at a low dilution rate so that the treated wastewater, from the on sight water treatment facility, has acceptable total dissolved solids (TDS) and conductivity (read: chloride concentration) levels to allow for direct discharge to the rivers.

Instead of disposing of the LCB, Leprino is seeking a beneficial use permit from the Colorado Department of Public Health and Environment (CDPHE) to allow for the use of LCB as a deicer in winter maintenance operations. Benefits from the reuse of LCB can be seen by both parties, such as;

- Leprino
    - Reduced environmental and carbon footprint of operations

- CDOT
    - Free salt brine with mild corrosion protection
    - Salt brine availability year round
    - Reduced water use to make salt brine
    - Reduced cost from the purchase of deicing materials
    - Reduced environmental and carbon footprint of operations

Historically Leprino cheese brine has been used for dust control but that is no longer done. By using the cheese brine that already exists in Colorado from the Leprino facility there will be *a net reduction of salts making it into the States watershed*, as less salt will need to be purchased and brought into the state by CDOT for use in winter maintenance operations.

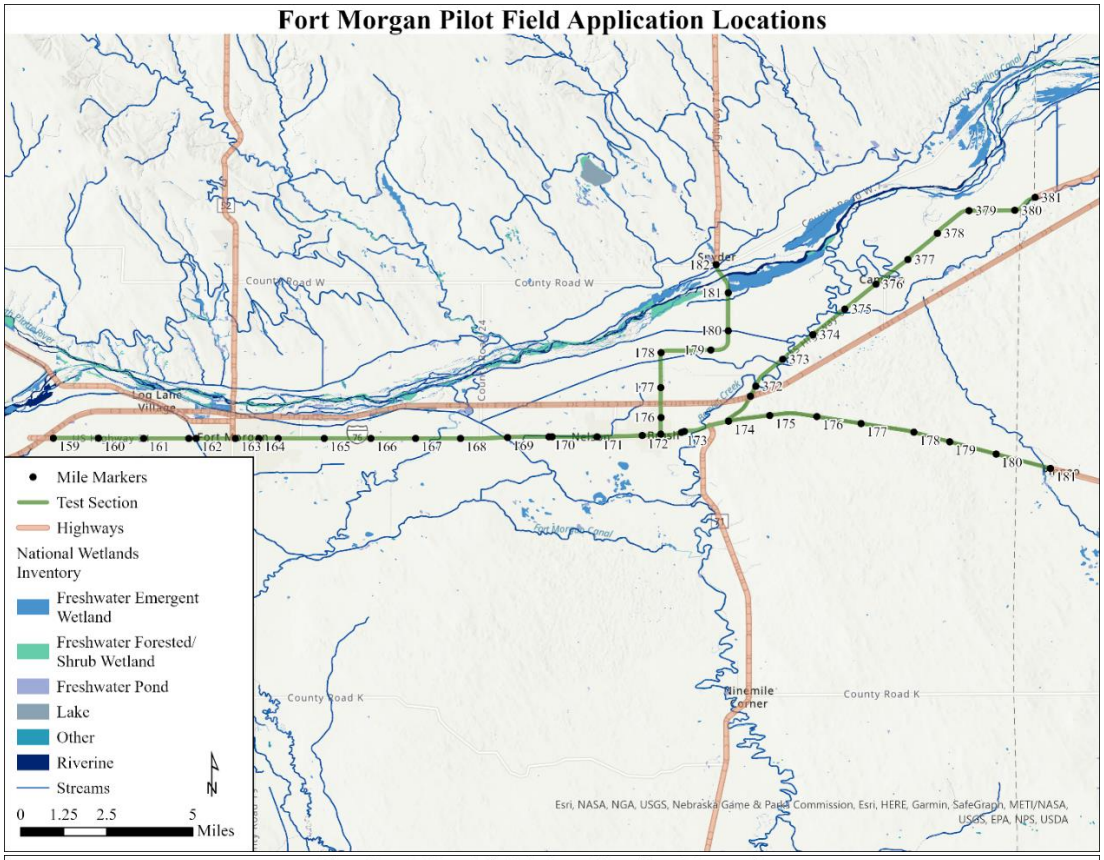
Test Plan Specifics

Roadway Environment

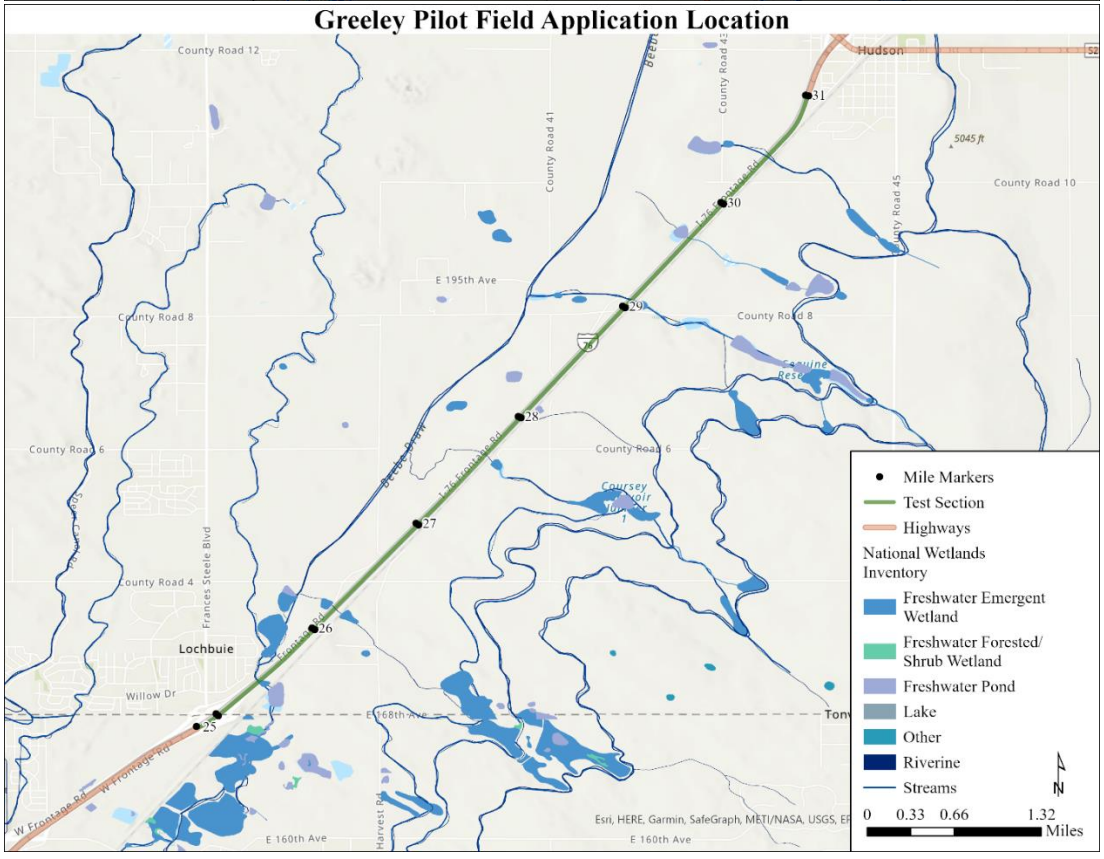
The following test sections have been identified to for field trials of LCB;

- Fort Morgan - US 34 from mile marker 159-180.7, Hwy 71 Mile marker 175.5-181.4, and Hwy 6 mile marker 371 to 380.5
- Greeley - I-76 frontage road from MM 25 to MM 31,

Fort Morgan Pilot Field Application Locations



Greeley Pilot Field Application Location



These locations were selected due in part to proximity to the Fort Morgan Leprino facility that is currently storing the LCB, as well as interest on the part of the maintenance mangers to participate in this effort.

As part of the CDPHE permit process, for each road segment where LCB will be used, environmentally sensitive areas including water ways, protected area, etc., will be identified, and application of LCB will be avoided if possible.

Winter Events

Application of the LCB will occur at the maintenance facilities discretion following normal protocols. Any and all winter conditions can and should be targeted in which normal deicer application would occur. No deviation from normal practices should occur.

Testing Methods & Equipment

LCB should be applied as a pre-wetting agent, a liquid added to solid material prior to application. LCB may be added to rock salt or sand-salt at normally prescribed rates for CDOT, or approximately 8 gallons per ton.

Test Material

As noted above in the introduction, Leprino cheese brine (LCB) is a complex chloride composed primarily of sodium chloride (NaCl) with small amounts of magnesium chloride ($MgCl_2$) and calcium chloride ($CaCl_2$). The LCB is available at approximately 13-16% NaCl concentration and is stored in large tanks at the Fort Morgan Leprino facility.

LCB will be picked up using DOT trucks at each driver's discretion. Communication between CDOT and Leprino for LCB pick up should be done via phone or email with:

Troy Gettman
Email: tgettman@leprinofoods.com
Phone: (970) 542-4256

Jim Volk
Email: jvolk@leprinofoods.com
Phone: (970) 867-9351

Data Collection Tools

Data will be collected on the following metrics:

- Logistics
    - Ease of pick up at the Leprino facility
    - Ease of use in normal winter maintenance operations
    - Does having a designated truck/tank for LCB work with your normal operations? (*Note that LCB cannot be mixed with magnesium chloride ($MgCl_2$) brines as it can cause clogging issues. A primary liquid used by CDOT is Apex, a magnesium chloride-based brine.)
    - Have you modified any logistics with getting, storing, or applying LCB since the start of the field trail?
    - Identify any challenges with logistics
- Functionality
    - How did the product perform?
    - Did it freeze in the tanks? Performance in storage?

    - Did any lines or equipment clog up or not work as well? (*Note that LCB cannot be mixed with magnesium chloride ($MgCl_2$) brines as it can cause clogging issues. A primary liquid used by CDOT is Apex, a magnesium chloride-based brine.)
    - Have you modified the application or use of LCB since the start of the field trial?
    - Identify any challenges in performance or functionality
- Costs and Benefits
    - Person and equipment hours and costs incurred from the pickup and storage of LCB by CDOT.
    - Amount of LCB applied in each location
    - Amount of normal deicing product saved by using LCB, and the costs (re: savings) associated with this.
    - Any additional costs, savings, or benefits identified?

This information will be captured through monthly conversations with the maintenance managers from Fort Morgan, Greeley, and Colorado Springs and from Leprino. An end of season conversation will be used to capture cost information and allow the maintenance manager to provide additional input.

Appendix C. Summary of WTI & Analytical Lab Testing Results

The following results are a summary of some of the testing used to characterize the Leprino cheese brine samples (Table 7). Note that LCB is Leprino cheese brine without any treatment, LCB1 are results from Weld Lab (see attached file), LCB2 and LCB3 are results from WTI-MSU testing, and Prewet (NaCl+LCB) is a blend made with Colorado DOT salt brine and LCB added at the equivalent rate of 8 gallons per ton of salt to mimic the prewet blend that is proposed for use by CDOT (testing conducted by WTI-MSU).

Table 7. Summary of chloride concentration, corrosion rate, total phosphorous, and BOD for LCB brines and blends.

	LCB1	LCB2	LCB3	Prewet (NaCl+LCB)
Chloride concentration (%)	13.8	14.2	13.4	23.7% NaCl
Corrosion Rate (%)*	NA	60.2	NA	67.2
Total Phosphorus (mg/L)	300	344	550	58
BOD (mg/L)	NA	NA	NA	800

*CDOT specific corrosion test, 3 day, TSI coupons, NACE Standard TM0169-95 (1995 Revision) as modified by Pacific Northwest Snowfighters.

The following summarizes ice melting test results for LCB, NaCl, and LCB:NaCl (50:50 blend) using two methods SHRP 205.1 (Chappelow et al., 1992[1]) and the Mechanical Rocker Test (Hansen and Halsey, 2019[2]). Preliminary results showed LCB had potential to be used in place of salt brine (**Error! Reference source not found.** and **Error! Reference source not found.**).

[1] Chappelow, C.C., McElroy, A.D., Darwin, D., de Noyelles, F.G., Locke, C.E. (1992) Handbook of Methods for Evaluation of Chemical Deicers. SHRP-H-332. Strategic Highway Research Program, Washington, D.C.

[2] Hansen, D. and Halsey, L. (2019) Validation of the Mechanical Rocker Test Method for Ice Melting Capacity (MRT-IMC). Nebraska Department of Transportation.

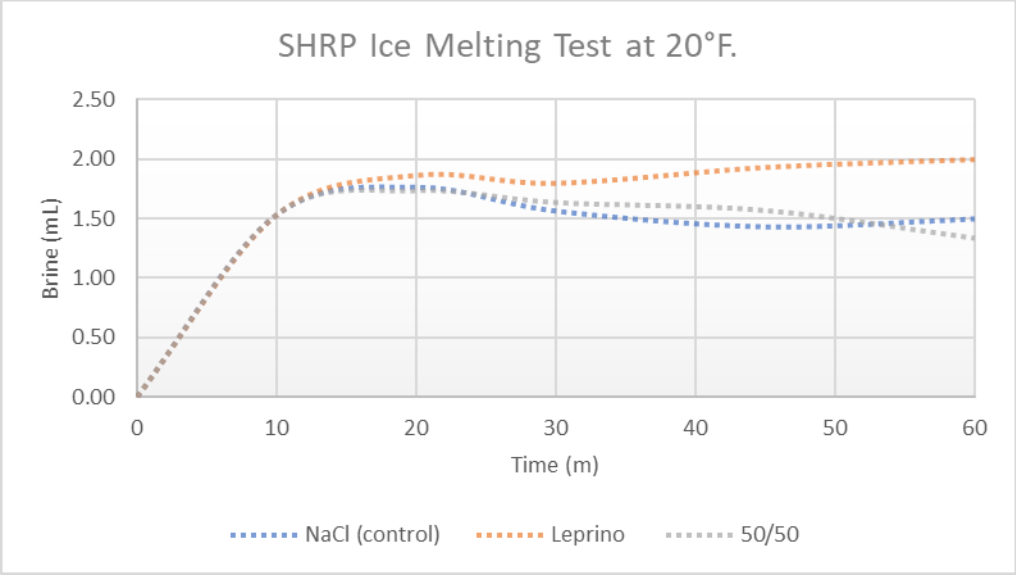


Figure 6. SHRP Ice melting test results at 20°F showing brine produced by each product over the course of one hour of testing.

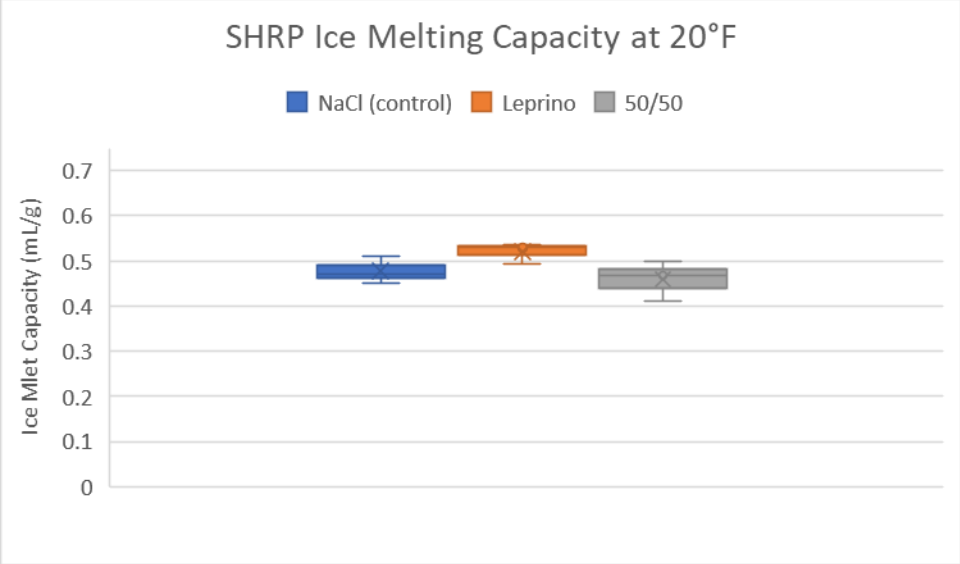


Figure 7. SHRP Ice melting capacity for each brine reported as milliliters of ice melted per gram of brine at 20°F.

Follow up work using the Mechanical Rocker Test to assess the brines melting capacity yielded the following results (Table 8).

Table 8. Summary of Mechanical Rocker Testing ice melting capacity results.

Ice Melting Capacity (mL/g)	NaCl brine (CDOT)	LCB	Prewet (NaCl + LCB)
	0.18 – 0.29	0.15 - 0.16	0.15 – 0.29

*Note that results between to the test methods cannot be compared, only the relative performance of each product within a test method can be compared.

Quantity of Phosphorus Added to the System

Assuming Colorado DOTs solid application rate of 150 pounds per lane mile (lbs/l-m) and pre-wet rate of 8 gallon per ton (gal/ton). The application of LCB prewetting rock salt or sand-salt will approximately add the following quantities of phosphorus to the environment:

Prewet (NaCl + LCB)

662 mg of Phosphorous added over the course of one lane mile (or 63,360 ft^2)

Prewet (NaCl + LCB) with phosphorus removed

17 mg of Phosphorous added over the course of one lane mile (or 63,360 ft^2)