

# **Economics of Using Calcium Chloride vs. Sodium Chloride for Deicing/Anti-Icing**

Final Report

TR488

By

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The opinions, findings, and conclusions expressed in this publication are those of the authors, and not necessarily those of the Iowa Department of Transportation.

## ABSTRACT

The use of chemicals is a critical part of a pro-active winter maintenance program. However, ensuring that the correct chemicals are used is a challenge. On the one hand, budgets are limited, and thus price of chemicals is a major concern. On the other, performance of chemicals, especially at lower pavement temperatures, is not always assured. Two chemicals that are used extensively by the Iowa Department of Transportation (Iowa DOT) are sodium chloride (or salt) and calcium chloride. While calcium chloride can be effective at much lower temperatures than salt, it is also considerably more expensive. Costs for a gallon of salt brine are typically in the range of \$0.05 to \$0.10, whereas calcium chloride brine may cost in the range of \$1.00 or more per gallon. These costs are of course subject to market forces and will thus change from year to year.

The idea of mixing different winter maintenance chemicals is by no means new, and in general discussions it appears that many winter maintenance personnel have from time to time mixed up a jar of chemicals and done some work around the yard to see whether or not their new mix “works.” There are many stories about the mixture turning to “mayonnaise” (or, more colorfully, to “snot”) suggesting that mixing chemicals may give rise to some problems most likely due to precipitation. Further, the question of what constitutes a mixture “working” in this context is a topic of considerable discussion.

In this study, mixtures of salt brine and calcium chloride brine were examined to determine their ice melting capability and their freezing point. Using the results from these tests, a linear interpolation model of the ice melting capability of mixtures of the two brines has been developed. Using a criterion based upon the ability of the mixture to melt a certain thickness of ice or snow (expressed as a thickness of melt-water equivalent), the model was extended to develop a material cost per lane mile for the full range of possible mixtures as a function of temperature. This allowed for a comparison of the performance of the various mixtures.

From the point of view of melting capacity, mixing calcium chloride brine with salt brine appears to be effective only at very low temperatures (around 0° F and below). However, the approach described herein only considers the material costs, and does not

consider application costs or other aspects of the mixture performance than melting capacity. While a unit quantity of calcium chloride is considerably more expensive than a unit quantity of sodium chloride, it also melts considerably more ice. In other words, to achieve the same result, much less calcium chloride brine is required than sodium chloride brine. This is important in considering application costs, because it means that a single application vehicle (for example, a brine dispensing trailer towed behind a snow-plow) can cover many more lane miles with calcium chloride brine than with salt brine before needing to refill. Calculating exactly how much could be saved in application costs requires an optimization of routes used in the application of liquids in anti-icing, which is beyond the scope of the current study. However, this may be an area that agencies wish to pursue for future investigation.

In discussion with winter maintenance personnel who use mixtures of sodium chloride and calcium chloride, it is evident that one reason for this is because the mixture is much more persistent (i.e. it stays longer on the road surface) than straight salt brine. Operationally this persistence is very valuable, but at present there are not any established methods to measure the persistence of a chemical on a pavement.

In conclusion, the study presents a method that allows an agency to determine the material costs of using various mixtures of salt brine and calcium chloride brine. The method is based upon the requirement of melting a certain quantity of snow or ice at the ice-pavement interface, and on how much of a chemical or of a mixture of chemicals is required to do that.

## 1: INTRODUCTION

In considering how well an anti-icing chemical performs, the very first question that must be addressed is what sort of performance should be measured. A number of recent studies have examined this issue (Nixon et al., 2007; Blackburn et al., 2004;) Table 1.1 lists possible areas of performance that might be of relevance in winter maintenance. Further possible areas are discussed in Nixon and Williams (2001).

<b>Chemical Performance</b>	<b>Mode of Measurement</b>
Range of Effective Temperature <sup>1</sup>	Phase Diagram
Speed of Ice Melting	SHRP Ice Melting Tests
Quantity of Ice Melted	SHRP Ice Melting Tests
Ice Undercutting Ability	SHRP Ice Undercutting Tests
Corrosion	Some form of corrosion test (e.g. PNS or NACE tests)
Environmental Impacts	Various tests, as discussed in NCHRP report
Persistence on Pavement	No easy test determined to date

**Table 1.1: Areas of Performance for Ice Control Chemicals**

Most of these tests have been discussed in a variety of reports (see Chapter 2: Literature Review for more discussion on this issue), but the issue of persistence on pavement is a relatively new area that has not been considered in any detail in the published literature to

date. It basically concerns how long a reasonable amount of chemical remains on the traveled way under the effects of traffic, before becoming ineffective. It appears to be a function of the stickiness or tackiness of the material applied, but also reflects how the material behaves when it is placed on the pavement. For example, salt brine tends to dry out after being placed on the pavement, and the dry residue may be swept away by passing cars. Anecdotes suggest that brine, used as a frost prevention treatment, may last about 2 to 4 days before a new application is required (absent any significant precipitation). In contrast, there are reports of a calcium chloride based liquid (calcium chloride mixed with a relatively small amount of beet juice, sold in the Pacific Northwest under the trade name of GeoMelt™) that is sufficiently “sticky” that it remains effective for periods of up to ten days when used in a frost prevention mode (again, absent any precipitation). Clearly the persistence of a chemical and the longevity of that chemical’s effectiveness would have a significant impact on the economics of using that chemical versus another, less persistent chemical. Unfortunately, at present there does not appear to be any consistent or suitably representative method of measuring this persistence. Accordingly, while it should be a factor in any decision regarding the use of particular chemicals, there is no way to incorporate this important factor into the models developed in this study. Users of those models should be particularly aware of this drawback in the models.

Perhaps the most widely used anti-icing and deicing chemical in the United States at present is Sodium Chloride. It is readily available, is cheaper to buy than any other deicing chemical and is very effective at melting snow and ice. Iowa uses about 190,000

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<sup>1</sup> Throughout this document the term “temperature” should be taken to indicate surface or pavement

tons of sodium chloride annually (this is a five year moving average from the Iowa DOT website<sup>2</sup>). However, there are limits to its ability. A phase diagram for the Sodium Chloride – water system shows that the eutectic temperature (the temperature below which no ice can be melted by adding salt) is around  $-6^{\circ}$  F (see e.g. Minsk, 1998). However, in practice, sodium chloride becomes an ineffective deicing agent at higher temperatures. Typically, salt is considered ineffective at between  $15^{\circ}$  and  $20^{\circ}$  F. Once the temperature drops below these levels, then agencies have two possible choices: use another chemical, or stop using chemicals altogether, and only plow and/or use abrasives. Two other chlorides (Calcium Chloride and Magnesium Chloride) both can be used at lower temperatures than Sodium Chloride, but both have some additional drawbacks, especially with regard to cost and corrosiveness. There are some newer, organic chemicals that have the ability to be effective at low temperatures (low in this case being considered to be below the  $15^{\circ}$  F cut-off for salt use). In particular, Potassium Acetate and Methyl Glucoside both have the ability to melt snow and ice at temperatures down to around  $0^{\circ}$  F. However, both are extremely expensive. In practice in Iowa, chemical usage is limited to Sodium Chloride and Calcium Chloride, although limited amounts of other chemicals are used, mostly on an experimental basis.

However, there is concern that winter maintenance practice in Iowa may be using Calcium Chloride in ways that are less than optimal. Iowa is typically rather cold in winter. This suggests that there are a significant number of occasions when use of Calcium Chloride might be more effective than use of Sodium Chloride. It's also

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temperature unless otherwise specified.



possible that a mix of the two chemicals might be a useful option to consider. The goal of this project is to examine how well various mixes of the two chemicals (Sodium Chloride and Calcium Chloride) perform over a range of temperatures. On that basis, a cost/benefit comparison can be run which would indicate which “mix” should be used under which conditions (primarily but not exclusively as a function of temperature). Further, because anecdotal reports indicate that occasionally Calcium Chloride applications can turn to “snot,” a range of mixes will be examined to determine whether any particular mixes seem prone to such degradation.

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<sup>2</sup> [http://www.dot.state.ia.us/dot\\_overview/transportationfacts\\_september2004.htm#Roads](http://www.dot.state.ia.us/dot_overview/transportationfacts_september2004.htm#Roads) referenced on January 28, 2008.

## 2: LITERATURE SEARCH

The basic performance issue here relates to the phase diagrams of the Sodium Chloride – Water and the Calcium Chloride – Water chemical systems. These are clearly well established in the literature, and can be found in typical reference works as well as in texts such as Minsk (1999) that are more focused on winter maintenance issues. Figure 2.1 shows the two phase diagrams on a single graph, thus allowing for direct comparison.

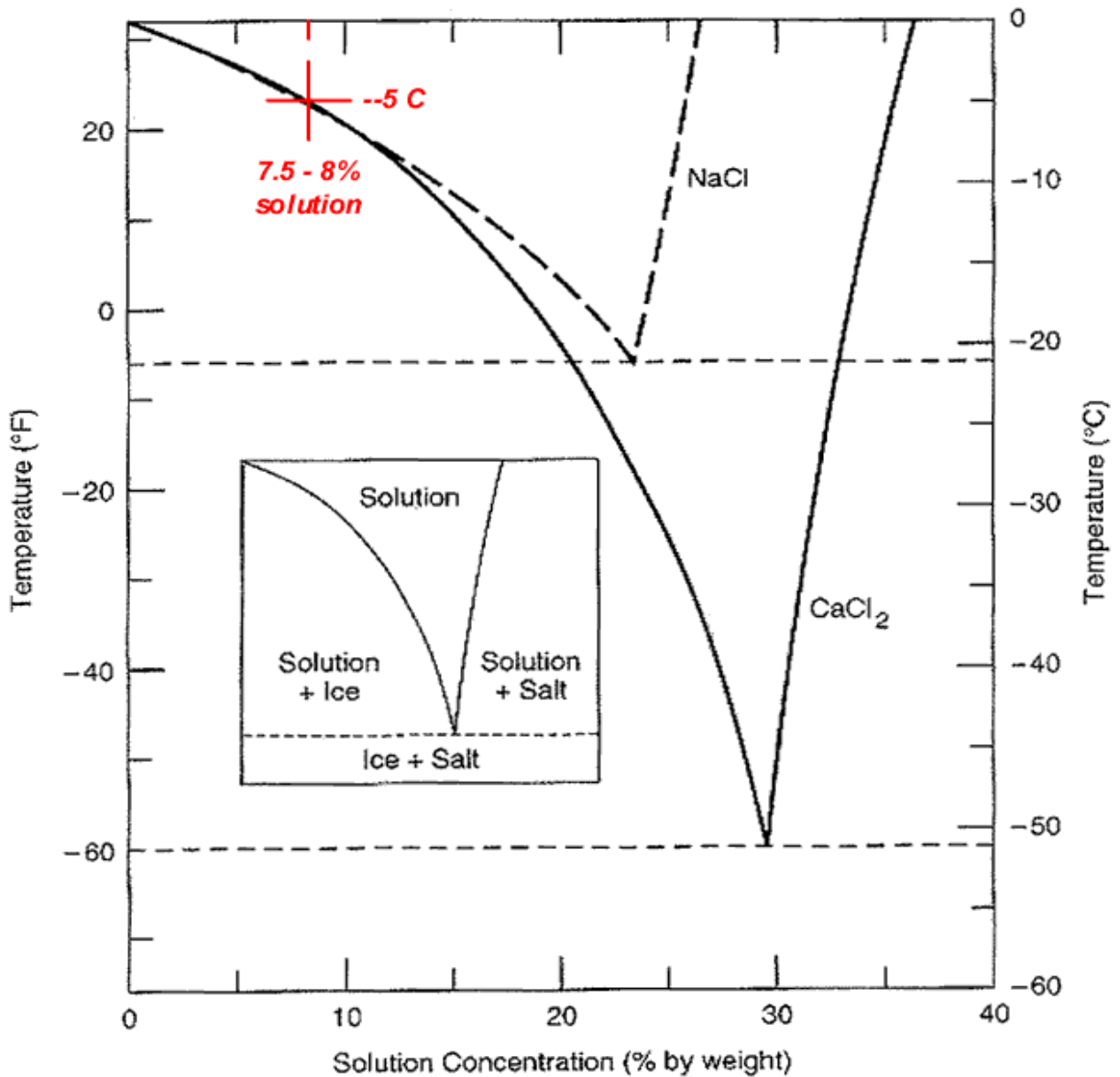


Figure 2.1: The Phase Diagrams for the NaCl – H<sub>2</sub>O and CaCl<sub>2</sub> – H<sub>2</sub>O systems

A number of points are apparent from Figure 2.1. First, at warmer temperatures (above 20° F) there is little difference between the melting curves for the two systems. Thus, as shown by the red cross on the diagram, at -5° C (or 23° F) the percentage of either salt or calcium chloride in a solution with water that will just begin to freeze is about 7.5 to 8%. It is only when the temperature drops below 20° F that calcium chloride begins to significantly out-perform sodium chloride.

Second, any phase diagram is an equilibrium based representation. That is, it properly represents the situation when all phase changes have occurred. In winter maintenance, this very rarely happens during a storm. Typically, the chemical applied to the road surface is only melting a very thin layer of snow or ice. Should enough time pass, more snow or ice will be melted, and the chemical will dilute out and start to freeze. Thus, we should not expect that the phase diagram relates directly to performance in the field. As one direct example, Figure 2.1 says nothing about how quickly the two chemicals act on the pavement. Nonetheless, experience in the field clearly identifies calcium chloride as a “hot” chemical that acts rapidly to melt snow and ice. The converse of this is that calcium chloride will dilute out more quickly than sodium chloride. The scraping tests conducted by Nixon (2003) confirm this comparative aspect of the two materials.

The report by Blackburn et al. (2004) addresses the issue of how much calcium chloride is required at a given temperature to be equivalent to a certain amount of sodium chloride. Thus in Table 9 of their report, they provide a multiplier that can be used to adjust the quantity of chemical required. These results are shown in Figure 2.2. On the basis of this, it would appear that calcium chloride begins to be more effective than sodium chloride at about 25° F. As the temperature lowers further, the calcium chloride

becomes significantly more effective. This increased effectiveness is made more apparent in Figure 2.3, taken from Table A-6 in Blackburn et al. (2004) which shows equivalent application rates of salt brine and calcium chloride brine as a function of temperature. According to Blackburn et al. (2004) these quantities are equivalent to an application of 100 lbs of salt per lane mile (or 28 kg per lane km).

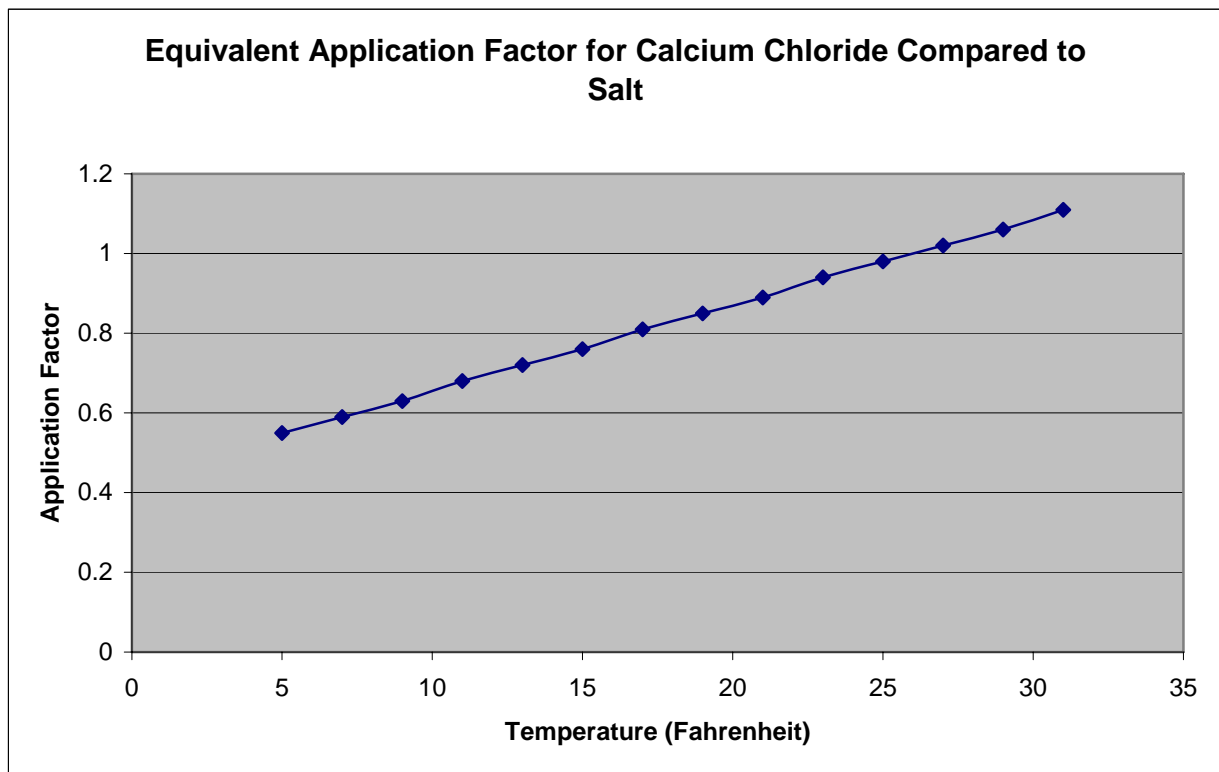


Figure 2.2: Equivalent Application Factor for Calcium Chloride Compared to Salt (with Data from Blackburn et al, 2004)

A more recent NCHRP Study (Levelton Consultants, 2007) provides a rational decision making tool for selecting the appropriate chemical according to a range of different factors. The report also includes a materials selection decision tool, which can be downloaded from the NCHRP web site<sup>3</sup>. The decision tool requires an agency to weight a number of factors, and on the basis of that, and the phase curve of the various materials

under consideration (primarily the five chemicals identified in Chapter 1 above) the tool generates a curve showing the score for each chemical as a function of temperature. The tool can use data from other chemicals as needed, on the basis of phase curve for the other chemicals. However, the tool does not have any feature allowing a mix of chemicals to be examined, unless a phase curve exists for that mix.

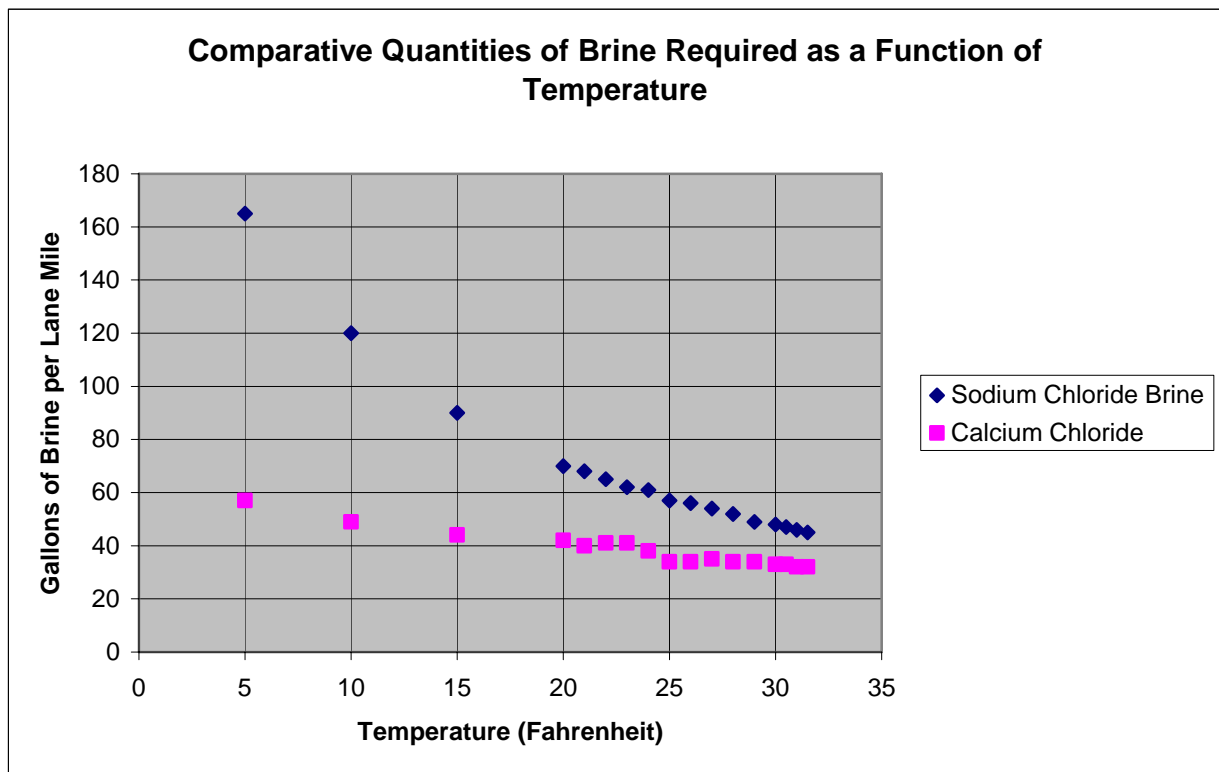


Figure 2.3: Comparative Quantities of Brine Required as a Function of Temperature (with Data from Blackburn et al, 2004)

Two agencies have been making use of mixtures of sodium chloride and calcium chloride (together with a beet juice based additive): the City of West Des Moines, Iowa, and McHenry County, Illinois. A number of presentations on their methods and their results are available on the APWA web site<sup>4</sup>. Their general experience has been that the mixture

<sup>3</sup> The tool can be downloaded from <http://www.trb.org/TRBNet/ProjectDisplay.asp?ProjectID=883>, accessed on January 30, 2008.

<sup>4</sup> Available at <http://www.apwa.net/Meetings/Snow/2007/handouts/> accessed on February 1, 2008.

they use, which they call Supermix, works better than straight salt brine in the winter weather conditions they face regularly. Most importantly, the blend remains effective for much longer than typical salt brine. This is an important point operationally, and should definitely be considered in any chemical selection decisions. A representative of one of the two agencies noted above stated explicitly that they use the mix not for improved low temperature performance but strictly for enhanced persistence (DeVries, Personal Communication, 2007). However, as indicated above, currently no standard test exists to measure the effective longevity of an ice control chemical on the pavement. The development of such a test was beyond the scope of this project, but may need to be considered in the future should this become a critical operational concern. It is perhaps worth noting that a number of other agencies have expressed considerable interest in the chemical mixing approach (again, see the APWA web site for details) and many agencies (including International agencies) have visited either West Des Moines or McHenry County to learn more.

To summarize the current literature as it pertains to the use of chemical mixtures as ice control products, there is little published that is of direct relevance in this regard. While tools are available to rate and evaluate ice control chemicals, in order to use these for chemical mixtures, a new phase curve would have to be developed for each such mixture. This is by no means impossible, but it suggests a great deal of labor to discover that a mixture may not, after all, be particularly effective.

### **3: DETERMINING PROPERTIES OF THE MIXTURES**

It was determined that two properties would be considered in constructing the economic model. These two properties were the ice melting capability, and the freezing point. The first step in gaining sufficient information to develop the model was to determine these capabilities for the two “baseline” products: salt brine and calcium chloride brine.

#### 3.1 Baseline Testing

There are two aspects to the baseline testing: the ice melting capacity, and the freezing point of the brines. The baseline tests and results are described in this section.

Baseline testing of ice melting capacity was conducted using the SHRP H-332 Report, entitled “Handbook of Test Methods for Evaluating Chemical Deicers” published in 1992. The use of the tests is described more fully in Nixon et al. (2007). The test used was H-205.2 Test Method for Ice Melting of Liquid deicing Chemicals. The two chemicals were tested at 30°, 20°, 10° and 0° F. Figure 3.1 shows how much ice was melted (measured in grams) by the application of 5 ml of ice control liquid after a period of one hour.

As expected, at 30° F there is relatively little difference between the two chemicals. The difference is much more pronounced at lower temperatures. The difference in chemicals is more clearly seen if the ratio of ice melted by calcium chloride to ice melted by sodium chloride brine is plotted as a function of temperature, as shown in Figure 3.2.

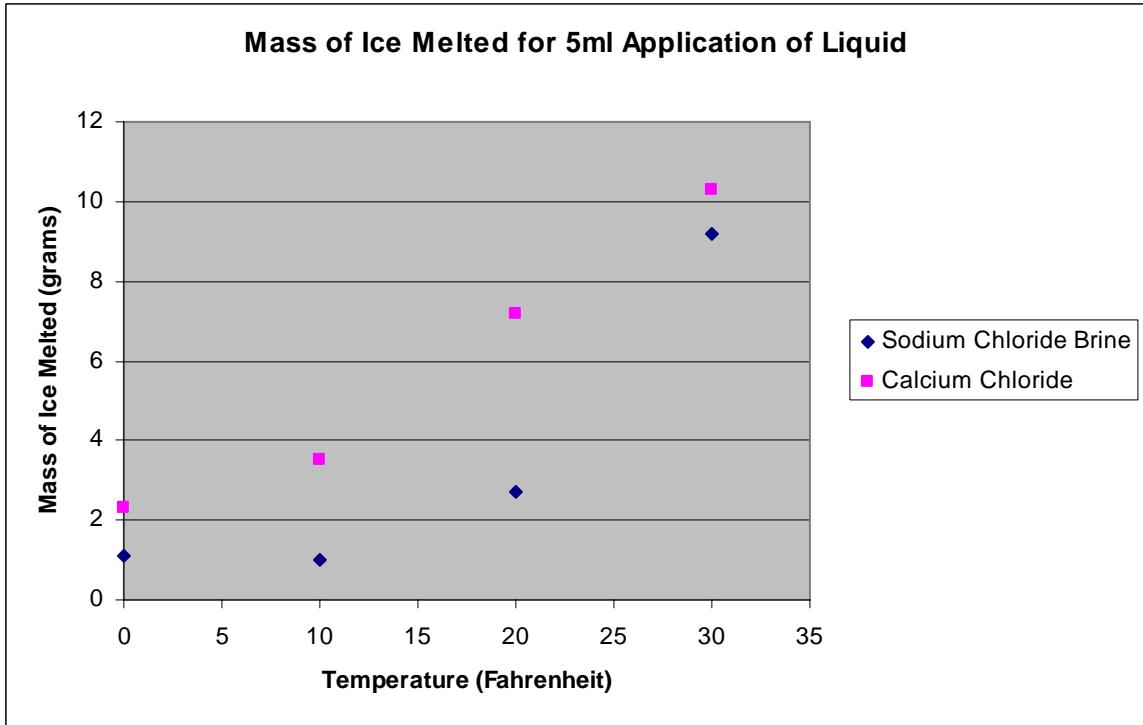


Figure 3.1: Mass of Ice Melted by Sodium Chloride Brine and Calcium Chloride as a Function of Temperature.

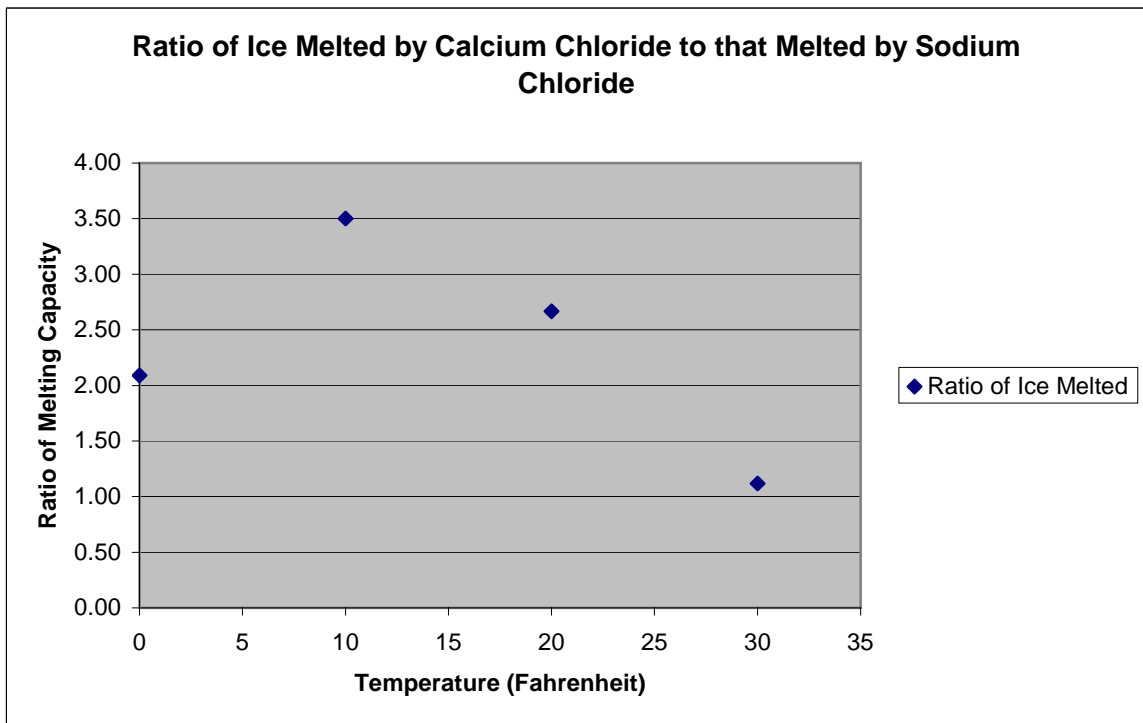


Figure 3.2: Ratio of Ice Melted by Calcium Chloride to that Melted by Sodium Chloride.



Figure 3.2 shows a rather interesting and anomalous result at 0° F. It would be expected that as the temperature continues to drop, the melting capacity of the Calcium Chloride brine would continue to outperform that of Sodium Chloride at an increasing rate. In particular, once the temperature drops below -6° F no further melting by salt brine will occur, while the Calcium Chloride brine will continue to melt ice down to about -60F (albeit very slowly at the latter temperatures). Even though the data at 0° F was obtained on the basis of five separate tests with less than 10% variance in test results, there may be an error in these data. In part this may arise because the quantity of material being measured was very small, and thus small errors in handling would be significantly magnified. Taking a ratio between two small numbers also will magnify any errors in those numbers.

With regard to freezing points of the two brines, the initial intent was to conduct freeze point testing as discussed in Nixon et al. (2007), using the standard test ASTM D 1177-94 (2000). However, such testing was ultimately deemed unnecessary because the baseline freezing point curves for the two materials are simply their phase diagrams (see Figure 2.1). These diagrams can be normalized with respect to the full strength of the brine that is to be applied to the pavement, and one such curve for a Calcium Chloride based product is shown in Figure 3.3. This has as the horizontal axis the variation of the product (expressed as a percentage) from its full as-applied strength (100%).

## Freeze Point Curve - Geomelt C (CaCl<sub>2</sub>)

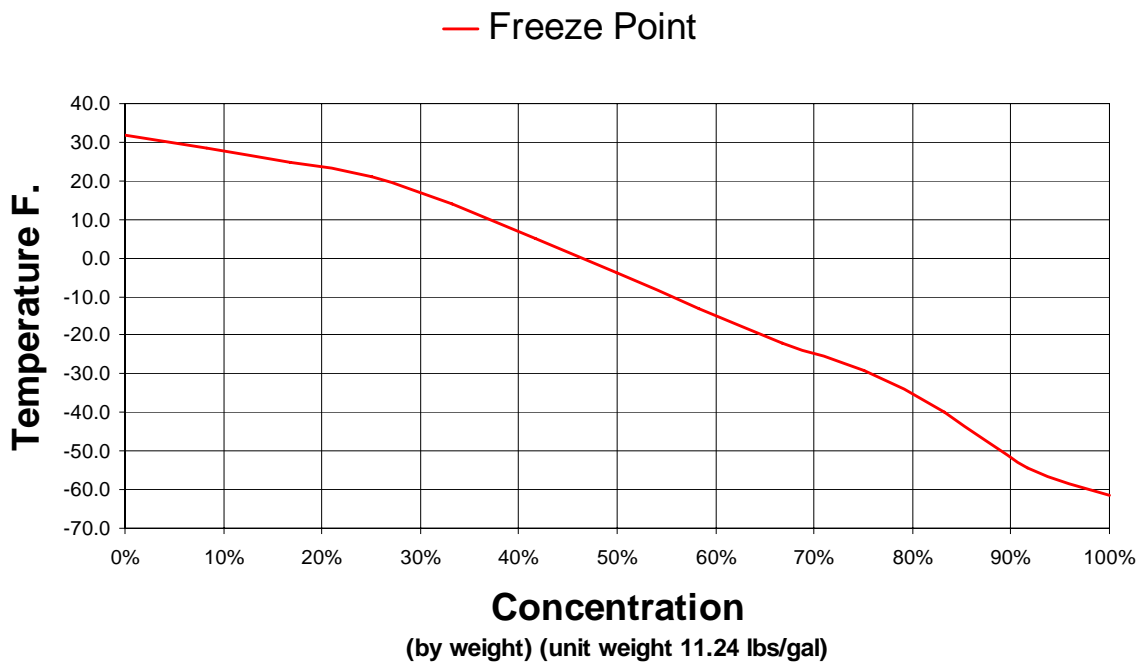


Figure 3.3: Freeze Point Curve for a Calcium Chloride based Product

In considering the freeze point curve, it became clear that any useful analysis of the relative economic benefits of mixtures of sodium chloride and calcium chloride would have to consider only representative points on the freeze point curve. Experience suggests that the lower end of the practical range of application for a chemical is the freeze point when that chemical has been diluted to half strength. Thus for sodium chloride, this would be about 18° F, while for calcium chloride it would be about -5° F.

### 3.2: Testing of Mixtures

The first aspect of testing of the mixtures was to determine whether any precipitation (referred to in the field as “turning to snot”) occurred with the mixtures investigated. No such behavior was observed, but some caveats should still be noted. First, it is entirely

possible that how the two chemicals are mixed may have an impact on whether any precipitation occurs. In our tests, calcium chloride was always added to salt brine, in general in small quantities and relatively slowly. Other methods of mixing may result in problems occurring, although it should be noted that the mixing methods used at West Des Moines and McHenry County have not shown any evidence of precipitation either. Second, many calcium chloride brines used in winter maintenance are in fact calcium chloride plus, where the “plus” may indicate a range of additives most often intended as corrosion preventatives. Only one type of calcium chloride brine was used in these tests, from the Davenport Garage of the Iowa DOT. Whether other additives to the calcium chloride may cause some sort of precipitation event is not known and has not been examined as part of this study.

The first stage of this part of the study was to examine certain mixes at certain degrees of dilution. Thus Figure 3.4 shows the freezing point of various mixtures, when the mixture had been diluted with water such that the mixture comprised 25% by weight of the final liquid tested. The mixtures ranged from 95% salt brine and 5% calcium chloride brine, to 5% salt brine, and 95% calcium chloride brine. Two complete ranges were run. The results seem to suggest only a minimal change in the freezing point of the mixture, and a re-examination of figure 2.1 would suggest why. At high levels of dilution the freeze point curves for salt and calcium chloride are essentially identical. At very high levels of calcium chloride there does appear to be some slight decrease in the freezing point, but the total range of the freezing points observed for this level of dilution ranged between  $-6^{\circ}\text{C}$  ( $21.2^{\circ}\text{F}$ ) and  $-12^{\circ}\text{C}$  ( $10.4^{\circ}\text{F}$ ).

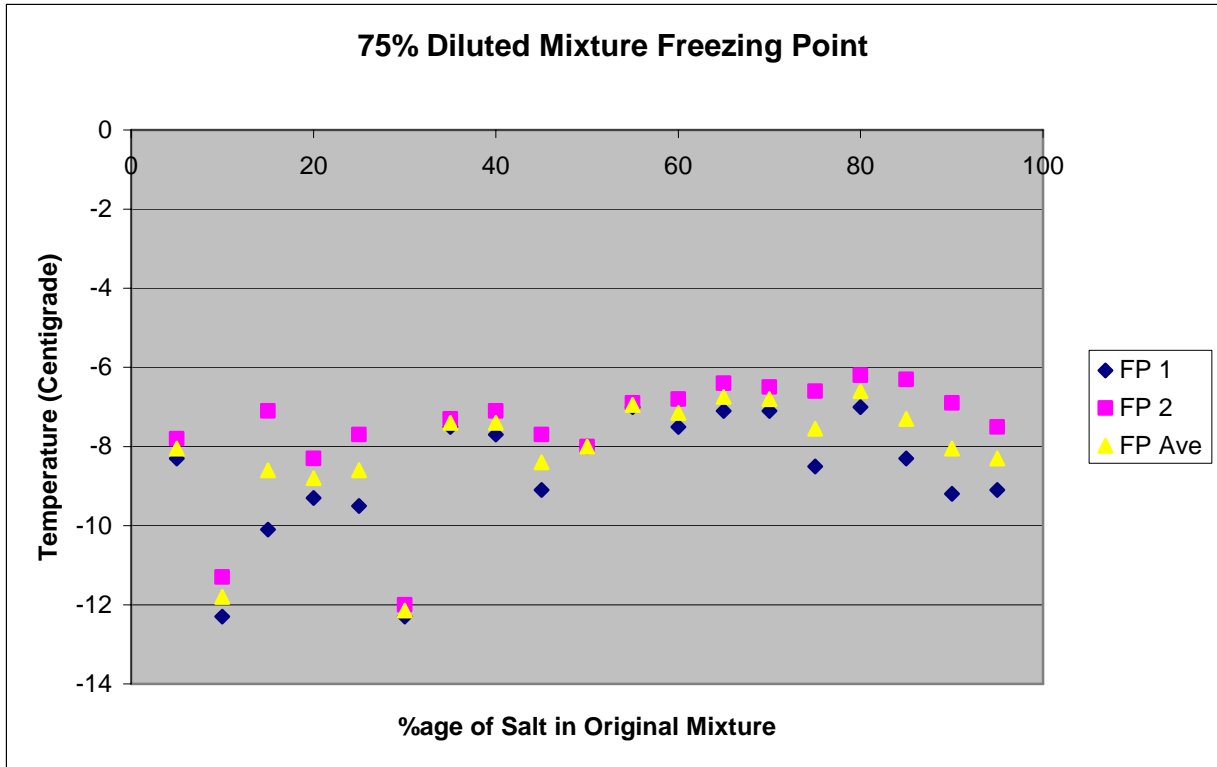


Figure 3.4: Variation of Freezing Point of Salt-Calcium Chloride Mixtures when Diluted with 75% water.

At lower levels of dilution some experimental problems were encountered. Figure 3.5 shows a freeze point test for a 50% Salt, 50% Calcium Chloride mixture that had been diluted to 50% of its original strength with water. The freeze point in this test is shown to be  $-20.4^{\circ}\text{C}$  ( $-4.72^{\circ}\text{F}$ ). This temperature is essentially at the capability of the cooling bath used for these experiments and thus a full range of mixtures could not be examined at the lower degrees of dilution. Nonetheless, this result is interesting in that this freezing point is very close to the freezing point of calcium chloride brine, diluted to 50% strength by water (see Figure 2.1).

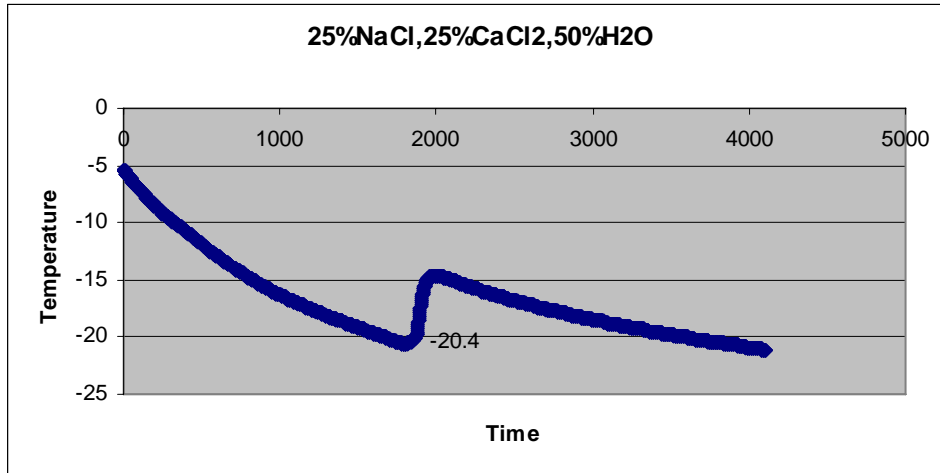


Figure 3.5: Freeze Point experiment Results for 50% Salt, 50% Calcium Chloride mixture that had been diluted to 50% of its original strength with water  
 Results from the ice melting tests showed that the quantity of ice melted by a given mixture could be modeled as a linear relationship between the ice melted by the two components of the mixture. Thus, at 10° F, a 50-50 mixture of the two chemicals would melt approximately 1.75 times as much ice as straight salt, compared with straight calcium chloride which melts about 3.5 times as much ice as straight salt. This is a very helpful relationship in terms of modeling the economic comparison of the mixtures. Figure 3.6 shows the base results that allowed this relationship to be developed.

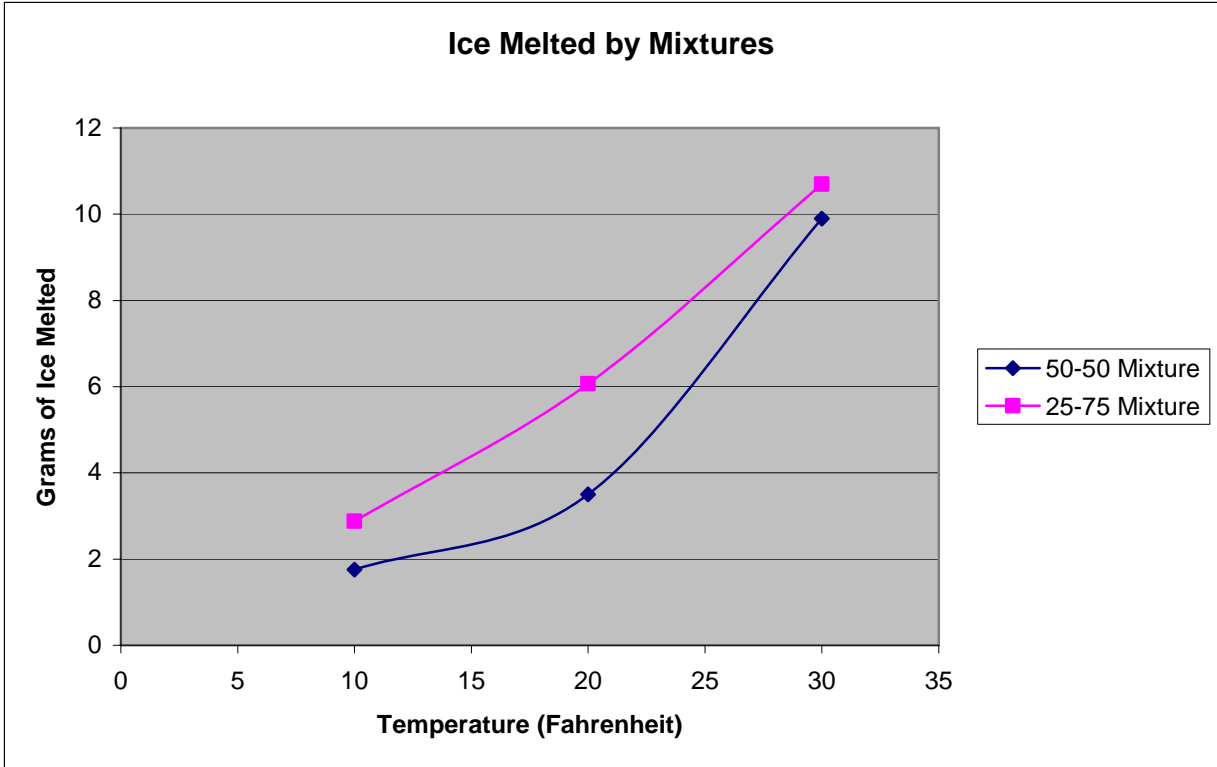


Figure 3.6: Ice Melted as a Function of Temperature for Two Mixtures

## 4: MODEL DEVELOPMENT

### 4.1: Initial Requirements

On the basis of the experimental results discussed in chapter 3 above, it is reasonable to model the behavior of mixtures of sodium chloride and calcium chloride brines with a linear model, directly proportional to the percentage of the mixture. While the relationship may not actually be linear, the data do not provide enough information to justify a more complex model.

While there are a number of things that could be used to model the ice melting performance of the mixture, the process by which ice is melted on the pavement is not yet fully clear (see Nixon et al., 2007). The quantity of ice or snow that can be melted by a reasonable application of salt is very small, as the following calculations show. If the phase diagram for salt (sodium chloride) is considered (see Figure 2.1) we can see that at a temperature of 23° F, a salt-water mixture will begin to freeze when the mixture comprises about 7.5% salt by weight. If we take a reasonably high application rate of 300 lbs per lane mile, we can use the phase diagram to calculate how much moisture will dilute this application to the point at which it starts to freeze. The first step in the calculation is a simple evaluation of how much water must be added to the 300 lbs of salt to create a 7.5% solution:

$$W = \frac{92.5\%}{7.5\%} (300 \text{ lbs} / \text{mile}) = 3700 \text{ lbs water/mile} \quad (4.1)$$

This quantity of water can now be converted to a depth of water across the lane mile over which the 300 lbs of salt is spread:

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

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

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

Given this result, it is clear that relatively little snow or ice needs to be melted. One way of modeling mixtures is to ask how much of a certain mixture is needed if a certain quantity of ice is to be melted. Clearly, finding this involves a combination of using the phase diagram, and using application quantities that have proven effective in the field. In that regard, the Iowa DOT application guide (shown in Table 4.1) is an excellent guide:

<b>Salt Application Rate Guidelines</b>							
<b>Prewetted salt @ 12' wide lane (assume 2-hr route)</b>							
<b>Surface Temperature (° Fahrenheit)</b>		<b>32-30</b>	<b>29-27</b>	<b>26-24</b>	<b>23-21</b>	<b>20-18</b>	<b>17-15</b>
	Heavy Frost, Mist, Light Snow	50	75	95	120	140	170
lbs of salt to be applied per lane mile	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
<b>Prewetted salt @ 12' wide lane (assume 3-hr route)</b>							
<b>Surface Temperature (° Fahrenheit)</b>		<b>32-30</b>	<b>29-27</b>	<b>26-24</b>	<b>23-21</b>	<b>20-18</b>	<b>17-15</b>
	Heavy Frost, Mist, Light Snow	75	115	145	180	210	255
lbs of salt to be applied per lane mile	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

Table 4.1: Application Rate Guide for Iowa DOT Plow Trucks



Using this table, we can take a condition that is relatively common, and use it and equations 4.1 and 4.2 to determine how much of any given mixture is required at any given temperature. If we consider a two hour cycle time, with a temperature of 23° F and medium snow at ½ inch per hour, we get an application rate of 145 lb per lane mile. This translates into melting approximately 0.006 inches of ice. Clearly other approaches could be used, but this has the benefit of simplicity, and a clear link to current practice which experience has shown to be effective.

#### 4.2 Linear Representation of the Mixtures

As indicated above, the performance of mixtures of the two brines will be based on a linear relationship between them. The approach to this will be to consider temperatures between 32° and -5° F. Since the low end of the effective temperature range for calcium chloride is generally taken to be close to -5° F, there is no value in going to lower temperatures, and of course, below -6.02° F, sodium chloride will not melt any ice at all.

For a given temperature, the percentage of each brine at which freezing just begins (specifically, the percentage at which the liquidus line is crossed) will be expressed as a percentage of the eutectic concentration. Thus, if at 23° F, sodium chloride just begins to freeze (crosses the liquidus line) then this is at a concentration of 7.5% salt by weight (see figure 2.1 and equations 4.1 and 4.2 above). Given that the eutectic concentration for sodium chloride in the sodium chloride-water system is approximately 23%, then the sodium chloride brine at 23° F will begin to freeze at 32.6% (7.5/23) of its eutectic concentration. Figure 4.1 shows this relationship for both sodium chloride and calcium chloride brines. Table 4.2 provides the values in tabular form.

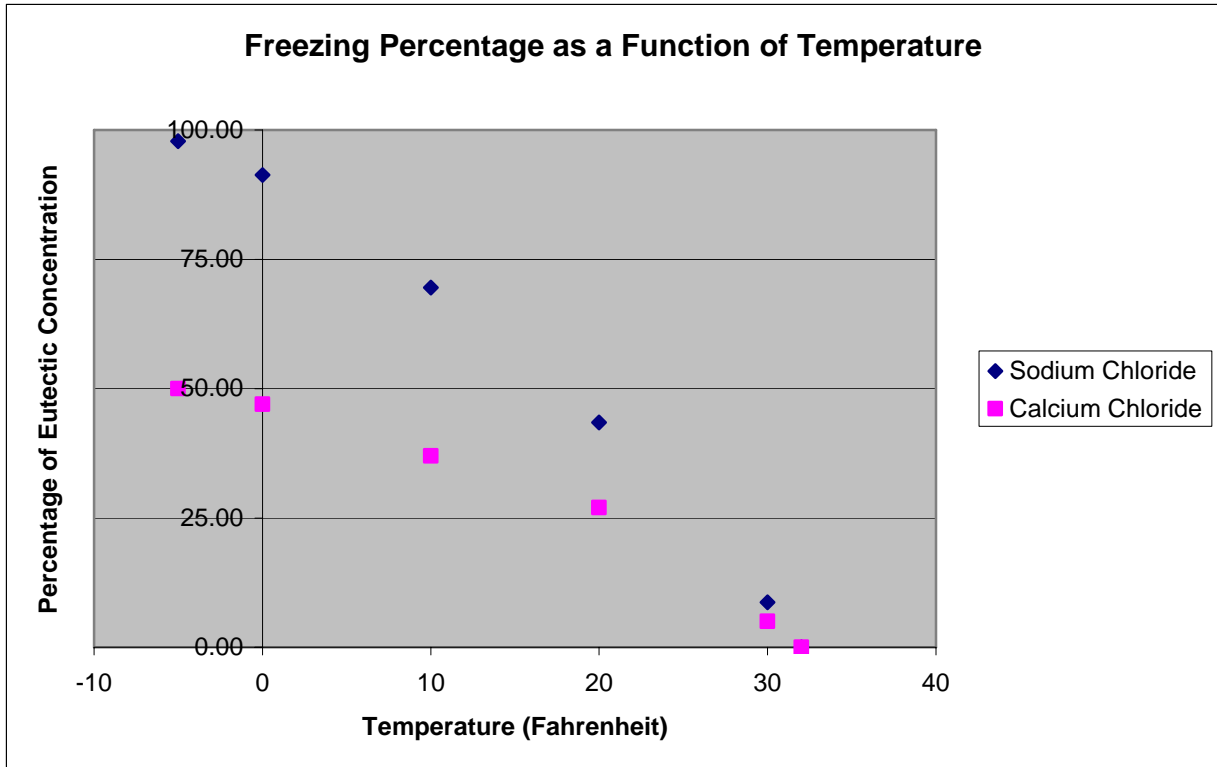


Figure 4.1: Freezing Eutectic Percentage as a Function of Temperature

Temperature (°F)	Sodium Chloride	Calcium Chloride
32	0	0
30	8.7	5.1
20	43.5	27.3
10	69.6	37.4
0	91.3	46.9
-5	97.8	50.1

Table 4.2: Percentage of Eutectic Concentration at which Freezing Occurs for a Given Temperature

If information is required for a temperature between the values listed in the table, linear interpolation will provide appropriate values. Thus for a temperature of 8° F, the percentage of eutectic concentration (P) at which freezing occurs is given as:

$$P_8 = P_{10} + (P_0 - P_{10}) \frac{T_{10} - T_8}{T_{10} - T_0} \quad 4.1$$

For Sodium Chloride this is 74.0% and for Calcium Chloride this is 39.3%. If a mixture of the two is then specified (e.g x% NaCl and y% CaCl<sub>2</sub>, where x+y = 100), then the final percentage of eutectic or applied concentration at which freezing will occur (P<sub>mix</sub>) is given as:

$$P_{mix} = \frac{xP_{8NaCl}}{100} + \frac{yP_{8CaCl2}}{100} \quad 4.2$$

So in a mix with 80% sodium chloride and 20% calcium chloride, the final percentage of applied concentration would be 67.1%.

#### 4.3 Determining the Quantity of the Mixture Required

Taking, from above, the goal of melting a water equivalent of 0.006” of ice or snow, the next step is to determine how much of the mixture is required to achieve this goal. A preliminary step is determining the weight of water (W<sub>w</sub>) that a 0.006” layer on the road surface equals per lane mile. This quantity is found as:

$$Weight = Volume \times Density \quad 4.3$$

where volume is expressed in cubic feet, and density in pounds per cubic foot. For the 0.006” layer thickness this gives:

$$W_w = \left( 12 \times 5280 \times \left[ \frac{0.006}{12} \right] \right) \times 62.4 = 1980 \text{ lbs} \quad 4.4$$

The quantity of mixture,  $Q_{mix}$  (measured in lbs), that must be added to the water on the road so that the mixture is diluted to the percentage at which it will begin to freeze ( $P_{mix}$ , from 4.2 above) is then found by:

$$\frac{Q_{mix}}{Q_{mix} + W_w} = P_{mix} \quad 4.5$$

which can be rearranged as:

$$Q_{mix} = \frac{P_{mix} W_w}{(1 - P_{mix})} \quad 4.6$$

The final step requires that  $Q_{mix}$  be converted from pounds into gallons, which is done simply by dividing by the specific weight (pounds per gallon) of the liquid mixture. The specific weight of the mixture will be the weighted average (weighted according to the relative percentages of each component of the mixture) of the two component specific weights (9.83 lbs per gallon for sodium chloride brine, 11.13 lbs per gallon for calcium chloride brine). Thus the specific weight of the mixture ( $SW_{mix}$ ) is:

$$SW_{mix} = \frac{xSW_{NaCl}}{100} + \frac{ySW_{CaCl2}}{100} \quad 4.7$$

From this, the volume ( $V_{mix}$ ) of the brine mixture required to achieve the desired melting, at the specified temperature for the given mixture is given (in gallons) by:

$$V_{mix} = \frac{Q_{mix}}{SW_{mix}} \quad 4.8$$

#### 4.4 Cost of the Mixture

One goal of this project was to be able to compare costs of possible mixtures with costs of straight brine, over a range of temperatures. To do this, three steps are needed. First, at a given temperature, determine how much sodium chloride brine would be required to achieve the desired amount of melting. This can be done by using equations 4.1 through 4.8 with the percentage of sodium chloride brine at 100%. Second, having chosen a mixture to investigate, the quantity of the mixed brine at the given temperature is again found, using equations 4.1 through 4.8. Finally, costs for the two brine quantities are calculated, using unit costs assigned as appropriate. The costs for the mixture can then be compared with the costs for the salt brine.

These costs can be calculated relatively simply, using a spreadsheet, and this has been done and is reported in Chapter 5 below. The inputs required for the spreadsheet calculations are the costs of sodium chloride brine and calcium chloride brine, and the percentage of each brine in the mixture to be investigated.

As discussed above, it should be noted that this comparison rests upon the need for a chemical application to melt a given, specified, quantity of ice or snow (0.006" inch of water equivalent). To the extent that this models ice melting performance, this approach will give a reasonable answer. This approach does not address other performance issues, such as persistence of chemical on the road. These other aspects may in certain circumstances be a great deal more important than ice melting performance.

## 5: MODEL RESULTS

### 5.1 Quantity Calculations

The first step was to conduct an interpolation of the data in table 4.2 for the whole temperature range (32° to -5° F) under consideration. Figure 5.1 shows the results of the interpolation.

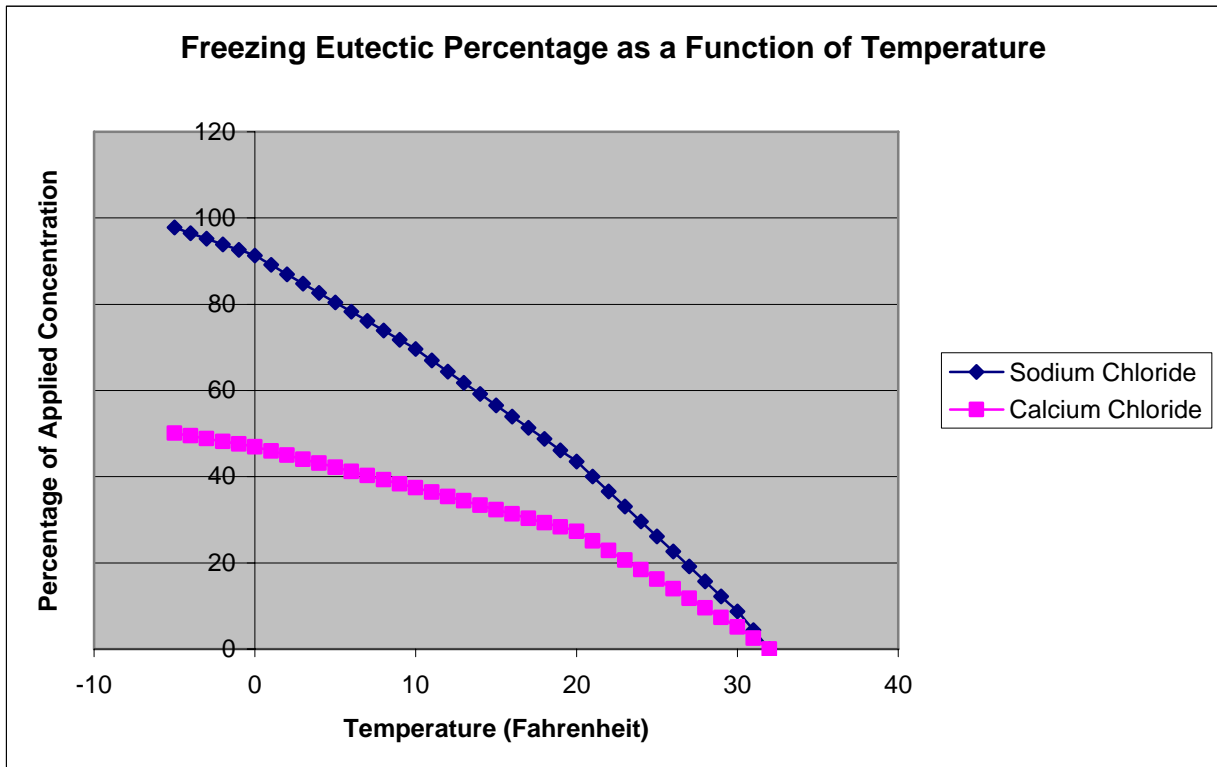


Figure 5.1: Interpolated Freezing Eutectic Percentage as a Function of Temperature.

As expected, the curves are relatively smooth and continuous.

Having determined the percentages for the two components of the mixtures to be considered, the next stage was to determine the percentage for various mixtures. Four Mixtures were considered: 80% NaCl, 60% NaCl, 40% NaCl, and 20% NaCl. The freezing percentages for these mixtures were obtained using equation 4.2.

The results of the application of equation 4.2 are shown in Figure 5.2 for the four different mixtures. Again, the curves are as expected.

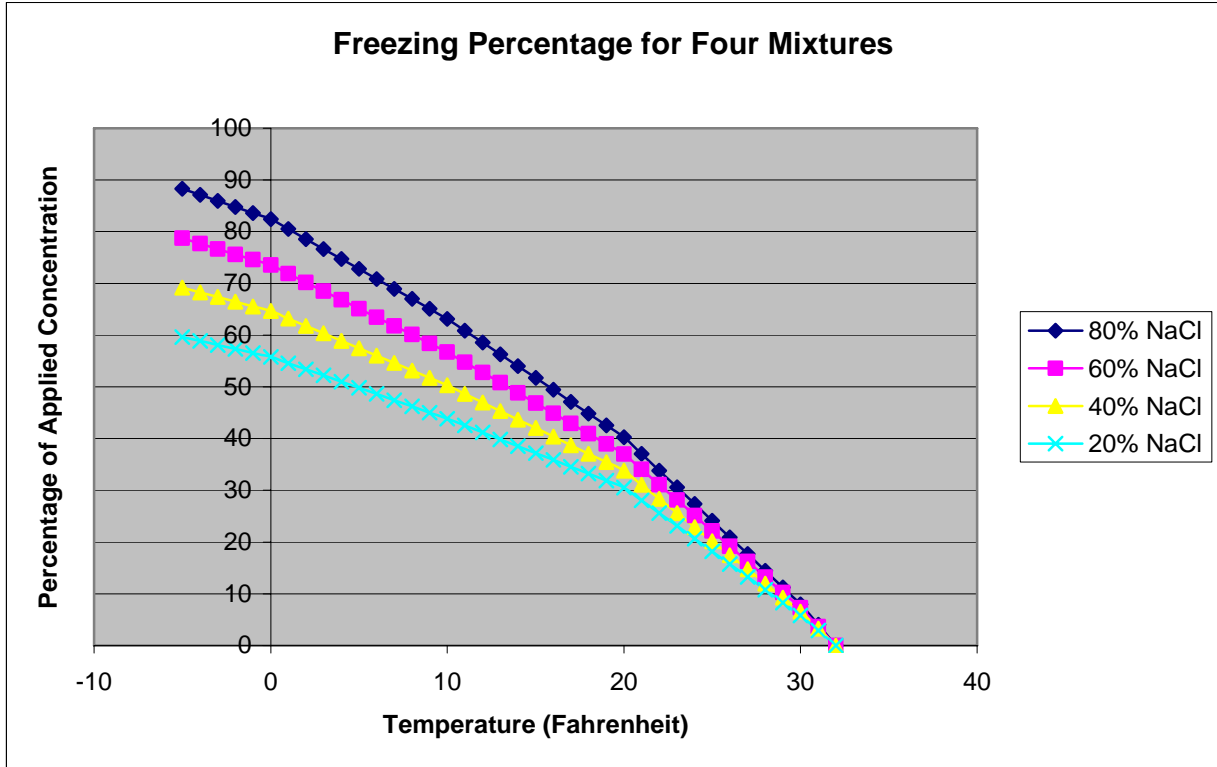


Figure 5.2: Freezing Percentage for Four Mixtures of Sodium Chloride and Calcium Chloride

Taking these percentages, and applying the results of equations 4.4, 4.5, and 4.6, the quantity of brine mixture, in pounds, that would be required to melt the appropriate thickness of ice or snow (0.006” of water equivalent) is shown in figure 5.3. As might be expected, the more calcium chloride brine in the mixture, the less quantity of mixture is required. Also, again as expected, the quantity required increases with decreasing temperature, and does so more rapidly the lower the temperature becomes.

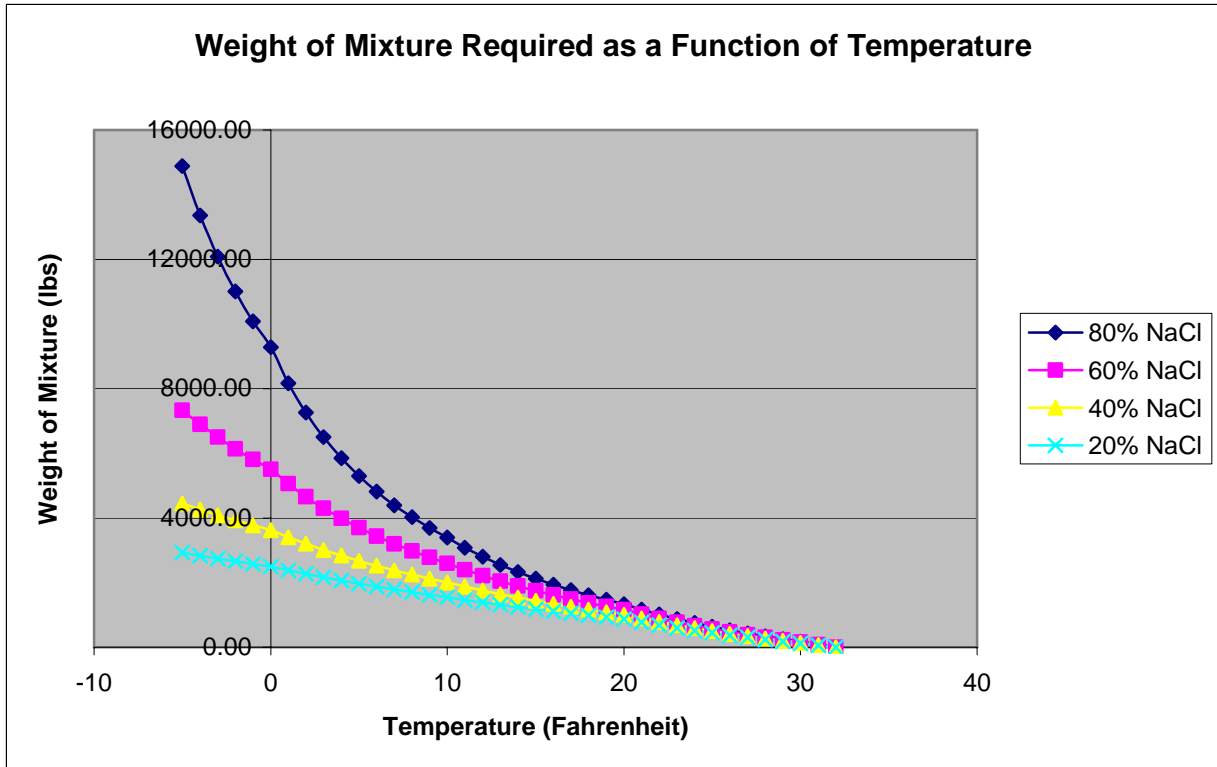


Figure 5.3: Weight of Mixture Required as a Function of Temperature

The next step is to convert the weight of mixture into a volume of mixture (expressed as gallons, and indicating the gallons per lane mile required to achieve the desired melt thickness). This is done by first finding the specific weight of the mixture (using equation 4.7) then calculating the volume using equation 4.8. The curves thus generated are very similar in shape to those in figure 5.3, albeit with a different scale on the vertical axis, as shown in Figure 5.4.



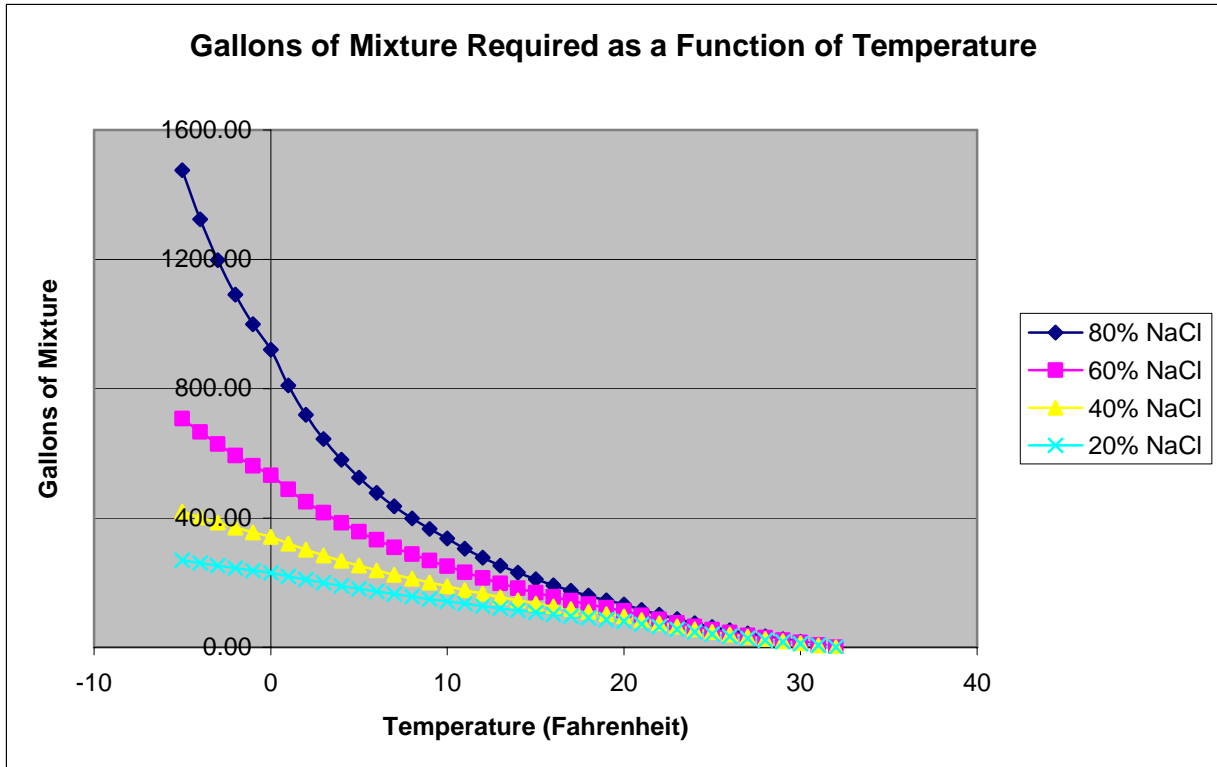


Figure 5.4: Gallons of Mixture Required as a Function of Temperature

## 5.2 Cost Calculations

The relative benefits of the mixtures from a cost standpoint can be determined by applying a cost per gallon to both the sodium chloride brine ( $C_{NaCl}$ ) and the calcium chloride brine ( $C_{CaCl_2}$ ). A cost for the mixture can then be calculated as:

$$C_{mix} = \frac{x C_{NaCl}}{100} + \frac{y C_{CaCl_2}}{100} \quad 5.1$$

where the mixture is x% sodium chloride brine and y% calcium chloride brine. This mixture cost can then be multiplied by the volume of mixture required at a given temperature to obtain a cost per lane mile as a function of mixture percentages and temperature.

Clearly the results of this calculation are extremely dependent upon the relative costs assigned for a gallon of sodium chloride brine and a gallon of calcium chloride brine.

Table 5.1 shows the combinations of costs that were considered in this study.

Sodium Chloride Brine Cost per Gallon	Calcium Chloride Brine Cost per Gallon
\$0.05	\$0.80
\$0.05	\$1.00
\$0.05	\$1.20
\$0.10	\$0.80
\$0.10	\$1.00
\$0.10	\$1.20

Table 5.1: Cost Combinations for the Two Brines

In considering these six costs combinations, comparisons will be made between applying straight salt and two different mixtures, the first with 80% NaCl, the second with 20% NaCl. This brackets the range of possible mixtures and provides insights into what sort of mixtures are likely to be most beneficial under which conditions.

Figure 5.5 shows the first cost combination comparing straight salt with 80% NaCl, while figure 5.6 shows the first cost combination comparing straight salt with 20% NaCl.

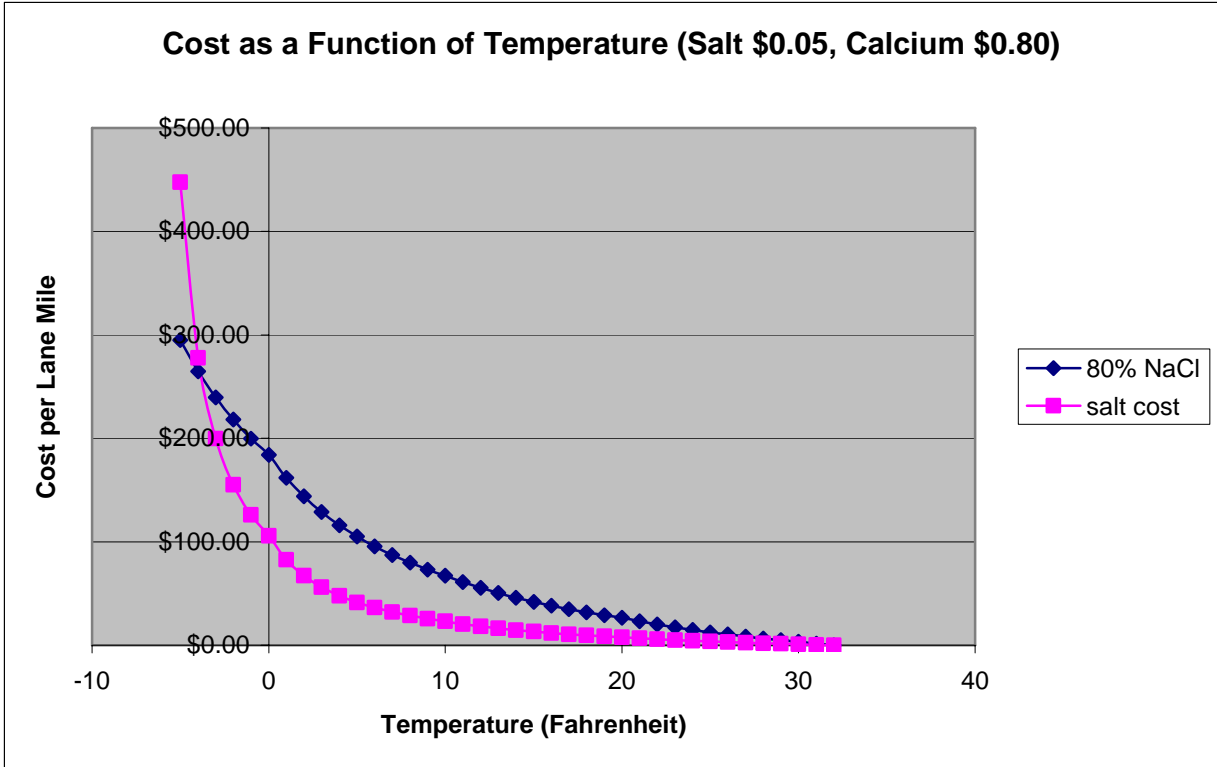


Figure 5.5: Cost Comparison, 80% NaCl, Salt \$0.05, Calcium Chloride \$0.80

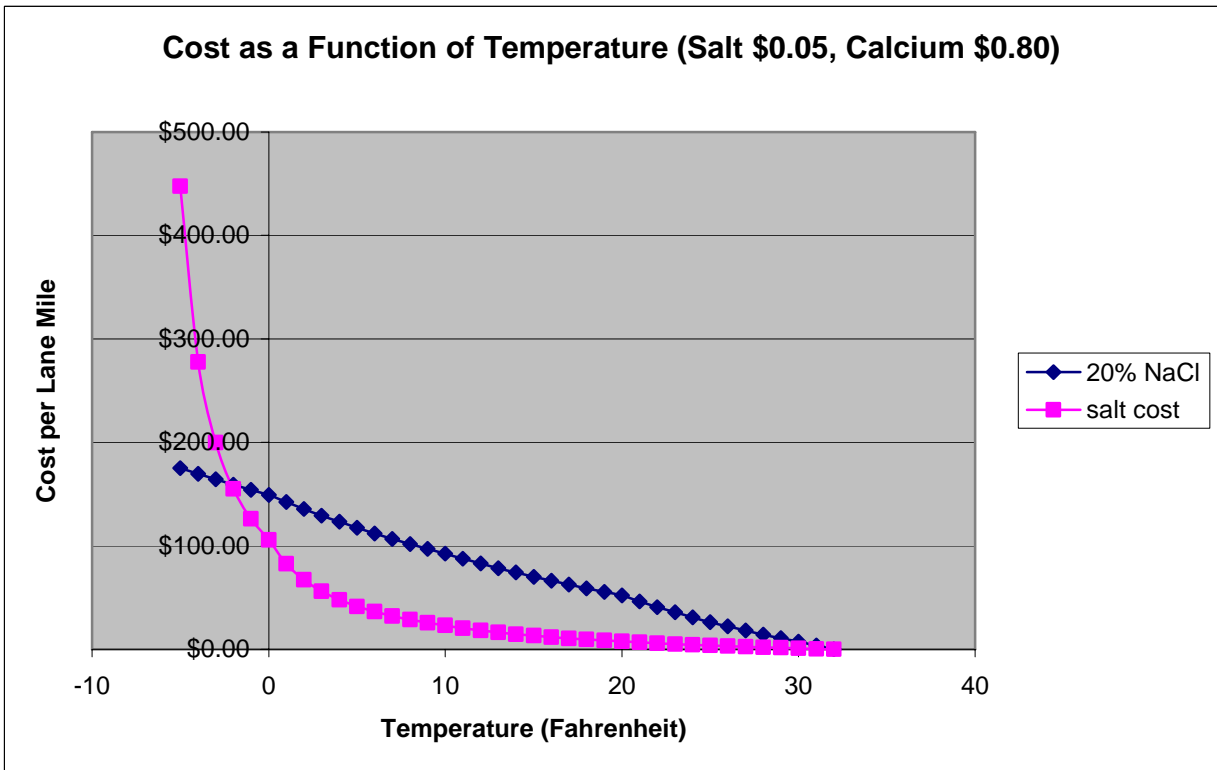


Figure 5.6: Cost Comparison, 20% NaCl, Salt \$0.05, Calcium Chloride \$0.80

It is of interest to note that the 80% NaCl mixture becomes more economical at a temperature of  $-4^{\circ}$  F, while the 20% NaCl mixture becomes more economical at a temperature of  $-2^{\circ}$  F. Operationally, there is little difference between these two “crossover” temperatures.

For the next cost combination (salt \$0.05, and calcium chloride \$1.00) the economic crossover points occur at even lower temperatures, as shown in figure 5.7. Now the 80% mixture is only economical at  $-5^{\circ}$  F and the 20% mixture is economical at  $-3^{\circ}$  F.

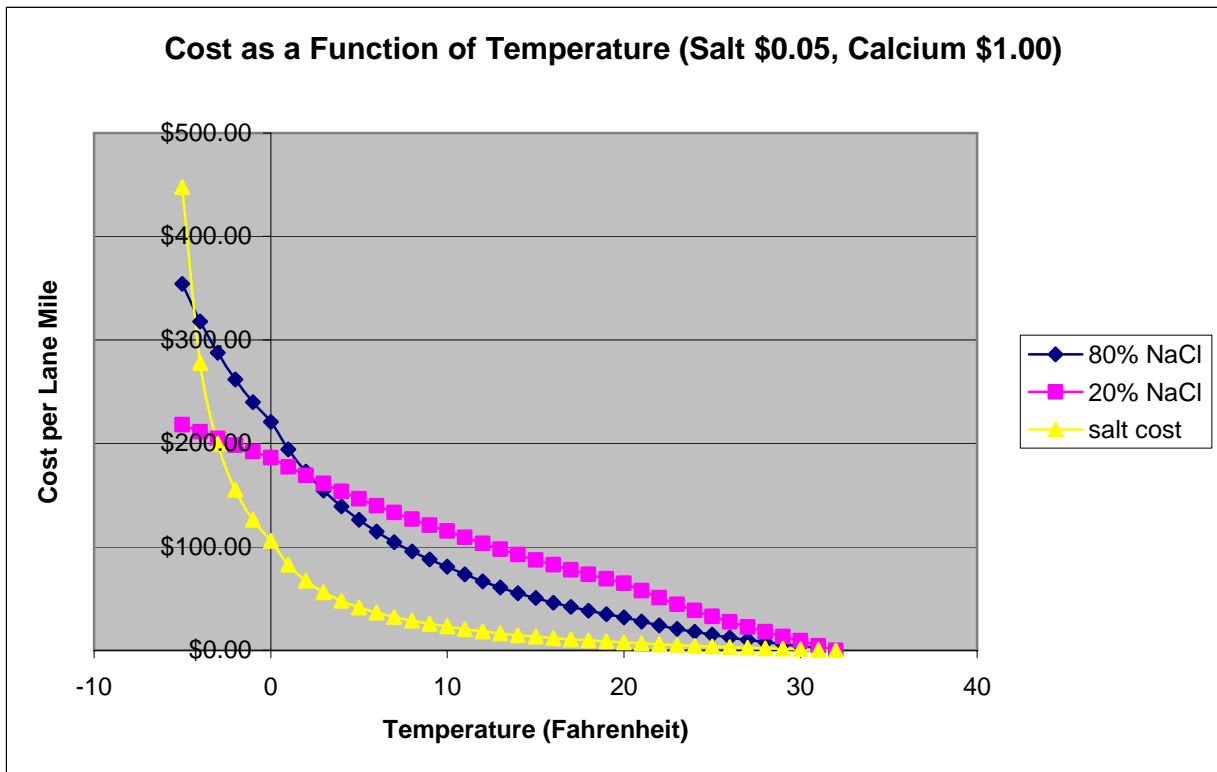


Figure 5.7: Cost Comparison, 20% NaCl and 80% NaCl Salt \$0.05, Calcium Chloride \$1.00

This trend continues further as the third category of cost (salt \$0.05, calcium chloride \$1.20) is considered. Figure 5.8 shows the results for this cost combination, and in this case, the 80% mixture is still economical only at  $-5^{\circ}$  F, and the 20% mixture is only economical at  $-4^{\circ}$  F.

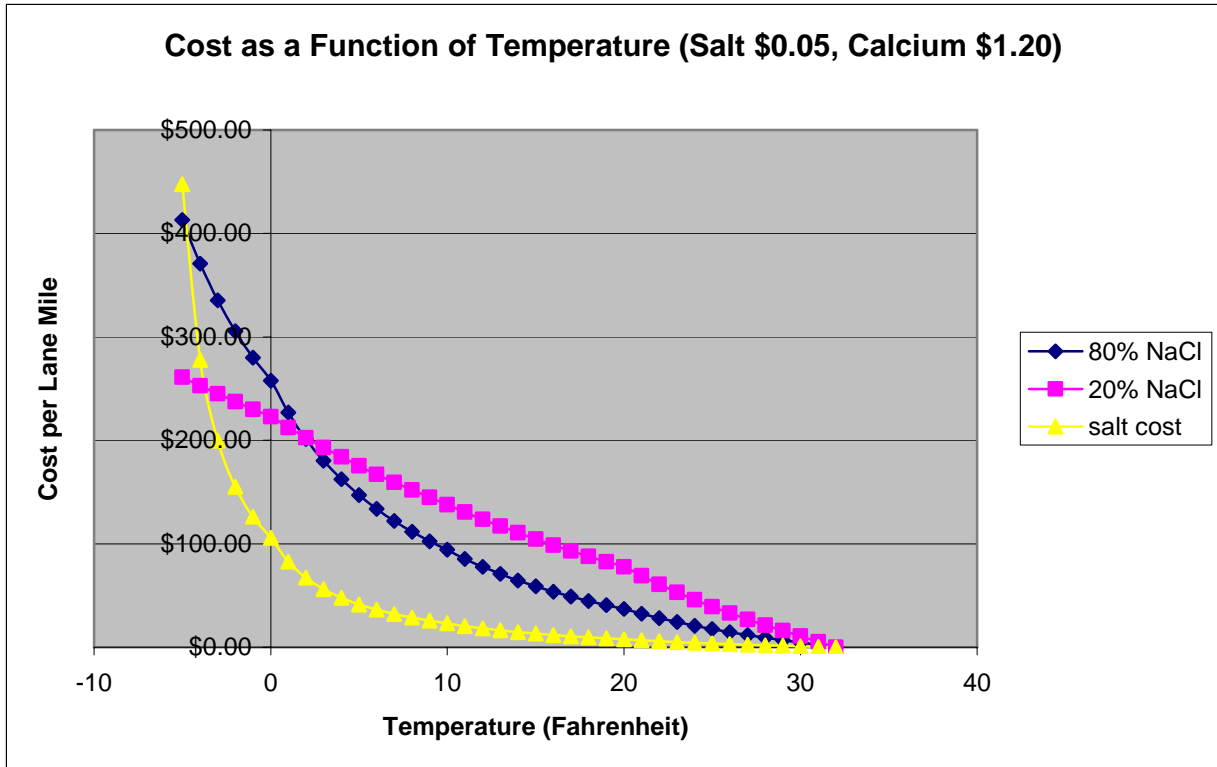


Figure 5.8: Cost Comparison, 20% NaCl and 80% NaCl Salt \$0.05, Calcium Chloride \$1.20

For the three final cost combinations, the cost of salt is set at \$0.10 per gallon, which would suggest a more favorable comparison with the calcium chloride based mixtures. This does indeed occur, but the benefits are not all that might be envisaged. Figure 5.9 shows the comparison for Salt at \$0.10 per gallon and Calcium Chloride at \$0.80 per gallon. The 20% NaCl mixture is now more economical at about +2° F, while the 80% mixture is economical at -1° F. As expected, these crossover temperatures decrease as the cost of the Calcium Chloride brine increases, as shown further in Figure 5.10 and 5.11. For Calcium Chloride brine at \$1.00 per gallon, the crossover temperatures are 0° and -2° F for 20% and 80% mixtures respectively. When that cost rises to \$1.20 per gallon, the crossovers become -1° and -3° F respectively.

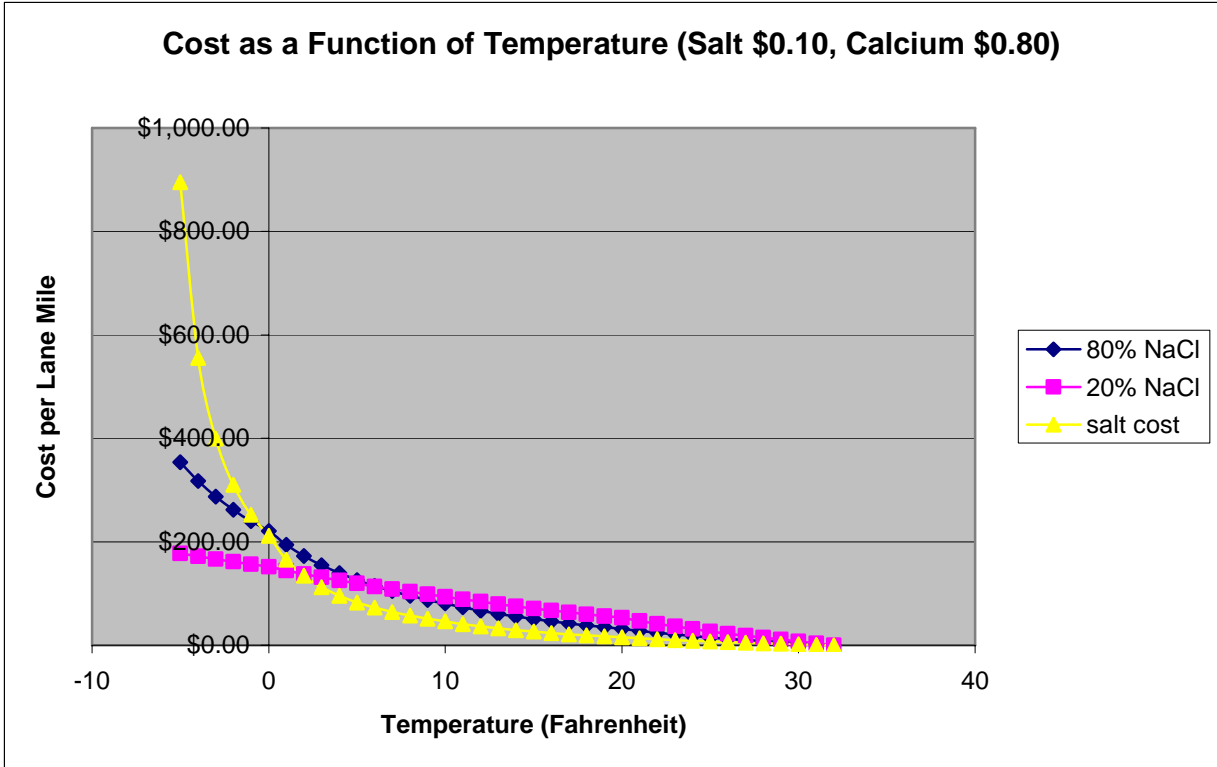


Figure 5.9: Cost Comparison, 20% NaCl and 80% NaCl Salt \$0.10, Calcium Chloride \$0.80

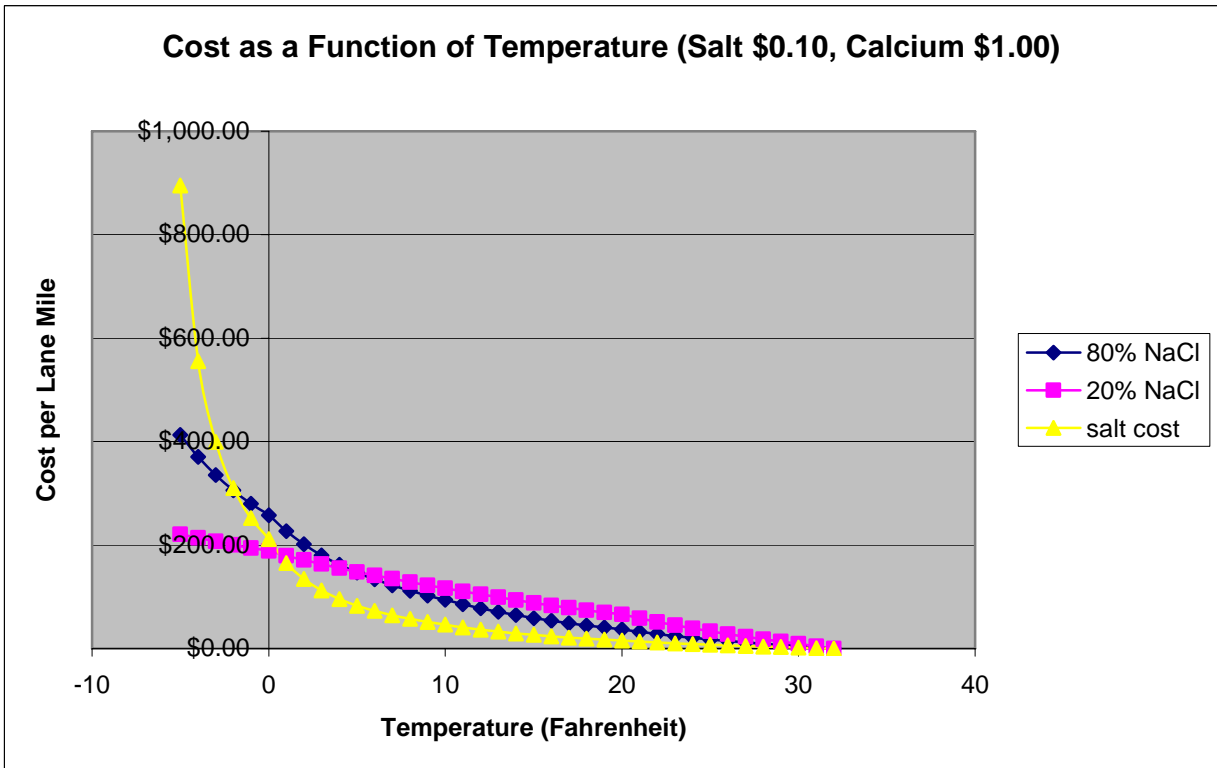


Figure 5.10: Cost Comparison, 20% NaCl and 80% NaCl Salt \$0.10, Calcium Chloride \$1.00

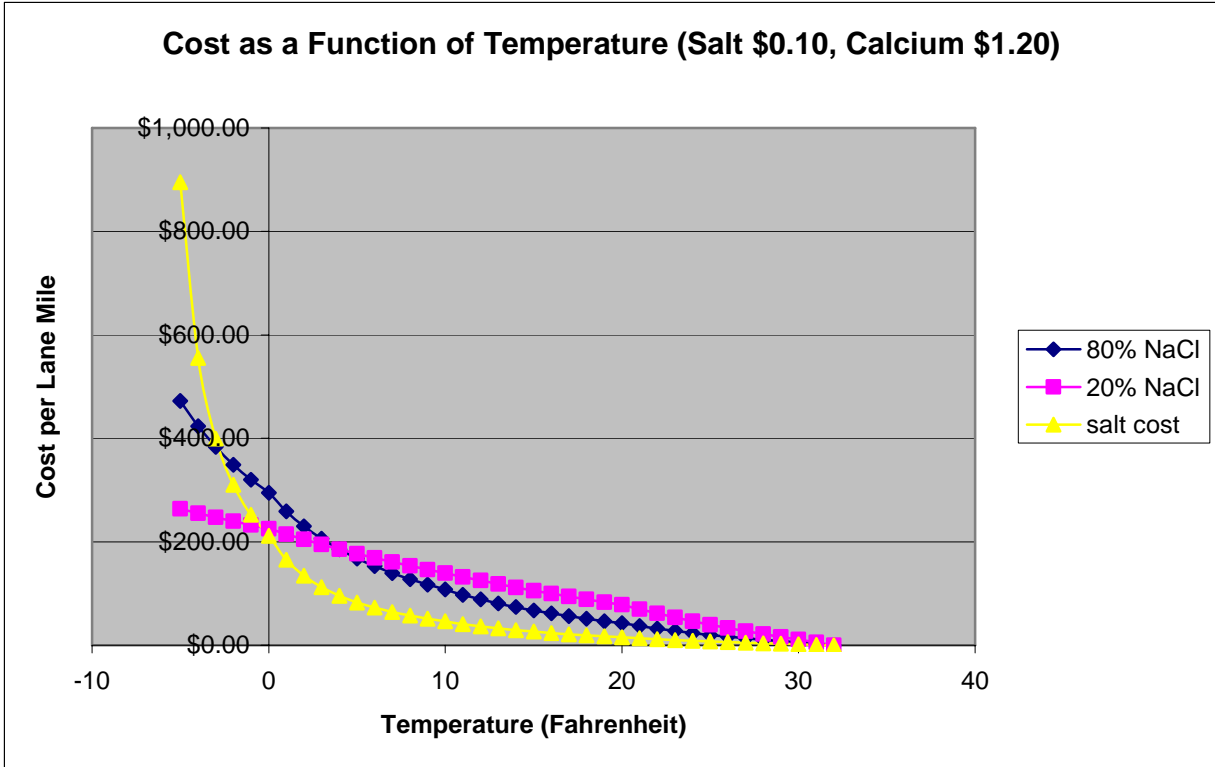


Figure 5.11: Cost Comparison, 20% NaCl and 80% NaCl Salt \$0.10, Calcium Chloride \$1.20

The implication of these results is relatively clear. From an economic standpoint based upon the melting capacity of brine mixtures alone, it is difficult to see any benefit in adding calcium chloride brine to salt brine, even at relatively high percentages until temperatures drop to zero or below. To some degree this is surprising, because the current practice suggests that salt loses effectiveness at about 15° F or thereabouts. However, it should be noted that at 15° F, in order to melt the required thickness of ice or snow, about 260 gallons of brine per lane mile (an amount that would likely be alarming to passing motorists) would be required as compared with less than 100 gallons per lane mile (still a substantial quantity of liquid) of calcium chloride brine. The material costs alone do not tell the full cost picture. Spray tankers would be able to cover 2.6 times as many lane miles using calcium chloride as they would using salt brine at 15° F. Even at

27° F, when the respective quantities would be about 50 gallons per lane mile of brine and 30 gallons per lane mile of calcium chloride, the use of calcium chloride would allow 66% greater coverage for each tank load of liquid. While the material costs for the two product applications at this temperature (and taking the two higher unit costs, \$0.10 and \$1.20 per gallon) would be about \$5.00 and \$36.00 per lane mile, the reduced number of trips may well be worth the additional material costs. Calculating these savings is in essence a route optimization problem, and as such lies beyond the scope of this project, but would be of interest to conduct in the future. However, it should be noted that should such an approach be taken, it would likely result in different optimal routes at different temperatures, and as such may not be operationally practical.



## 6: CONCLUSIONS

The purpose of this study has been to examine how well various mixes of the two chemicals (Sodium Chloride and Calcium Chloride) perform over a range of temperatures. On that basis, a cost/benefit comparison has been run. The following findings have been made:

- None of the mixtures of sodium chloride and calcium chloride brine showed any tendency to create precipitates, such that the mixture would become slippery.
- However, it should be noted that only one particular calcium chloride brine was tested in this study. Other calcium chloride brines, with other additives, may be more prone to producing precipitates, and as such care should be taken when mixing these products together.
- Experiments were conducted to determine the ice melting capacity and the freezing point of various salt-calcium chloride mixtures. These tests showed that behavior of the mixtures could be reasonably approximated by a linear interpolation between the performance of the two base brines.
- The performance of the brine mixtures was modeled using the linear interpolation described above, together with an assumption that a particular quantity of ice or snow needs to be melted on the pavement to allow for clean and effective plowing of the pavement.
- An economic model was constructed to allow comparison of the costs of different mixtures of brines at different temperatures.

- A variety of cost combinations for salt brine and calcium chloride brine were investigated to determine which mixtures were most economical. This part of the study showed that on a purely material cost basis, the mixtures do not become effective in comparison with straight salt brine until temperatures of about 0° F.
- While the previous result suggests that mixtures will rarely be of economic benefit, it was noted that this study does not consider the reduced volume of the mixtures (and the concomitant enhanced range of the spraying vehicles). Such a study would likely include a significant route optimization component and was thus significantly beyond the scope of this study. Nonetheless, this may be a topic of future interest.
- Discussions with winter maintenance supervisors who are currently using mixtures suggest that the primary benefit they observe from using the mixtures is the persistence of the liquid on the road surface. At present, no tests exist to determine such persistence and this too may be a topic of future interest.

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