1157

TRANSPORTATION RESEARCH RECORD

Deicing Chemicals and Snow Control

Transportation Research Record 1157

Contents

Foreword

Users seek assurance that the substitution of a much more expensive deicing chemical, calcium magnesium acetate (CMA), for sodium chloride will not introduce environmental problems the chemical is intended to solve. Studies, including those reported in this Record, indicate that CMA is somewhat less effective as an ice control agent than sodium chloride (commonly called salt). CMA systemic toxicity potential is similar to that of sodium chloride, but CMA is much less deleterious to highway-related and automotive-related materials than sodium chloride.

Other studies compare several classes of deicers with regard to their ability to melt and penetrate ice over various time and temperature ranges, evaluate the value of encapsulated calcium chloride pellets (Verglimit) in asphalt as an ice retardant, report the results of a study of stockpile wetting with calcium chloride, and compare several newer and faster bench-scale methods of study and materials evaluation.

The Verglimit study results in the New Jersey tests are similar to results from tests in other states and countries; the agent was effective in retarding pavement icing and made removal of snow accumulations easier.

Comparative Study of Chemical Deicers

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The ice-penetration and ice-melting characteristics of seven commercially available chemical deicers that were tested at temperatures ranging from 0°F to 25°F are examined in this paper. The materials tested included four discrete deicing chemicals and three blends: sodium chloride, calcium chloride, potassium chloride, urea, sodium chloride with traces of carboxymethylcellulose, a sodium chloride/potassium blend, and a sodium chloride/urea blend. The ice penetration tests were conducted using a Plexiglas™ apparatus consisting of small cavities. Water was frozen in the cavities and penetration observed when pellets of deicer were placed on the exposed ice surface. The ice-melting tests were conducted using an apparatus consisting of a 9-in.-diameter Plexiglas™ dish containing a $1/8$-in.-thick layer of ice. Deicers were placed on the ice surface at a selected rate. Melt brine was collected, measured, and reintroduced periodically with a syringe. The extensive data base resulting from the tests was used to compare the several classes of deicers with regard to their ability to melt and penetrate ice as a function of time and temperature, to establish lower temperature limits for deicer use, and to relate observed behavior to chemical and thermochemical properties of deicers.

There are many manufacturers of chemical-based deicers. They are available for use in several market areas but generally compete in the industrial/institutional/residential markets. The objective of this research was to obtain valid data on the performance of several chemical deicers.

A study of the major products was conducted and it was determined that four discrete deicing chemicals and three blends are primarily used. They are

- Sodium chloride,
- Calcium chloride,
- Potassium chloride,
- Urea,
- Sodium chloride with traces of carboxymethylcellulose,
- A sodium chloride/potassium chloride blend with 1 percent urea, and
- A sodium chloride/urea blend.

Information on these chemical deicers (manufacturer, name, and assay) is presented in the Appendix. Calcium magnesium acetate (CMA) was also reviewed, but it is not included in this research. The test results of this material are discussed in a separate paper in this Record.

The two major concerns of deicer performance selected for testing were (a) the rate and extent of penetration of the deicers through a layer of ice and (b) the total ice-melting rate and volume. All deicers were evaluated over a range of selected temperature and time intervals. This is because penetration is a measure of a deicer's ability to burrow through the ice and begin ice/pavement disbonding. The ice-melt volume is a measure of the amount of ice that has been melted and, in conjunction with penetration, is an indication of how much ice undercutting has occurred.

TESTING METHODOLOGIES

At the time this program was initiated, there were no standard methodologies and procedures for specifically testing a deicer's penetration and ice-melting capabilities. Therefore, various means for carrying out these tests were researched and evaluated. Several approaches were rejected because they lacked reproducibility. The testing methodologies ultimately selected provided the type of results that were hypothesized and are fully reproducible.

An important consideration in the selection of these methodologies was that the tests could be photographed for documentation purposes without affecting the test results. The deicer particles were treated with a blue dye, Rhodamine B, so that particle penetration and the resultant brine would be visible in photographs. It is believed that this dye had no significant effect on the performance of the deicers.

All deicers were stored in predried, screw-cap bottles and kept inside a glove box until testing time. Special care was given to hygroscopic deicers in order to prevent them from absorbing moisture.

For temperature control, tests were conducted in a 42-in.-long × 30-in.-wide × 30-in.-high insulated box placed inside a walk-in cold room. This arrangement prevented temperature changes caused by the opening and closing of the room's access door and body heat generated by researchers. The box was equipped with a hinged Plexiglas™ window that had two hand ports and was completely insulated on all sides. Hand ports were equipped with lab jacket sleeves through which the operator's arms were inserted for manipulation of the apparatuses. Temperature inside the box was controlled by a thermostat and a small fan which circulated cold air. The cold room was maintained at a temperature slightly lower than that of the box.

Penetration Test

The apparatus developed for the penetration tests consisted of an 11-in. × 2-in. Plexiglas™ plate, $3/8$-in. thick in which 15 holes were drilled at $5/8$-in. intervals, each $1/8$-in. in diameter and $1\frac{1}{2}$ in. deep (Figure 1). These holes were countersunk to
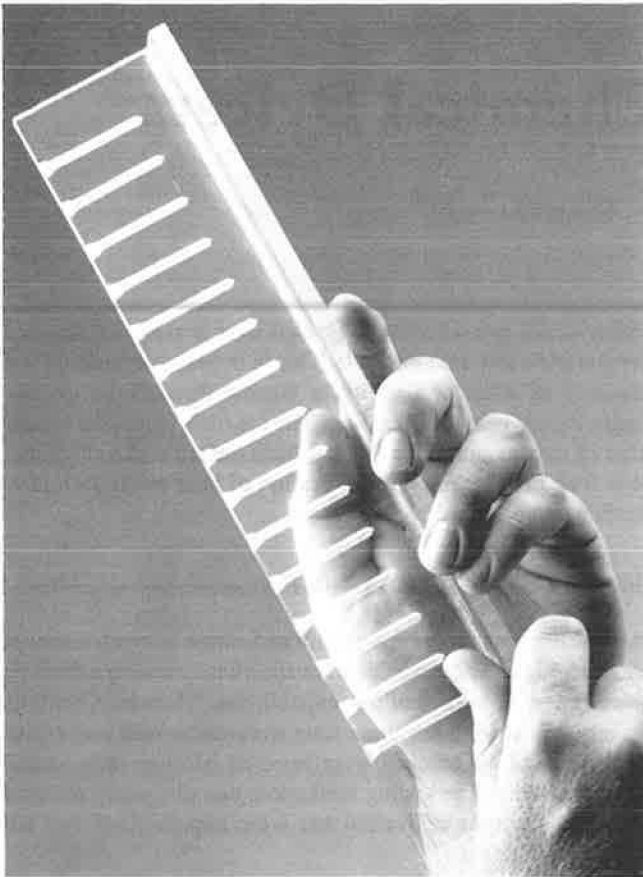
FIGURE 1 Penetration apparatus.

produce an opening 6 mm in diameter and 3.5 mm deep, at the point where the cone and the 1/8-in. hole meet. This configuration provides a deicer particle the freedom of movement it needs as it begins penetration (Figure 2).

Degassed (by boiling), deionized water was partially cooled and placed in the cavities with a syringe and needle, taking care to force out any air bubbles. The apparatus was placed overnight in the freezer compartment of a refrigerator. Because water expands when it freezes, a globule of ice formed on top
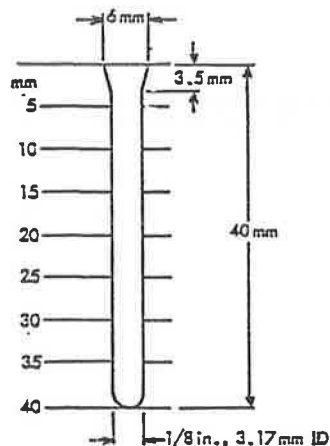
FIGURE 2 Dimensions of penetration apparatus.

of each cavity. With an aluminum plate, the surface ice was melted but an excess of water was left. The apparatus was again placed in the freezer and allowed to equilibrate to temperature for about 5 hr.

Approximately 1 hr before test time, the surface ice was subjected to a final "ironing" with the aluminum plate. At this time excess water was removed and the surface of the ice was made flush with the Plexiglas™ surface. This final surface preparation near the time of the test start effectively sealed the ice/Plexiglas™ interface at the surface. With these precautions, no evidence of preferential melting was observed at the ice/Plexiglas™ interface.

Two particle sieve-sizes were used for each deicer: +10 mesh and +8 mesh. Twenty to thirty calcium chloride pellets were weighed to determine the average weights for the two mesh sizes. These average weights were then used for all deicers. The weights were 11.5 to 14 mg for the +10 mesh material and 22 to 24 mg for the +8 mesh material. If necessary, the sieved, nonhygroscopic deicers were typically filed to achieve these weights.

For the sodium chloride/potassium chloride blend, chemical analysis, physical separation, and weighing of the individual particles revealed its composition to be approximately 50:50 by weight. Therefore, particles used in testing this material consisted of one particle of sodium chloride and one particle of potassium chloride, each weighing 6 to 7 mg for the +10 mesh sample and 11 to 12 mg for the +8 mesh sample. The combined weight of these two materials was equal to the weight of one nonblended deicer. For the sodium chloride/carboxymethylcellulose mix, only trace amounts of the carboxymethylcellulose were found. Therefore, the particle primarily used in testing this material was sodium chloride taken directly from the deicer as supplied from the manufacturer's package.

One hour before testing, all deicers were brought to the cold room so the materials could reach equilibrium temperature to simulate actual winter conditions. To ensure that each deicer was placed on the penetration apparatus simultaneously, a Plexiglas™ caddy was constructed which measured 15 in. long × 2 in. high × 1/2 in. wide. Small cups were drilled in the caddy and the penetration apparatus was inverted over it so that the cups and the cavities were aligned; then both pieces were inverted again so that the particles dropped on top of the ice columns. Forceps were used to center each particle over an ice-filled cavity (Figure 3). The loaded penetration apparatus was immediately placed in position inside the cold box located in the cold room and a timer was started.

The penetration depth for each deicer was recorded as follows. When penetration occurred uniformly and evenly in the cavity, one depth was recorded [e.g., second cavity in Figure 3 (15 mm)]. When penetration deviated and tendrils appeared (due to pellet size, density, or shape; the thermodynamics of ice/deicer interaction; or temperature), two depths were recorded. The first represented the uniform depth, or the point at which penetration continued to occur uniformly and evenly (Figure 3, fourth cavity, 7 mm). The second represented the maximum depth, or the farthest point reached by a tendril (Figure 3, fourth cavity, 20 mm). These two numbers were added together and the result divided by 2 to obtain the average penetration depth (13.5 mm).

FIGURE 3 Representative penetration behavior.

Ice-Melting Rate and Volume Test

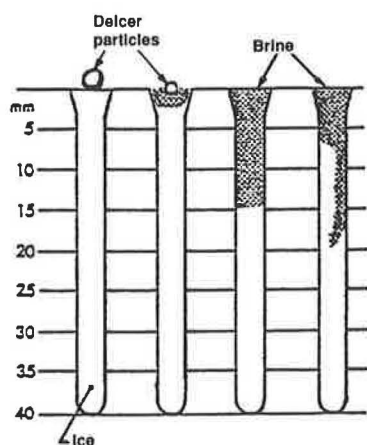There were two primary considerations to the ice-melting test: the ability to (a) isolate and measure the brine at various time intervals and (b) return that brine to the ice/deicer system so that melting could continue and further measurements be made.

The apparatus used in the ice-melting test consisted of two pieces of Plexiglas™, one ¼ in. thick, one ½ in. thick, and both 11 in. square. A hole 9 in. in diameter was cut through the ½-in.-thick piece. The two pieces were then glued together under pressure, thereby producing a hole 9 in. in diameter and ½ in. deep (Figure 4). Ten dishes were constructed in this manner so that simultaneous testing could be carried out.
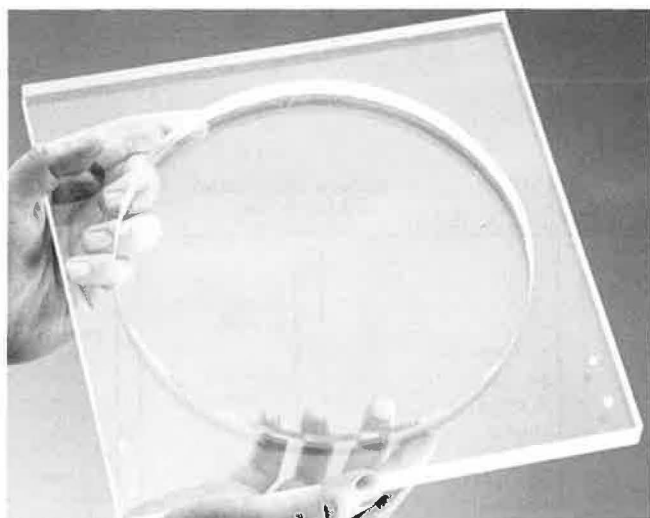
FIGURE 4 Melting apparatus.

For each test, the dishes were charged with 130 ml of deionized water and placed overnight in a level freezer compartment of a refrigerator. This volume of water corresponded to an ice thickness of ⅛ in. Before each test, it was necessary to smooth the ice surface. Therefore, a thick aluminum plate was placed on the ice surface and rotated by hand for several seconds until the surface ice was melted. The dishes were then placed on a level surface inside the testing cold room until the melted water was refrozen.

Next, the dishes were placed on edge in the temperature control box and allowed to equilibrate for a minimum of 2 hr. Placing the dishes on edge (a) assured that the dish and ice were exposed principally to the cold air and (b) permitted circulation of the air over and around the specimens causing more rapid temperature equilibration.

The deicers to be used for the day's operation were also placed inside the temperature control box before testing and allowed to equilibrate to simulate actual winter conditions. Material was taken directly from samples submitted by the manufacturer.

The deicer application rate used was 3 oz/yd^2 (1,320 lb per lane mile). This rate created amounts of brine from each deicer that were both measurable and manageable at all test temperatures and within the test time limitations. The application rate also corresponded to recommendations from the deicer manufacturers for use as residential/commercial deicers.

Samples for the ice-melting tests were taken from bulk samples of packaged commercial products. Accordingly, particle size distributions in these samples were representative of distributions in package products. The deicer designated as sodium chloride is commonly known as rock salt or halite. The particle size distribution of this product conformed to ASTM Specification D632 for highway deicing sodium chloride (percent passing: ⅜ in., 95 to 100; 4 mesh, 20 to 90; 8 mesh, 10 to 60; 30 mesh, 0 to 10). The several products consisting chiefly of sodium chloride or potassium chloride (or both) generally conformed to this specification, with the exception that most of the materials passed a 4-mesh screen. Thus, these materials contained few of the larger particles commonly present in sodium chloride, designated as halite or rock salt. Approximately 90 percent of the calcium chloride particle passed a 6-mesh screen with the bulk of the material being distributed among +8-mesh, +10-mesh, and +12-mesh screens. Essentially all of the urea passed a 6-mesh screen, with the majority being held by 8-mesh and 10-mesh screens.

To measure the amount of melt after a specified time period, each dish was tipped so that the brine flowed to the perimeter of the dish. Using a syringe and needle, the brine was quickly withdrawn and measured. The amount was recorded, then replaced in the deicer holes using the same syringe and needle.

RESULTS

Penetration Test

To ensure accurate and consistent test results, a minimum of three runs were recorded for each time period and temperature level and the average of those results was recorded. After each test run, the cavities were thoroughly flushed and rinsed with distilled water before preparing the next test.

Penetration tests for both +10-mesh and +8-mesh sieve sizes were conducted at temperatures of 5°F, 15°F, 20°F, and 25°F. Depths were recorded at 3, 5, 10, 15, 20, 30, 45, and 60 min.

Penetration test results with the +8-mesh-size material are presented in Table 1 and Figures 5, 6, 7, and 8 as a function of time and temperature. (Note: For simplicity, 3- and 15-min data and 3-, 5-, and 15-min data are omitted from Table 1 and Figures 5–8, respectively.) The +8-mesh-size material is representative of the bulk material found within the tested deicers. Consequently, +10-mesh-size test results are not provided.

TABLE 1 AVERAGE PENETRATION DEPTH MEASUREMENTS FOR CHEMICAL DEICERS TESTED AS A FUNCTION OF TIME AND TEMPERATURE

Time (min)	Sodium Chloride	Calcium Chloride	Potassium Chloride	Urea	Sodium Chloride with Carboxymethyl-cellulose	Sodium Chloride/ Potassium Chloride	Sodium Chloride/ Urea
25°F							
5	2.3	3.6	1.3	1.7	2.4	1.7	2.6
10	3.7	7.2	2.3	2.5	3.6	2.8	4.0
20	8.8	11.9	4.1	4.3	8.4	5.3	8.3
30	13.8	14.3	6.7	5.9	12.8	7.8	13.7
45	18.7	16.5	12.3	7.8	17.7	11.0	18.7
60	21.3	18.5	15.8	9.3	20.8	13.8	20.6
20°F							
5	1.1	2.8	1.0	0.4	1.7	1.5	1.1
10	2.3	4.5	1.4	0.9	2.8	2.7	2.7
20	4.8	8.9	2.6	2.0	5.1	4.8	5.1
30	7.8	10.3	3.6	3.1	9.4	7.3	9.0
45	12.0	11.8	5.2	4.5	14.2	8.8	15.7
60	14.0	13.1	7.1	6.1	16.5	10.7	17.6
15°F							
5	1.4	2.3	0.0	0.0	1.4	1.7	0.9
10	2.2	5.5	0.1	0.1	2.3	3.0	2.1
20	4.2	9.7	0.6	0.7	4.1	5.6	3.8
30	6.4	11.1	1.0	1.4	6.2	8.3	6.0
45	9.9	11.7	1.2	1.6	9.7	10.4	9.6
60	12.2	12.0	1.7	2.0	13.4	10.9	12.5
5°F							
5	0.9	1.1	0.0	0.0	0.7	0.3	0.8
10	1.7	2.1	0.0	0.0	1.4	0.8	1.4
20	2.2	4.8	0.0	0.0	2.1	1.9	2.5
30	3.1	6.9	0.0	0.0	2.8	3.0	3.1
45	3.8	8.1	0.0	0.0	3.6	4.7	4.0
60	4.7	8.5	0.0	0.0	4.5	7.0	4.9

NOTES: Penetration depth measurements in mm.
Deicer particle sieve size: +8 mesh.
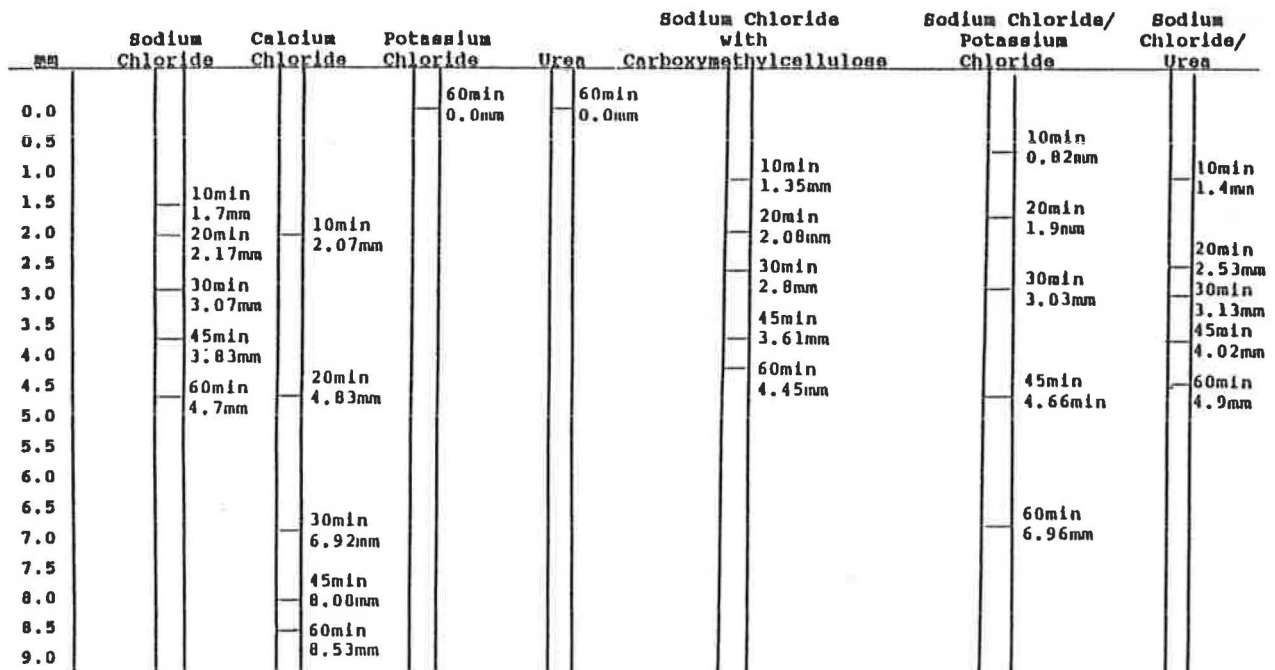
FIGURE 5 Average penetration depth (mm) at 5°F for No. 8 sieve size.
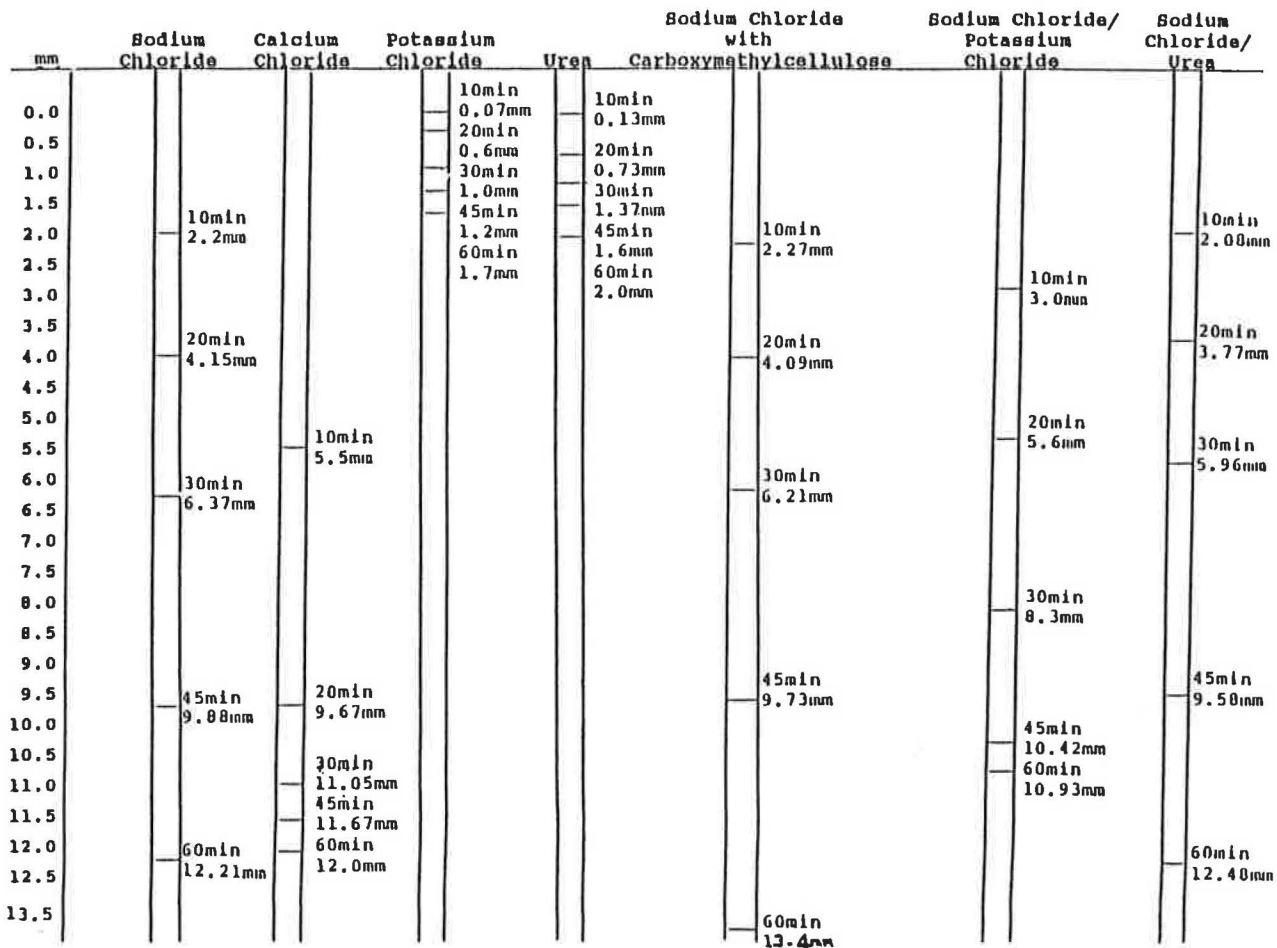
FIGURE 6   Average penetration depth (mm) at 15°F for No. 8 sieve size.

Examination of these data reveals the following:

• At all test temperatures, calcium chloride deicer penetrates to substantially greater depths than do the remaining deicers, at 10, 20, and 30 min.

• At 15°F, 20°F, and 25°F, penetration depths achieved by calcium chloride and sodium-chloride-based deicers are approximately the same after 45 and 60 min.

• At 5°F, penetration by calcium chloride deicer is substantially greater than that by the other deicers at all time intervals.

• Potassium chloride and urea penetrate little (1.7 to 2.0 mm) at 15°F and, as expected, do not penetrate ice at 5°F.

There is a significant difference between the penetration behavior of calcium chloride and the other deicers, which is not indicated by the penetration data. The calcium chloride deicer tends strongly to melt all the ice above the penetration front. The other deicers tend strongly to produce slender melt tendrils, and thus only partially melt the ice above the penetration front. This difference is consistent with the exothermic heat of dissolution of calcium chloride in water and the slighty endothermic heat of dissolution of the other deicer in water. This fundamental difference in thermochemistry is likewise believed to be the primary reason that calcium chloride deicers

penetrate more rapidly in the early stages (up to 30 min) of penetration events.

Evaluation of the penetration data in terms of effectiveness under field-use conditions leads to the conclusion that the calcium chloride deicers should be substantially more effective in promoting disbondment of ice from pavement materials. For example, undercutting of a 1/8-in.-thick layer of ice should commence in the following time intervals for the various deicers, considering only +8-mesh-size particles.

Temper-ature (°F)	Time Interval (min)			
	CaCl$_2$	NaCl	KCl	Urea
25	5	10	15	15
20	6–7	15	30	30
15	7–8	17–18	>60	>60
5	15	30	— No penetration —

Ice-Melting Rate and Volume Test

Tests were conducted at temperatures of 0°F, 5°F, 10°F, 15°F, 20°F, and 25°F. The melt volume at each temperature was measured at 10, 15, 20, 25, 30, 45, and 60 min. These results are presented in Table 2 and Figures 9–13. (Note: For simplicity, 15- and 25-min data and 0°F and 10°F data are

mm	Sodium Chloride	Calcium Chloride	Potassium Chloride	Urea	Sodium Chloride with Carboxymethylcellulose	Sodium Chloride/ Potassium Chloride	Sodium Chloride/ Urea
0.0				10min 0.9mm			
1.0			10min 1.43mm				
1.5	10min 2.33mm			20min 2.0mm			
2.0						10min 2.67mm	10min 2.67mm
2.5			20min 2.63mm	30min 3.07mm	10min 2.83mm		
3.0							
3.5			10min 1.6mm				
4.0		10min 4.5mm		45min 4.5mm		20min 4.75mm	
4.5	20min 4.83mm						20min 5.08mm
5.0			15min 5.2mm		20min 5.08mm		
5.5				60min 6.07mm			
6.0							
6.5						30min 7.33mm	
7.0			60min 7.07mm				
7.5	30min 7.83mm						
8.0						45min 8.83mm	30min 8.95mm
8.5		20min 8.87mm					
9.0					30min 9.42mm		
9.5						60min 10.7mm	
10.0		30min 10.25mm					
10.5							
11.0							
11.5	45min 11.97mm	45min 11.8mm					
12.0							
12.5		60min 13.08mm					
13.0							
13.5							
14.0	60min 14.0mm				45min 14.17mm		
14.5							
15.0							
15.5							45min 15.67mm
16.0					60min 16.45mm		
16.5							
17.0							
17.5							60min 17.58mm
18.0							

FIGURE 7 Average penetration depth (mm) at 20°F for No. 8 sieve size.

omitted from Table 2. Likewise, 15- and 25-min data and 10°F data are omitted from Figures 9–13.)

Examination of the results of the ice-melting tests indicates that the trends and comparative differences of the data generally parallel those exhibited by the penetration data, as enumerated below:

• Calcium chloride deicer melts substantially more ice than sodium chloride deicers after 10 to 45 min at 15°F, 20°F, and 25°F. At 10 min the ratio of melt volumes is of the order of 2:1. At 45 min the ratio of melt volumes is of the order of 1.3:1.

• At 5°F, calcium chloride deicer melts three to five times the quantity of ice melted by sodium chloride deicers at 10 to 45 min, and more than twice the quantity of ice melted by sodium chloride deicers at 60 min.

• Urea and potassium chloride are inferior to sodium chloride and calcium chloride at all temperatures and times and melt little ice at 15°F and none at 5°F.

• At 60 min calcium chloride is modestly superior to sodium chloride at 25°F, and is increasingly superior to sodium chloride as the temperature is lowered. Visual observations of the

dissolution of deicer pellets indicate that all calcium chloride pellets dissolve completely in the early stages of melting tests and that larger sodium chloride pellets are only partially dissolved at lower temperatures—5°F in particular.

CONCLUSIONS

Penetration Test

• Calcium chloride deicers initially penetrate ice at all temperatures, at a rate approximately twice the rates exhibited by other deicers.

• Sodium chloride deicers penetrate ice at a lower rate initially than does calcium chloride; perform similarly to calcium chloride over a 45- to 60-min period at 15°F to 25°F; and are substantially inferior to calcium chloride at 5°F.

• Urea and potassium chloride are substantially less active than sodium chloride and calcium chloride, and they become essentially nonpenetrating at 15°F and lower temperatures.
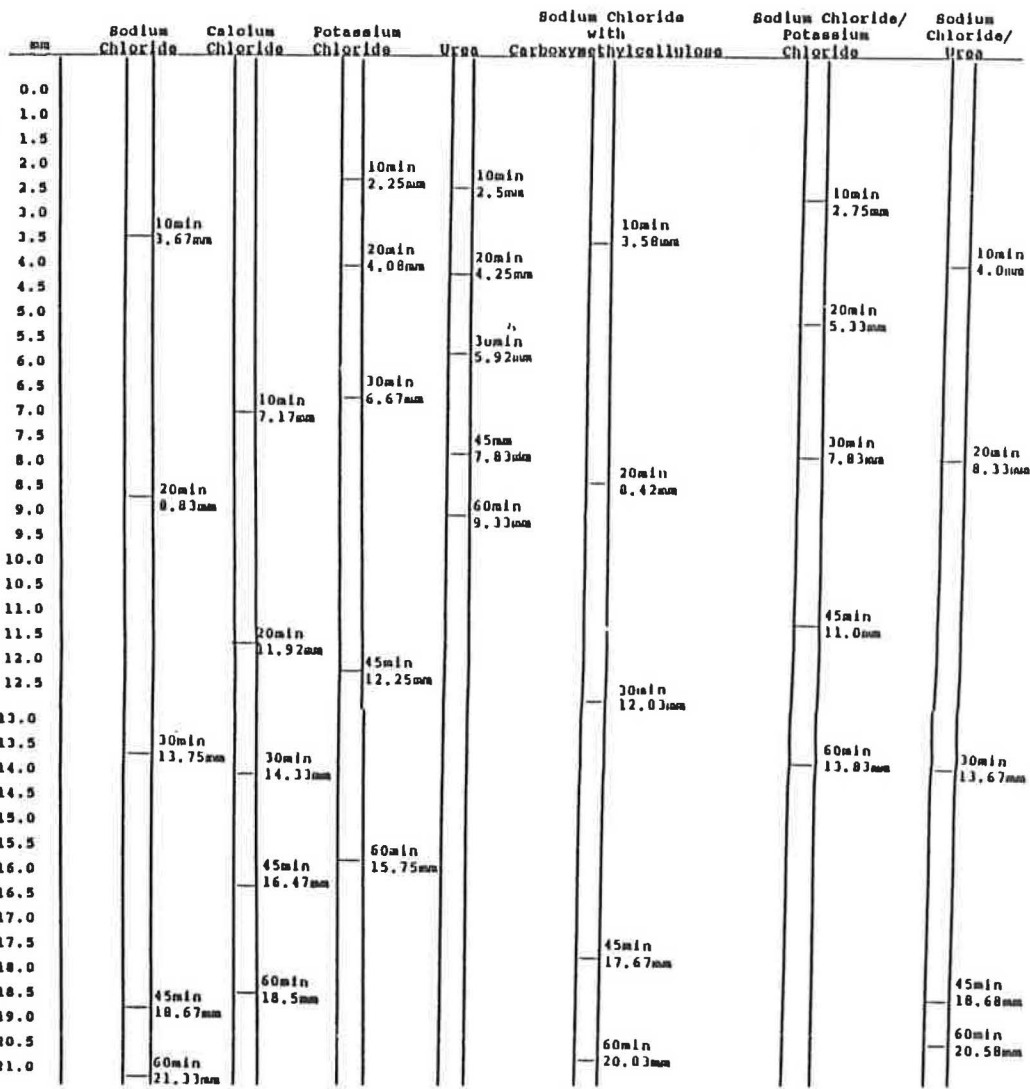
FIGURE 8   Average penetration depth (mm) at 25°F for No. 8 sieve size.

- From the standpoint of undercutting and ice disbondment, the order of preference is CaCl₂ > NaCl > KCl and urea.
- Sharp-edged crystal deicers, such as sodium chloride, tend to behave differently than spherical deicers. Spherical deicers tend to produce a uniform penetration front; crystal deicers penetrate with a nonuniform melting front with tendrils.

Ice-Melting Rate and Volume Test

- At all temperatures and in equal lengths of time, calcium chloride outperformed the other chemical deicers in melt-volume products.
- The performance differences in melt volume increased between calcium chloride and the other deicers as temperature decreased.

Penetration and Ice Melting

- Calcium chloride deicers are substantially superior to other deicers, from the standpoint of ice-melting volumes and

ice penetration/undercutting in the early stages (30 min or less) of ice melting.

- Potassium chloride and urea are indicated to be substantially less effective as expected from theoretical considerations. Both are essentially inert at the lower end of the range of temperatures tested in this program.
- Deicer blends tested were equal to or less effective than the sodium chloride at all test temperatures.
- Rapid melting of ice/snow in the first 15 min after deicer application is critical in determining deicer usefulness.

SUMMARY

In summary, calcium chloride appeared to be more effective than the other deicers in terms of ice penetration and melt volume, particularly at lower temperatures and in shorter lengths of time.

TABLE 2   AVERAGE MELT VOLUME MEASUREMENTS FOR CHEMICAL DEICERS TESTED AS A FUNCTION OF TIME AND TEMPERATURE

Time (min)	Sodium Chloride	Calcium Chloride	Potassium Chloride	Urea	Sodium Chloride with Carboxymethyl-cellulose	Sodium Chloride/ Potassium Chloride	Sodium Chloride/ Urea
25°F							
10	6.1	13.8	3.8	4.9	5.3	5.0	6.5
20	13.0	21.4	9.3	6.4	12.7	10.3	13.6
30	19.5	25.3	13.8	8.9	20.1	16.0	21.5
45	24.8	28.9	18.6	11.1	25.2	21.3	26.9
60	29.0	31.3	21.9	12.9	29.6	25.4	30.2
20°F							
10	3.0	8.4	1.6	3.6	4.1	5.7	5.7
20	7.8	15.7	3.2	4.8	9.1	8.8	9.9
30	12.3	18.8	6.1	6.0	14.0	12.4	14.8
45	15.8	20.8	8.5	6.6	17.9	16.2	19.5
60	20.2	22.7	11.2	7.2	21.5	18.3	21.8
15°F							
10	2.3	5.2	0.4	1.1	2.1	1.8	2.4
20	5.2	11.2	1.0	2.0	4.3	4.7	5.8
30	8.2	14.3	1.4	2.6	7.8	7.6	9.3
45	10.3	15.3	1.9	2.9	10.3	9.7	12.6
60	12.2	16.3	2.4	3.2	12.8	11.8	14.7
5°F							
10	1.0	4.1	0.0	0.0	0.8	0.5	0.7
20	1.5	8.7	0.0	0.0	1.3	1.2	1.8
30	2.6	10.5	0.0	0.0	2.1	1.8	2.9
45	3.8	11.3	0.0	0.0	3.6	2.4	3.8
60	5.2	12.1	0.0	0.0	4.8	3.2	5.2

NOTES: Melt volume measurements in ml.
Deicer application rate: 3 oz/yd^2.

FIGURE 9   Average melt volume (ml) at 0°F (application rate, 3 oz/yd^2).

FIGURE 10

mL axis (Figure 10): 0.0, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 5.5, ≈, 8.5, 9.0, 9.5, 10.0, 10.5, 11.0, 11.5, 12.0, 12.5

Sodium Chloride
10min 1.0mL
20min 1.53mL
30min 2.63mL
45min 3.8mL
60min 5.23mL

Calcium Chloride
10min 4.1mL
20min 0.67mL
30min 10.5mL
45min 11.32mL
60min 12.13mL

Potassium Chloride
60min 0.0mL

Urea
60min 0.0mL

Sodium Chloride with Carboxymethylcellulose
10min 0.8mL
20min 1.27mL
30min 2.13mL
45min 3.57mL
60min 4.83mL

Sodium Chloride/Potassium Chloride
10min 0.45mL
20min 1.23mL
30min 1.8mL
45min 2.37mL
60min 3.2mL

Sodium Chloride/Urea
10min 0.67mL
20min 1.77mL
30min 2.07mL
45min 3.83mL
60min 5.17mL

FIGURE 10 Average melt volume (ml) at 5°F (application rate, 3 oz/yd^2).

FIGURE 11

mL axis (Figure 11): 0.0, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 5.5, ≈, 7.0, 7.5, 8.0, 8.5, 9.0, 9.5, 10.0, 10.5, 11.0, 11.5, 12.0, 12.5, 13.0, 13.5, 14.0, 14.5, 15.0, 15.5, 16.0, 16.5

Sodium Chloride
10min 2.25mL
20min 5.17mL

Calcium Chloride
10min 8.17mL
45min 10.33mL
60min 12.17mL

Potassium Chloride
10min 5.23mL
20min 11.18mL
30min 14.25mL
45min 15.25mL
60min 16.32mL

Urea
10min 0.4mL
20min 1.03mL
30min 1.4mL
45min 1.9mL
60min 2.37mL

(Urea column second set)
10min 1.07mL
20min 2.0mL
30min 2.63mL
45min 2.93mL
60min 3.17mL

Sodium Chloride with Carboxymethylcellulose
10min 2.08mL
20min 4.33mL
30min 7.67mL
45min 10.25mL
60min 12.03mL

Sodium Chloride/Potassium Chloride
10min 1.83mL
20min 4.67mL
30min 7.58mL
45min 9.67mL
60min 11.77mL

Sodium Chloride/Urea
10min 2.42mL
20min 5.75mL
30min 9.33mL
45min 12.50mL
60min 14.67mL

FIGURE 11 Average melt volume (ml) at 15°F (application rate, 3 oz/yd^2).

FIGURE 12 Average melt volume (ml) at 20°F (application rate, 3 oz/yd²).

Columns: Sodium Chloride | Calcium Chloride | Potassium Chloride | Urea | Sodium Chloride with Carboxymethylcellulose | Sodium Chloride/Potassium Chloride | Sodium Chloride/Urea

mL scale: 0.0 to 23.0

Sodium Chloride: 10min 3.0mL; 20min 7.8mL; 30min 12.27mL; 45min 15.83mL; 60min 20.17mL

Calcium Chloride: 10min 8.42mL; 20min 15.67mL; 30min 18.75mL; 45min 20.83mL; 60min 22.67mL

Potassium Chloride: 10min 1.6mL; 20min 3.23mL; 30min 6.07mL; 45min 8.5mL; 60min 11.2mL

Urea: 10min 3.63mL; 20min 4.70mL; 30min 6.02mL; 45min 6.58mL; 60min 7.2mL

Sodium Chloride with Carboxymethylcellulose: 10min 4.13mL; 20min 9.06mL; 30min 14.0mL; 45min 17.08mL; 60min 21.54mL

Sodium Chloride/Potassium Chloride: 10min 5.67mL; 20min 8.83mL; 30min 12.4mL; 45min 16.23mL; 60min 18.33mL

Sodium Chloride/Urea: 10min 5.67mL; 20min 9.90mL; 30min 14.83mL; 45min 19.5mL; 60min 21.83mL
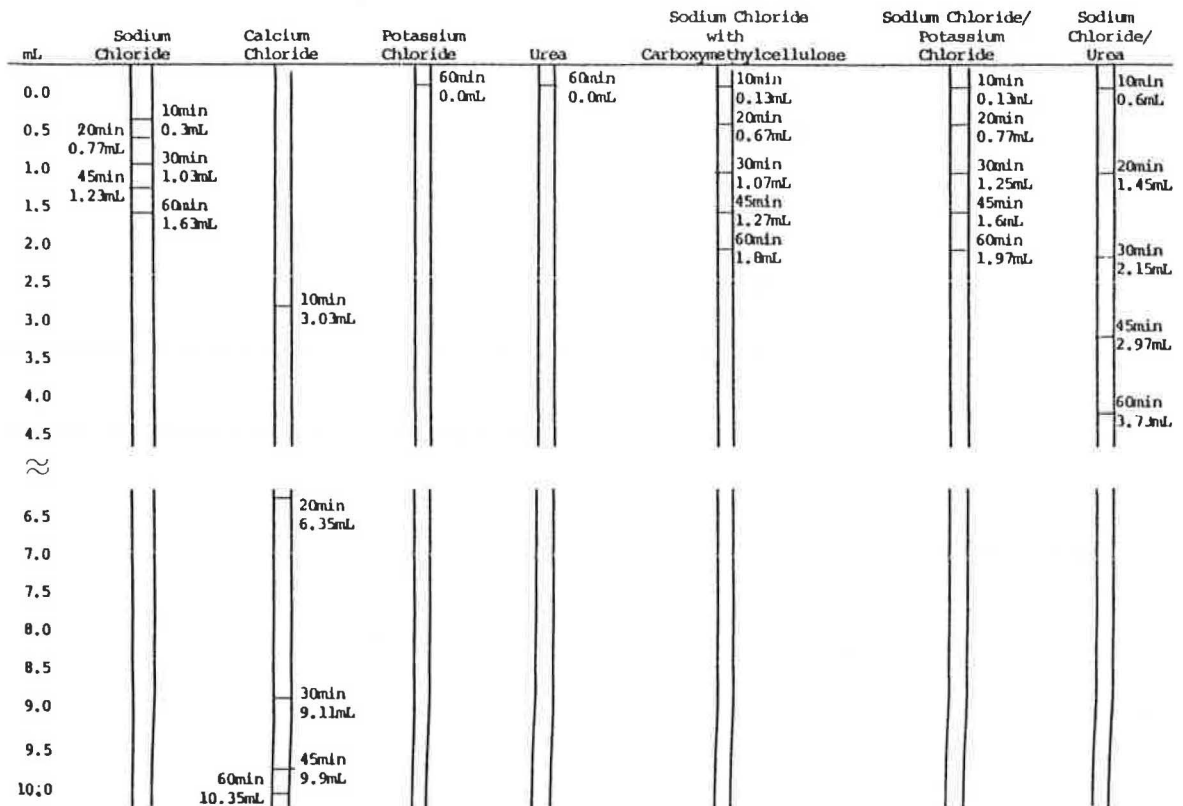

FIGURE 13 Average melt volume (ml) at 25°F (application rate, 3 oz/yd²).

Columns: Sodium Chloride | Calcium Chloride | Potassium Chloride | Urea | Sodium Chloride with Carboxymethylcellulose | Sodium Chloride/Potassium Chloride | Sodium Chloride/Urea

mL scale: 0.0 to 32.0

Sodium Chloride: 10min 6.08mL; 20min 12.97mL; 30min 19.47mL; 45min 24.83mL; 60min 29.0mL

Calcium Chloride: 10min 13.83mL; 20min 21.42mL; 30min 25.33mL; 45min 28.92mL

Potassium Chloride: 10min 3.83mL; 10min 13.83mL; 20min 9.33mL; 45min 18.6mL; 60min 21.93mL

Urea: 10min 4.07mL; 20min 6.43mL; 30min 9.92mL; 45min 11.1mL; 60min 12.93mL

Sodium Chloride with Carboxymethylcellulose: 10min 5.33mL; 20min 12.68mL; 30min 20.07mL; 45min 25.17mL; 60min 29.58mL

Sodium Chloride/Potassium Chloride: 10min 5.0mL; 20min 10.33mL; 30min 16.0mL; 45min 21.33mL; 60min 25.4mL

Sodium Chloride/Urea: 10min 6.49mL; 20min 13.55mL; 20min 21.46mL; 45min 26.94mL; 60min 30.18mL

APPENDIX

Sodium Chloride

Manufacturer:	Morton-Thiokol, Inc.
Trade Name:	Halite Safe-T-Salt™
Assay:	99 percent sodium chloride

Calcium Chloride

Manufacturer:	The Dow Chemical Company
Trade Name:	PELADOW™ calcium chloride pellets
Assay:	90.8 percent calcium chloride

Potassium Chloride

Manufacturer:	Howard Johnson Enterprises, Inc.
Trade Name:	Zero Ice™ Melting Crystals
Assay:	99 percent potassium chloride

Urea

Distributor:	Lange Stegmann
Principal Ingredient:	Fertilizer grade urea, spherical particles
Assay:	100 percent urea

Sodium Chloride with Carboxymethylcellulose

Manufacturer:	Morgro Chemical Company
Trade Name:	Ice-Fighter Plus™
Assay:	99 to 100 percent sodium chloride with traces of carboxymethylcellulose

Sodium Chloride/Potassium Chloride

Manufacturer:	Koos, Inc.
Trade Name:	Safe Step™ Ice Melter
Assay:	44 percent sodium chloride, 54 percent potassium chloride, 1 percent urea by assay; physical separation of particles: 51.5 percent potassium chloride, 48.5 percent sodium chloride

Sodium Chloride/Urea

Manufacturer:	Chemopharm
Trade Name:	Superior Sno-N-Ice™ Melter
Assay:	92.5 percent chloride, 5.3 percent urea by assay; physical separation of particles: 93 to 94 percent sodium chloride, 6 to 7 percent urea

Comparative Evaluation of Calcium Magnesium Acetate and Rock Salt

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Described in this paper are laboratory tests conducted to determine the ice-melting and ice-penetration characteristics of rock salt, calcium magnesium acetate (CMA) manufactured by RAD Services, CMA manufactured by Chevron (Ice-B-Gon™), and a Chevron CMA/sand product. Ice penetration by the three CMA products was very inferior to ice penetration by rock salt, and diminished to essentially no penetration at temperatures at which rock salt continued to penetrate. RAD Services CMA melted ice in quantities, relative to rock salt, somewhat higher than estimated from theoretical differences at 15°F and 25°F, and exhibited an approximate lower temperature limit for melting of 10°F. Chevron Ice-B-Gon™ CMA melted ice in quantities, relative to rock salt, substantially less than estimated from theoretical differences, and exhibited an approximate lower temperature limit for melting of 15°F. Results of ice-melting capacity tests indicate that in the 20°F to 25°F range, 1 ton of rock salt is equivalent to 2.5 to 3 tons of Ice-B-Gon™ CMA. Given the need for high application rates and high costs of CMA relative to rock salt, simplified cost analyses do not indicate that benefits accruing from the use of CMA will counterbalance the high costs associated with general CMA use for snow and ice control.

Snow and ice control on highways is clearly essential to the nation's economy and for public safety. The use of chemical deicers has been and will continue to be a major part of snow and ice control methods.

Extensive use of rock salt (sodium chloride) is, however, the source of substantial cost penalties due to its corrosive action and its ability to degrade roadway surface materials. In some regions of this country, sodium chloride poses an environmental threat to groundwater quality.

The Federal Highway Administration's research programs (1) accordingly address both of the following: (a) alternatives to chemical deicers and (b) alternative chemical deicers which ideally will not exhibit the undesirable properties of rock salt and will compare reasonably favorably to rock salt in performance and in cost.

Research and development programs conducted in the last 10 to 15 years have identified calcium magnesium acetate (CMA) as a potentially viable chemical deicer. This material potentially can be manufactured in quantity from readily available raw materials (i.e., biomass and dolomitic limestone); in theoretical terms will require about 1.7 lb to melt the same

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quantity of ice as 1 lb of rock salt; and is not expected to be the source of adverse impacts on highways, highway structures, automobiles, and the associated environment. The latter advantages have been supported by laboratory-based studies but have yet to be adequately verified in the field. A major deterrent to extensive use in the field is cost, which is projected to be on the order of 15 times the cost of rock salt.

Important steps in the development of CMA were as follows:

1. The identification of CMA, by Bjorksten Research Laboratories under the support of FHWA (2), as the principal viable alternate to rock salt.
2. Research on fermentation processes by the University of Georgia.
3. The development of fermentation processes for production of acetic acid and subsequent production of CMA at costs less than costs for production with "synthetic acetic acid," by SRI International (3).
4. The manufacture of 200 tons of CMA (4), by the Bowling Green, Kentucky, plant of the R&D Chemicals Division of RAD Services, Inc., under subcontract to SRI International (FHWA Contract DTFH61-81-C-00122).
5. The distribution of tonnage quantities of the above CMA to the states of Michigan and Washington and 50-lb quantities to several states for testing and evaluation.
6. The conduct of field tests, principally in Michigan and Washington, with this material.
7. The development of a process in Iowa for manufacturing CMA-coated sand, accompanied by field tests in Iowa.
8. Implementation of research, by the New York State Energy, Research, and Development Authority, on methods to inexpensively produce acetic acid.
9. Process development and product manufacture by Chevron Chemical Company, activities focused on manufacture of CMA with improved physical and handling characteristics, and on production of CMA-coated sand.
10. Studies by the California Department of Transportation, the University of Oklahoma, Daedalian Associates, and others focused on defining impacts of environment and materials on corrosion properties of CMA.

These activities have yielded results that generally support the following:

- In highway uses, CMA must be applied at rates approximately twice those used for rock salt to get equivalent results.
- CMA effectiveness varies considerably with environmental conditions and traffic conditions, and CMA accordingly appears to be not as universally usable as rock salt.

• Cost considerations tend to signify specialized use (i.e., on bridge structures as opposed to general highway ice control).

• The use of CMA in conjunction with abrasives (sand) may be a preferred mode of use.

• Elimination of adverse environmental impacts would appear to be justified.

• Reduction or elimination of corrosion is still to be demonstrated and quantified for production-quality CMA.

The tests of CMA reported in this paper were undertaken to provide a firmer basis for evaluating the performance capabilities of CMA compared to those of rock salt. The test program consisted of measurement of two deicer characteristics—ice melting and ice penetration—as a function of time and temperature. The authors want to emphasize the fact that the two types of tests used to compare deicers are laboratory tests rather than field tests. Conclusions relative to field use are thus subject to some uncertainties, particularly with regard to the probable influence of traffic and other field factors on deicer performance. A specific example consists of measurement of ice-melting and ice-penetration capabilities of CMA-coated sand in a manner that does not allow for factoring in the effect of traffic, and thus does not permit the assessment of whether or not CMA is effective in promoting the effect of an abrasive, or vice versa.

MATERIALS AND TEST PROCEDURES

Ice-melting and ice-penetration tests were conducted in an insulated enclosure placed inside a cold room. The cold room was maintained at a temperature 5°F to 10°F colder than the test temperature. The temperature in the insulated enclosure was maintained by enclosure lighting augmented on demand by a thermostatically activated fan. The box was provided with two hand ports and a hinged Plexiglas™ window.

Temperatures used in the two tests were 25°F, 15°F, 10°F, and 5°F. With exceptions as noted later, deicer materials were applied at a rate of 3 oz/yd² in the ice-melting tests, and pellets weighing approximately 24 mg were used in the ice-penetration tests.

Materials

Deicer materials tested in this investigation were as follows:

• Rock salt—the two rock salt materials used in this study were supplied by the American Salt Company and by Morton-Thiokol under the commercial name of Safe-T-Salt™.

• RAD Services CMA (CMA-1)—supplied by the state of Michigan, the CMA-1 was relatively finely divided, with maximum particle weights of 12 to 15 mg. Production data (4) indicate that essentially all of this material passes a 6-mesh screen, about 55 percent passes a 12-mesh screen, 10 percent passes a 20-mesh screen, and 6 percent passes a 30-mesh screen.

• Chevron Ice-B-Gon™ CMA (CMA-2)—the CMA-2 consisted of white, essentially spherical particles with a size distribution approximately as follows, in weight percent passing: 5 mesh, 84 percent; 8 mesh, 39 percent; and 10 mesh, 28 percent.

• CMA-coated sand, manufactured by Chevron—the approximate size distribution (in percent passing) of the CMA-

coated sand was 6 mesh, 69 percent; 8 mesh, 54 percent; 10 mesh, 47 percent; 12 mesh, 37 percent; and 14 mesh, 25 percent. The average CMA contents of size fractions and of a composite sample were determined by weighing dried sand and insolubles retained on filters, after washing with 4 percent acetic acid and water, with results as follows: +6 mesh, 3.95 percent CMA; −6+8 mesh, 7.85 percent CMA; −8+10 mesh, 10.5 percent CMA; −10+12 mesh, 12.2 percent CMA; −12+14 mesh, 14.3 percent CMA; −14 mesh, 27.65 percent CMA; calculated composite, 13 percent CMA; and measured composite, 14.6 percent CMA. Because of the difficulty of isolating a small representative sample, the calculated composite CMA percentage of 13 percent was used for specifying the application rate in ice-melting tests.

CMA-1 (RAD Services) was analyzed and subjected to solubility/freezing-point determination with results as follows: CMA content, 96.01; calcium acetate, 51.2 percent; magnesium acetate, 44.8 percent; mole ratio, Mg:Ca = 1:1.027; moisture, 3.0 percent; and insolubles, 1.0 percent.

The maximum solubility of filtered material at ambient temperatures was 28.22 percent CMA. Temperatures at which initial ice crystals formed from CMA solutions were 28.22 percent, 2.3°F; 26.0 percent, 6.3°F; 24.0 percent, 9.5°F; 20.0 percent, 15.5°F; and 15.0 percent, 19.7°F.

CMA-2 (Chevron Ice-B-Gon™) was similarly analyzed, with results as follows: CMA content, 90.22; calcium acetate, 33.71 percent; magnesium acetate, 56.51 percent; mole ratio, Mg:Ca = 1.865:1; moisture, 2.03 percent; and insolubles, 7.75 percent.

Maximum solubility of filtered material from CMA-2 at ambient temperatures was 29.6 percent. Temperatures at which initial ice crystals formed from CMA-2 solutions were 29.6 percent, −3.75°F; 28.4 percent, −1.3°F; 27.3 percent, 2.5°F; 26.3 percent, 3.6°F; 25.0 percent, 5.3°F; 20 percent, 14.5°F; 15 percent, 19.6°F; and 10 percent, 24.8°F.

Ice-Melting Test

The ice-melting test used a flat Plexiglas™ dish, 9 in. in diameter. A ⅛-in.-thick layer of ice was frozen in the dish and smoothed to remove surface irregularities. The dish containing the ice was then equilibrated to operating temperature in the enclosure for a minimum of 2 hours.

The deicer sample, usually in a quantity (4.17 g) sufficient to yield a loading rate of 3 oz/yd², was cooled to operating temperature and scattered uniformly over the ice surface. Melted brine was collected, measured, and reinjected to the ice system at intervals of 10, 15, 20, 25, 30, 45, and 60 min. This operation was effected in about 2 min by tilting the dish, syringing out the brine, and reinjecting brine into ice cavities.

The application rate of 3 oz/yd² is about three times the rates used for application of highway deicing salt. The rate was selected to ensure that measurable quantities of brine were generated in test equipment. Comparisons between deicers are considered to be valid because the deicers were tested under identical conditions. Extrapolations to field conditions and field application rates will be subject to some uncertainty.

CMA-coated sand containing 13 percent CMA was applied in the ice-melting test at the rate calculated for application of 3 oz CMA/yd² (i.e., 23 oz/yd² for CMA/sand combination).

Visual observation of CMA-coated sand applied to the ice indicated a substantial variation in particle-size distribution from one test to the next. Accordingly, the quantity of CMA actually applied was determined on test termination by recovering and weighing the sand.

A series of tests was conducted with CMA-2 to determine the application rate required to yield approximately the same quantity of brine as rock salt. Application rates of 1.5, 3.0, 4.5, 6, 8, 11, and 15 oz/yd^2 were used in this series of tests.

Ice-Penetration Test

The ice-penetration test used an 11-in. × 2-in. × ^{3}/$_8$-in.-thick Plexiglas™ plate, placed on edge. Fifteen ^{1}/$_8$-in.-diameter, 1^1/$_2$-in.-deep cavities were drilled in the Plexiglas™ at ^{5}/$_8$-in. spacings. The upper end of each cavity was enlarged with a conically shaped bit, yielding a cone 6 mm (0.24 in.) in diameter at the surface and 3.5 mm (0.14 in.) deep at the point of intersection of the cone with the ^{1}/$_8$-in. cavity.

Each cavity was filled with deionized and deaerated water. After freezing, the surface was melted with a metal piece and excess water removed. The apparatus was placed in the test enclosure and brought to temperature. A drop of dilute Bulls Eye™ (Milliken Chemical Company, Inman, South Carolina) dye was placed on the surface of the ice in each cavity approximately 30 minutes before test start. A weighed, pre-cooled deicer pellet was centered on the surface ice of each cavity, and depths of melting/penetration were recorded at selected intervals over a 1-hr period.

The penetration test with CMA-coated sand posed a special problem relative to selection of particles containing a quantity of CMA approximately equal to the quantity (24 mg) of deicer used with other materials. The several size fractions, which had been analyzed for CMA content, were further segregated into coated (as evidenced visually by a fairly uniform coat of CMA) and uncoated or poorly coated sand/CMA particles. The overall analyses showed the following:

- The large particles (+6 mesh) contain little CMA;
- Average CMA percentage of particle weight increases as particle size decreases;
- As particle size decreases, an increasing fraction of the pellets contain no sand; and
- A majority of the CMA is contained by the well-coated sand particles.

Thus, −6+8 mesh and −8+10 mesh coated particles contained about 40 percent CMA, while poorly coated sand grains in these size fractions contained 3 to 5 percent CMA. Well-coated −10 mesh material contained about 50 percent CMA, and a substantial fraction of the particles in this size range contained no sand. The coated −6+8 mesh particles weigh about 30 mg, and thus contain 10 to 12 mg of CMA on an average basis. Single CMA/sand pellets containing 24 mg CMA were not available, with the probable exception of fairly large pellets containing no sand core. Accordingly, penetration tests with CMA-coated sand used visually coated pellets isolated from the −6+8 mesh fraction. The average CMA content (10 to 12 mg) of these pellets was approximately 50 percent of the deicer weight used in penetration tests with CMA-1, CMA-2, and rock salt.

Single pellets of CMA-1 (RAD Services) having desired weights (23 to 26 mg) were not available in the supplied material. Accordingly, three 7 to 9 mg pellets were used for penetration tests with CMA-1.

DISCUSSION OF TEST RESULTS

On a theoretical basis, the normally cited comparative performance figure for CMA and rock salt is 1.7, that is, 1.7 lb of pure CMA with equimolar proportions of calcium acetate and magnesium acetate should have the melting capacity of 1 lb of sodium chloride, or 1 lb of CMA should melt 59 percent of the quantity of ice melted by 1 lb of sodium chloride. Factoring in the purities of the two CMA products tested in this investigation and the proportions of magnesium acetate and calcium acetate, CMA-1 (RAD Services) should melt 57 percent of the quantity of ice melted by the same quantity of rock salt; and CMA-2 (Chevron), 54 percent. The CMA/sand product should perform similarly to CMA-2 at rates adjusted for the CMA content of CMA/sand.

Comparative ice-penetrating capabilities for CMA and rock salt can be expected generally to reflect theoretical differences in ice-melting capacities, that is, it might be predicted that with pellets of equal weight, CMA will penetrate approximately 55 to 60 percent of that observed with rock salt. However, the penetration process is probably affected more by factors such as particle density, particle size, and thermochemistry than is the melting process. Ice melting may thus be more likely to parallel theoretical comparisons than will ice penetration.

Freezing-point data for the two products indicate that ice melting should occur down to a few degrees above 0°F for CMA-1 and to a few degrees below 0°F for CMA-2. Useful melting under field conditions usually does not occur at temperatures approaching eutectic temperatures, however. One of the objectives of this investigation consisted of defining a lower practical temperature limit for melting.

Ice-Melting Results

Data on volumes of brine generated at seven time intervals up to 1 hr are presented in Table 1 for 25°F and in Table 2 for 15, 10, and 5°F. The deicer application rate in these tests was 3 oz/yd^2 for rock salt, CMA-1, and CMA-2; and 23 oz/yd^2 for

TABLE 1   ICE-MELTING TEST RESULTS AT 25°F

Time (min)	Average Brine Volume (ml)					
	Rock Salt	CMA-1	CMA-2	CMA/Sand (23 oz/yd^2) by CMA Application Rate (oz/yd^2)		
				3.16	3.58	4.83
10	5.8	4.2	1.8	1.0	1.6	3.6
15	9.3	6.8	3.6	2.7	4.0	6.7
20	12.2	9.0	4.6	4.0	6.0	10.2
25	15.4	11.6	5.5	5.9	8.3	12.6
30	18.0	12.8	6.8	7.5	10.0	14.0
45	23.3	16.0	8.9	9.8	14.5	19.0
60	27.4	18.3	11.4	12.3	18.0	22.8

NOTE: Averaged data for tests with Morton-Thiokol Safe-T-Salt and American Salt. Deicer application rate, 3 oz/yd^2.

TABLE 2 ICE-MELTING TEST RESULTS AT 15°F, 10°F, AND 5°F

Temperature (°F)	Time (min)	Average Brine Volume (ml)			
		Rock Salt	CMA-1	CMA-2	CMA/Sand (23 oz/yd^2)
15[a]	10	2.2	0.2	0.0	0.0[b]
	15	3.7	1.2	0.0	0.0
	20	5.2	2.7	0.3	0.0
	25	6.7	3.2	0.7	0.0
	30	8.1	4.2	1.1	0.3
	45	10.4	6.9	1.8	1.2
	60	12.4	8.1	2.3	2.7
10[c]	10	1.2	0.0	Not tested	
	15	1.7	0.0		
	20	2.2	0.0		
	25	2.9	0.2		
	30	4.0	0.5		
	45	5.4	1.1		
	60	7.2	2.3		
5[a]	10	1.0	0.0	0.0	0.0[b]
	15	1.3	0.0	0.0	0.0
	20	1.5	0.0	0.0	0.0
	25	1.9	0.0	0.0	0.0
	30	2.6	0.0	0.0	0.0
	45	3.8	0.0	0.0	0.0
	60	5.2	0.0	0.0	0.0

[a]Averaged data for tests with Morton-Thiokol Safe-T-Salt and American Salt.
[b]Values in this column correspond to a nominal CMA application rate of 3 oz/yd^2.
[c]Averaged data for tests with Morton-Thiokol Safe-T-Salt.

CMA/sand. The rate of 23 oz/yd^2 for CMA/sand nominally provides 3 oz/yd^2 of CMA.

Inspection of results with CMA-1 at 25°F and 15°F indicates that this CMA product melts ice in about the quantities expected relative to rock salt. At 10°F, CMA-1 appears to be on the verge of becoming inactive as an ice melter; at 5°F, no ice was melted over the 1-hr test period.

Inspection of results with CMA-2 indicates a considerably lower melting capacity than CMA-1 at 25°F; CMA-2 at 15°F performs similarly to CMA-1 at 10°F, and yielded no melted ice at 5°F. At the end of the 1-hr test period, the larger pellets of CMA-2 were only slightly dissolved at 15°F and 25°F; large pellets in fact failed to dissolve in an additional 2-hr period with the test apparatus at ambient (72°F to 75°F) temperatures.

The intent was to apply CMA/sand at a rate that would apply 3 oz/yd^2 of CMA. In the 25°F tests, insufficient care was taken to isolate representative samples. The wide variability of results in these tests prompted recovery, drying, and weighing of sand after each test. The variability is in part explained by the differences in actual application rates of CMA (3.16, 3.58, and 4.83 oz/yd^2). CMA/sand at 3.16 oz CMA/yd^2 performed moderately better than CMA-2 at 3 oz/yd^2. The performance of CMA/sand at 3.58 and 4.83 oz CMA/yd^2 is considerably better relative to CMA-2 than can be explained by the higher CMA application rates.

One general observation is applicable to CMA-1, CMA-2, and CMA/sand. With rock salt as well as with other deicers tested in related studies, ice melting occurs with extensive penetration through the 1/8-in. layer of ice, even at the lower range (5°F to 10°F) of temperatures tested. This penetration is accompanied by undercutting and creation of an expanding

network of under-the-ice channels through which brine flows to the brine collection area of the test apparatus. The CMA materials largely fail to penetrate through the ice layer, except in the final 20 to 30 min of a 25°F test; brines remain principally on the surface of the sheet of ice and tend strongly to float undissolved deicer particles to the brine collection area. (The latter behavior is much less noticeable with CMA/sand—the sand particles have little tendency to float in the brine.)

The ice-melting capacity of CMA-1 and CMA-2 is compared to that of rock salt in Table 3. The column labeled "I"

TABLE 3 CMA ICE-MELTING CAPACITY RELATIVE TO ROCK SALT

Deicer	Temperature (°F)	Time (min)	Theoretical CMA:Rock Salt (I)	Observed CMA:Rock Salt (II)	CMA Obs.:Theor. (II:I)
CMA-1	25	60	0.57	0.64	1.12
		45		0.69	1.21
		30		0.71	1.25
		20		0.75	1.28
		15		0.73	1.28
		10		0.73	1.28
CMA-1	15	60	0.57	0.66	1.16
		45		0.67	1.17
		30		0.52	0.91
		20		0.52	0.91
		15		0.33	0.58
		10		0.09	0.16
CMA-1	10	60	0.57	0.31	0.54
		45		0.21	0.37
		30		0.12	0.21
		20		0	0
		15		0	0
		10		0	0
CMA-1	5		No ice melting		
CMA-2	25	60	0.54	0.40	0.74
		45		0.38	0.70
		30		0.38	0.70
		20		0.33	0.61
		15		0.32	0.59
		10		0.32	0.59
CMA-2	15	60	0.54	0.18	0.33
		45		0.18	0.33
		30		0.14	0.26
		20		0.07	0.13
		15		0	0
		10		0	0
CMA-2	5		No ice melting		

NOTE: Rock salt equals 1.0.

indicates that CMA-1 theoretically should melt 57 percent of the ice melted by the same quantity of rock salt; and CMA-2, 54%. The column labeled "II" presents the observed percentages as a fraction. The column labeled "II:I" basically presents numbers that indicate whether CMA has performed better (numbers > 1.0) or worse (numbers < 1.0) than expected from the simple theoretical differences (0.54 and 0.57 versus 1.0 for rock salt).

The data in Table 3 indicate the following:

• At 25°F CMA-1 performs better than theory, relative to rock salt, from beginning to end of the test period.

• At 15°F CMA-1 is a slower starter (10- to 30-min data), but over the 1-hr period performs better than theory, relative to rock salt.

- At 10°F CMA-1 generates measurable brine only after about 25 minutes. Over the 1-hr period, CMA-1 at 10°F yields about 55 percent of the melting expected, relative to rock salt.
- At 25°F CMA-2 melts ice at 60 to 75 percent of its theoretical capability, relative to rock salt.
- At 15°F CMA-2 is on the verge of becoming inactive or inert, in this respect resembling CMA-1 at 10°F.

Results of a series of tests undertaken to determine CMA-2 application rates required to yield a melting capacity equal to that of rock salt at 3 oz/yd^2 are presented in Tables 4 and 5.

TABLE 4   CMA-2 ICE-MELTING TESTS AT VARIOUS APPLICATION RATES: 25°F

Time (min)	Average Brine Volume (ml)					
	CMA-2 by Application Rate (oz/yd^2)					Rock Salt (3 oz/yd^2)
	1.5	3	4.5	6	8	
10	0.7	1.8	2.6	3.9	4.1	5.8
15	1.4	3.0	4.3	6.2	7.3	9.3
20	2.2	4.0	6.3	8.8	10.2	12.2
25	2.7	5.5	8.3	10.8	12.5	15.4
30	3.5	6.9	10.4	13.1	15.6	18.0
45	4.8	8.9	13.5	17.4	21.3	23.3
60	6.4	11.4	16.3	21.3	26.4	27.4

TABLE 5   CMA-2 ICE-MELTING TESTS AT VARIOUS APPLICATION RATES: 15°F

Time (min)	Average Brine Volume (ml)					
	CMA-2 by Application Rate (oz/yd^2)					Rock Salt (3 oz/yd^2)
	1.5	3	4.5	6	11	15	
10	0.0	0.0	0.1	0.0	0.0	0.0	2.2
15	0.0	0.0	0.4	0.5	0.5	0.4	3.7
20	0.2	0.3	1.0	1.1	1.2	1.3	5.2
25	0.3	0.7	1.3	1.8	2.3	2.2	6.7
30	0.5	1.1	2.0	2.5	3.6	3.7	8.1
45	0.6	1.8	3.3	4.5	6.1	6.9	10.4
60	0.8	2.3	4.6	6.0	9.0	10.3	12.4

From the data, it is apparent that at 25°F an application rate of 8 oz CMA-2/yd^2 yields brine in approximately the quantities given by 3 oz rock salt/yd^2. At 15°F, an equivalence point having any real significance could not be established. As higher and higher rates of CMA-2 were applied, it became evident that melted ice was increasingly absorbed in the masses of CMA present on the ice surface.

Ice-Penetration Results

Ice-penetration data are presented in Table 6. At 25°F the rock salt pellets penetrated through about 21 mm (0.8 in.) of ice in 60 min, compared to 4 to 5 mm (0.16 to 0.2 in.) of ice by CMA-1 and CMA-2, and 2.9 mm (0.11 in.) of ice by CMA/sand. The CMA/sand pellets, however, contained about 10 to 12 mg CMA compared to 23 to 26 mg CMA in CMA-1 and CMA-2 pellets. The times required for penetration of 3.2 mm (^{1}/$_8$ in.) of ice at 25°F are about 5 min for rock salt and 40 to 45 min for CMA-1 and CMA-2.

The rock salt exhibits significant ice-penetrating capabilities at 5°F, that is, 3.2 mm (^{1}/$_8$ in.) in about 40 min, and 4.4 mm (0.18 in.) in 60 min.

TABLE 6   ICE-PENETRATION TEST RESULTS

Temperature (°F)	Time (min)	Average Penetration Depth (mm)			
		Rock Salt	CMA-1	CAM-2	CMA/Sand[a]
25	3	1.8	0.0	0.0	0.0
	5	3.0	0.0	0.0	0.0
	10	4.7	0.5	0.2	0.3
	15	7.6	0.9	0.6	0.6
	20	9.5	1.5	1.3	1.0
	30	13.9	2.1	2.1	1.8
	45	18.1	3.3	3.4	2.3
	60	20.7	4.1	4.7	2.9
15	3	0.6	0.0	0.0	0.0
	5	1.1	0.0	0.0	0.0
	10	2.4	0.0	0.0	0.0
	15	3.3	0.05	0.0	0.0
	20	3.9	0.07	0.0	0.0
	30	5.4	0.2	0.0	0.0
	45	8.6	0.7	0.0	0.0
	60	10.6	1.1	0.0	0.0
5	3	0.3	0.0		
	5	0.5	0.0		
	10	1.3	0.0		
	15	1.6	0.0		
	20	1.9	0.0		
	30	2.7	0.0		
	45	3.5	0.0		
	60	4.4	0.0		

NOTE: Mesh-size-8 pellets: 23–26 mg.

[a]Mesh-size-8 pellets of visually coated CMA/sand, average CMA per pellet: 10 to 12 mg.

Comparative ice-penetration data relative to rock salt are presented in Table 7. At 25°F, the three CMA products penetrate ice to about 20 percent of the depth penetrated by rock salt in 60 min. Rock salt penetrates significantly within 3 min while it takes about 10 min for the CMA products to produce even slight depths of penetration.

At 15°F CMA-1 penetrates about 10 percent of the distance in ice penetrated by rock salt in 60 min, while CMA-2 and CMA/sand exhibit no observable penetration of ice.

In summary, the three CMA products are markedly less effective than rock salt from the standpoint of ice penetration; and they have essentially no ability to penetrate ice at 15°F and lower. The differences in ability to penetrate ice perhaps are best illustrated by the fact that CMA at 25°F is about equivalent to rock salt at 5°F.

SUMMARY OF LABORATORY TEST RESULTS

Theoretical comparisons of CMA and rock salt indicate a 1.7 to 1.8:1 difference in ice-melting capacities, and lower temperature limits of potential utility which are slightly in favor of rock salt (i.e., −6°F for NaCl, −3.75°F for CMA-2, and +2.3°F for CMA-1).

Results of the tests performed in this investigation generally indicate that one CMA product, CMA-1, melts ice at rates and quantities somewhat better than predicted from theoretical comparisons, at 25°F and 15°F; that the second CMA product (CMA-2) performs substantially less well than predicted at 25°F and 15°F; and that the lower temperature limits for melting are about 15°F for CMA-2, 10°F with CMA-1, and 5°F and lower with rock salt. The results of the tests thus indicate

TABLE 7 COMPARATIVE ICE PENETRATION

Temperature (°F)	Time (min)	CMA-1 ÷ Rock Salt	CMA-2 ÷ Rock Salt	CMA/Sand ÷ Rock Salt[a]
25	3	0.0	0.0	0.0
	5	0.0	0.0	0.0
	10	0.11	0.04	0.07
	15	0.13	0.09	0.09
	20	0.16	0.14	0.10
	30	0.15	0.15	0.16
	45	0.18	0.19	0.17
	60	0.20	0.23	0.20
15	3	0.0	0.0	0.0
	5	0.0	0.0	0.0
	10	0.0	0.0	0.0
	15	0.015	0.0	0.0
	20	0.018	0.0	0.0
	30	0.037	0.0	0.0
	45	0.08	0.0	0.0
	0	0.10	0.0	0.0

NOTE: CMA relative to rock salt = 1.

[a]CMA/sand compared to 10- to 12-mg pellets of halite.

that the CMA products are seriously limited relative to rock salt for use at lower temperatures.

The relative inferiority of the CMA products is considerably more pronounced with regard to ice-penetrating capabilities. Rock salt has some penetrating ability at temperatures as low as 5°F; the CMA products penetrate reasonably well only at 25°F.

The following marked differences between CMA-2 and rock salt are probably caused by the inferior ice-penetrating ability of CMA. First, CMA products tend strongly to yield surface films of brine, in which smaller particles float; rock salt particles generate melt cavities into which the pellets sink, and the rock salt brine increasingly undercuts the ice with time. Second, the larger pellets of CMA-2 are only partially dissolved at the end of 60-min tests, while the larger rock salt pellets are fairly completely dissolved, even at the lower temperature tested. It can be concluded from these observations that the inherent rate of interaction between ice/brine and CMA is lower than the corresponding rate with rock salt; and that as a consequence, conditions conducive to rapid and efficient melting (i.e., immersion of pellets in brine) are precluded from developing.

The principal cause of the marked difference in the ice-melting capacities of CMA-2 and CMA-1 is attributed to the above effect. CMA-1 is a much more finely divided material; initially it has the benefit of substantially greater ice surface to deicer particle contact, and, as a consequence of higher surface area/smaller particle size, is enabled to interact more readily with ice and the surface film of brine.

EXTENSION OF ICE-MELTING RESULTS TO HIGHWAY USE

Extension of the ice-melting data to highway use permits the estimation of application rates needed to obtain comparable ice melting, excluding the effects of traffic and other possible effects. An application rate of 300 lb rock salt per lane mile should yield ice melting equal to that of about 460 lb of CMA-1 at 15°F to 25°F; approximately 790 lb of CMA-2 at 25°F; and approximately 1,800 to 1,900 lb of CMA-2 at 15°F.

One ton of rock salt is accordingly equivalent to about 1.5 tons of CMA-1 at 15°F to 25°F, 2.6 tons of CMA-2 at 25°F, and 6 tons of CMA-2 at 15°F. However, due to its marked dusting tendency, CMA-1 cannot be considered to be a practical deicer with existing highway equipment. Evaluations of CMA as a highway deicer must accordingly be based on the CMA-2 product applied at the high rates indicated for CMA-2.

The CMA/sand product can be less clearly evaluated and compared with rock salt. The somewhat limited data and accompanying observations indicate that the CMA content of CMA/sand is more useful than an equivalent quantity of CMA in CMA-2, consistent with the fact that the CMA in CMA/sand is concentrated in finer particles and on the surfaces of medium size particles (particles retained by 8- and 10-mesh screens). At 25°F the two CMA/sand samples containing a higher-than-average percentage of CMA yielded significantly higher quantities of brine per unit weight of CMA than did CMA-2.

COST ANALYSIS

Comparative costs for field use can be developed only with considerable uncertainty because snow and ice removal or control is a complicated function of weather and temperature; traffic; rate, frequency, and timing of deicer application; and other control measures. The point in question concerning relative costs is whether substitution of CMA for rock salt at the application rates presented above will result in the same or acceptable levels of snow and ice control.

Since the RAD Services product (CMA-1) is not a practical material with current highway equipment, cost comparisons at present should be based on the Chevron Ice-B-Gon™ product (CMA-2). For this product, a minimum application rate is about two and one-half times the application rate of rock salt, with rates five to six times that being required at temperatures of the order of 15°F. If the following are accepted: a factor of 3 (3 tons of CMA equivalent to 1 ton rock salt), $16.00 FOB plant as the cost per ton of rock salt, and $500.00 FOB plant as the cost of CMA, the relative deicing materials costs, excluding transportation, storage, and handling costs, are 1 ton rock salt: $16.00 and equivalent CMA (3 tons): $1,500.

The reported annual consumption of highway deicing salt in the United States is about 10 million tons (5), for a total FOB plant cost of $160 million. Substitution of CMA for rock salt would result in a total FOB plant cost of $15 billion, or $14.84 billion greater than the cost of rock salt. The FOB plant cost differential of $14.84 billion will be increased by added costs for transporting, storing, and handling the larger quantity of CMA. Annual costs of corrosion attributed to highway salt usage (6, 7) have been estimated as $1.2 billion for automobile corrosion, and $1.6 billion for bridge maintenance and replacement, for a total cost of $2.8 billion.

It is apparent that the added costs of across-the-board substitution of CMA for rock salt will be five to six times the benefit which might accrue from elimination of the corrosion attributed to highway salt use. Given the uncertainties about the extent of reduction of corrosion attending the use of production grade CMA, it is probable that the cost benefit from corrosion reduction will be less than the reported cost of $2.8 billion.

CONCLUSIONS

The CMA product (CMA-2) currently commercially available in a form suitable for highway snow and ice control can be thought of as being technically equivalent to rock salt in one of two important control characteristics—ice melting—when approximately three times as much material is used at the upper end of the ambient temperature range of interest (i.e., 20°F to 25°F). It is unacceptably inferior to rock salt with respect to ice melting at lower temperatures with no utility at temperatures of 15°F and lower. From the standpoint of ice penetration and undercutting/disbondment, CMA-2 is indicated to be much less effective than rock salt at all temperatures.

Costs for general use of CMA-2 as an alternate to rock salt are much higher than costs of rock salt. The additional cost for CMA-2 is not adequately counterbalanced by cost benefits that might result from corrosion control.

It can be concluded that the current CMA will be limited to special uses, exemplified by its incorporation in sand and its use on bridge structures and in areas where continued use of rock salt is environmentally objectionable.

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DISCUSSION

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The conclusions drawn from the research discussed in this paper are in direct conflict with independent findings from the field demonstrations of CMA by federal, state, local, and provincial transportation organizations. As such, the laboratory study discussed demonstrates that current methods are inadequate for the reliable evaluation of a deicer's efficacy in the field.

It has been widely known that CMA melts less ice than sodium chloride. However, highway snow and ice control is not accomplished through the mere melting of ice from the nation's roads—not even when sodium chloride is the deicer employed. Rather, chemical deicers work by breaking the bond of snow or ice with the highway surface, allowing traffic and plows to move the pack off the roadway and restore safe conditions. CMA has been shown to be effective in maintaining and restoring safe driving conditions at field demonstration sites across the United States and Canada.

McElroy et al. conclude that Chevron CMA (Ice-B-Gon™ deicer) must be applied at roughly 3 times the rate for sodium chloride to be effective. This is in direct conflict with the findings in field use. Indeed, a recent report of field experience on the Queen Elizabeth Way by the Ontario Ministry of Transportation (*1*) showed year-long Chevron CMA usage ratios to be 1.19 on high-speed highways and 0.95 on low-volume service roads. These data also reflect at least one instance in which salt application was deemed to be ineffective and was suspended during a severe storm whereas Chevron Ice-B-Gon deicer continued to keep the roadway track bare or better. A similar report by the Massachusetts Department of Public Works showed a year-long ratio of only 0.73 in use on urban streets.

The authors also conclude that the use of Chevron CMA as an alternative to rock salt is not cost-effective. Another recent report, issued by the New York State Energy Research and Development Authority (*2*) in the interest of reducing fuel use by motorists and contractors in the repair of highway damage, concluded that the total cost of salt-related damage in New York is between $920 and $2,080 per ton of salt now used. With the bulk price of Chevron CMA currently $600/ton, Ice-B-Gon deicer is indeed a cost-effective alternative to conventional deicing chemicals.

In addition, we would like to point out that the material described as Chevron CMA in the research does not meet Ice-B-Gon deicer specifications. Chevron was not asked to supply a sample for this research (which we do frequently) and does not know its origin or the sampling method used to obtain it.

Highway snow and ice control is an extremely complex subject. The effective maintenance of our infrastructure requires more than the simple melting of ice. It requires the use of responsible methods for keeping roads safe while minimizing the impact of these programs on the environment and on the roads themselves. It is toward this goal that the transportation community, and Chevron, continues to strive in the development of alternative deicers such as calcium magnesium acetate and Chevron Ice-B-Gon deicer.

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DISCUSSION

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In this paper, ice-melting data for a calcium magnesium acetate (CMA) deicer are presented and compared to corresponding information on rock salt. On the basis of information compiled, it was concluded that (a) rock salt is a much better ice-melting material than CMA and (b) CMA is unacceptably inferior to rock salt with respect to ice melting at low temperatures.

This paper does not point out that there are other methods by which deicing can occur and by which CMA works in deicing highways. Recent field studies have shown that although rock salt does melt ice much faster and to a larger extent than CMA, CMA deices by penetrating to the road surface, debonding and dislodging the snow or ice pack from the surface, and converting the pack to a loose, mealy mixture for easy removal by traffic or snowplows. These field observations showed that CMA, in quantities 1.2–1.6 times that of rock salt, worked as well as salt in its overall deicing ability by this method.

Thus there is more than one mechanism that a deicer can use to deice highways. CMA should not be judged solely by its melting capabilities for deicing ice and snow.

AUTHORS' CLOSURE

We appreciate Walters' comments but do not believe that our findings are in direct conflict with independent findings from field demonstrations, as he states. Review of CMA research by the states of Michigan, Iowa, and Washington as well as by the Province of Ontario suggests that a higher application rate of CMA is required to achieve a degree of effectiveness comparable with that of rock salt. Unfortunately, field research to date has compared winter storms that are usually above 25°F. CMA ice-melting and ice-penetrating abilities outlined in our paper are at 25°F and lower; thus the results do not rigorously apply to current field studies. Moreover, the laboratory tests do not represent the effects of traffic, wind or air currents, or the abrasive action of the deicer.

The study by Manning mathematically averages the CMA:rock salt used and arrives at a ratio of 1.19, as Walters correctly points out. However, according to Manning, the initial ratio of 1.7 for the application rate of CMA to salt was used, and after 2 months it was reduced to 1.5 to 1. Manning

states: "The relatively small number of storms (15) prevented the investigation of other application rates," and "the optimum application ratio was not determined."

In 2 of 15 storms, rock salt/sand was compared directly with CMA/sand. One storm ratio was 0.76 to 1 and the second was 2.34 to 1. In the remaining storm events, rock salt, rock salt/sand, CMA, and CMA/sand were employed in varying combinations with varying numbers and rates of application. Sand was the major ice and snow control agent directed at snow control and did not include provisions for determining optimum comparative application rates.

Given the relative randomness of spread timings, rates per application, and intermingling of deicer with deicer/sand, in our opinion the 1.19 to 1 ratio of CMA to salt averaged in the field testing by Manning is low.

The current cost of CMA is approximately 25 to 27 times higher than rock salt based upon FOB average cost. Societal cost per ton of rock salt has been set at $101.50 in 1976 by The Institute for Safety Analysis (TISA), $300 in 1976 by EPA, and, as Walters notes, $920 to $2,080 in 1987 by the New York State Energy Research and Development Authority. Vehicle corrosion accounts for 67 percent (EPA study) and 63 percent (TISA study) of the overall societal cost. In our opinion, vehicle corrosion can be better approached economically by rustproofing.

In response to the question of the quality of the Ice-B-Gon CMA employed in our research, we elected to secure material made available for purchase by a state highway department rather than material supplied in response to a request for a research project. The material used in the tests appears to meet all product specifications with the exception of water insolubles (7.75 percent versus ≤ 3.0 percent).

In summary, we submit the following comments:

1. Research results indicate that the CMA product tested was sluggish, as related to rock salt, in its ice-melting and ice-penetrating capabilities and in this respect was substantially limited at temperatures below 20°F within the tested time frame (1 hr).

2. Field experience to date does not adequately indicate how much CMA relative to rock salt is required for acceptable snow control, and therefore an adequate basis for establishing a ratio does not now exist. The theoretical ratio is 1.7 CMA to 1.0 rock salt.

3. The cost benefits of using either rock salt or CMA for ice and snow control are subject to debate and questions. Corrosion reduction is also subject to the same questions.

4. We suggest that the reader or potential deicer user should evaluate costs and cost benefits in terms of factors and considerations unique to his use situation.

Calcium Magnesium Acetate: Comparative Toxicity Tests and an Industrial Hygiene Site Investigation

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A commercial formulation of calcium magnesium acetate (CMA), an alternative deicing agent for salt-sensitive areas, was evaluated for toxicity. A subchronic toxicity test was performed, as was a full complement of short-term toxicity tests including acute oral toxicity, acute inhalation toxicity, acute dermal toxicity, eye irritation, skin irritation, and dermal sensitization tests. Presented in this report are the results of those tests, conducted through the Chevron Environmental Health Center, Inc., which are compared to similar toxicity data on sodium chloride and some worker experience with CMA. The goal was to identify and characterize any immediate or short-term toxic effects CMA may produce in humans and compare the results with data on sodium chloride (common salt). This series of tests showed CMA to have very low mammalian toxicity. In general, the effects produced by CMA are similar to those caused by sodium chloride in similar toxicity tests. The systemic toxicity potential of CMA is similar to that of sodium chloride, as are the eye and skin irritation potentials. In the subchronic feeding study, CMA produced no toxicity at a "limit" dose of 1,000 mg/kg/day for 28 days. The acute inhalation toxicity of CMA is also low and CMA produced no evidence of immunologic reactivity in a dermal sensitization test. In spite of the low irritation potential evidenced in the acute eye and skin tests, highway workers at one field test site complained of eye and skin irritation when handling CMA. An industrial hygiene site investigation was conducted to attempt to reconcile this human experience with the laboratory data. Dust exposures at the site in question were found to greatly exceed the threshold limit value for occupational exposure to nuisance dusts; respirable dust levels were much lower. In summary, laboratory and human evidence indicate CMA to have a toxicity comparable to that of sodium chloride.

Calcium magnesium acetate (CMA) is being evaluated as an alternative road deicing agent in the United States and abroad, especially in environmentally sensitive areas. Two attractive features of CMA, as compared to traditional road salt, are that it is (a) less corrosive and (b) less damaging to the environment. CMA has been shown to be less corrosive to concrete, zinc, aluminum, and steel than has salt; it is therefore expected to produce less damage to bridges and other road structures and to automobiles. CMA contains no sodium or chloride to contribute to groundwater contamination and is expected to have less effect on salt-sensitive vegetation.

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If CMA is to play a major role as a deicing agent, other factors must also be considered; prime among these is toxicity. Toxicity is the capability of a compound to injure living organisms. The mitigating factor to toxicity is dose, the amount of the compound to which a living organism is exposed. Virtually all compounds have some toxicity; the extent of its expression depends on the level of exposure required for injury to occur (injury from a compound of low toxicity requires exposure to a larger amount).

Salt is perceived by the public as "nontoxic"; it has a low mammalian toxicity in comparison with other compounds common to society. Therefore, before the public can be expected to accept an alternative deicing agent, its toxicity should be evaluated and compared to that of salt.

CHEMICAL INFORMATION

Toxicity studies were conducted on the Chevron Ice-B-Gon™ deicer formulation of CMA. This CMA formulation has a nominal 3:7 calcium:magnesium ratio and is approximately 91 percent CMA (dry basis). Formulations of Chevron Ice-B-Gon™ deicer having different proportions of calcium and magnesium may be developed in the future. It is believed that the results of the studies described in this paper will be generally representative of the toxicity of these other formulations. Because of potential differences in manufacturing processes, physical and chemical properties, and impurities present, however, it is not known if these data will be relevant to CMA prepared by other manufacturers.

An actual commercial sample from an early production run of the CMA was used for toxicity evaluation. For testing, the normally hard, spherical pellets were ground into a fine powder, a procedure that usually increases biological reactivity and allows for precise exposure control.

Following is the structure of the commercial formulation of CMA used in the toxicity studies and the field tests that form the basis of this report:

$$CMA = Ca_xMg_y(C_2H_3O_2)_{2(x+y)}$$

where

$$x = 3 \text{ to } 4$$
$$y = 7 \text{ to } 6$$

TOXICITY OF CALCIUM MAGNESIUM ACETATE

The toxicity tests performed on CMA included acute oral toxicity, acute inhalation toxicity, acute dermal toxicity, eye irritation, skin irritation, and a subchronic oral test. This series of tests is appropriate for a deicing agent, a compound which is expected to be used daily, but only on a seasonal basis. The tests were performed in accordance with federal guidelines for toxicity testing, where applicable (*1, 2*).

A review of the toxicology literature for similar data on sodium chloride did not identify any toxicity studies on road salt itself. Since road salt is primarily sodium chloride, the toxicity data on sodium chloride were used for the comparison to CMA; any toxicities of the additives and impurities present in road salt are not represented by these data.

Short-term toxicity tests are conducted using unrealistically high doses of the test compound, the rationale being that these high doses will exaggerate any subtle effects that might not otherwise be apparent. In addition, these tests characterize any risk associated with one-time or occasional use of the test compound.

These tests showed CMA to have low mammalian toxicity. In general, the effects produced by CMA were similar to those caused by sodium chloride (common salt) in the same tests. As evidenced by the acute and subchronic oral toxicity tests, the systemic toxicity potentials of the two compounds are very similar. Dermal and ocular testing showed the skin and eye irritation potentials of CMA to be equivalent to or less than those of sodium chloride. Few inhalation data on sodium chloride are available for comparison; however, CMA exhibited very low toxicity by this route of exposure. Signs of respiratory difficulty developed in some animals during the inhalation study, but this was in response to an exposure level 450 to 500 times that of the threshold limit value (TLV) for occupational exposure to nuisance dusts (which is 10 mg/m^3).

Acute Oral Toxicity

An acute oral toxicity test provides a basic indication of the level of toxicity of the compound being studied. This test is most relevant to single or occasional human overexposures. In addition to indicating the potential of the substance to cause harm, the test yields information about the symptoms and time course of any poisoning that may occur in humans.

This test also provides a value (the LD_{50}) for use in comparing the toxicity of different chemicals. The LD_{50} is the theoretical dose predicted to be fatal to one-half of the animals tested. Compounds with lower LD_{50}'s are more toxic than those with higher LD_{50}'s.

Calcium Magnesium Acetate

The acute oral LD_{50} for CMA was found to be 3,150 mg/kg (milligrams CMA per kilogram body weight) in rats. This LD_{50} places CMA in the "slightly toxic" category of a standard classification scheme (Table 1) for chemical toxicities (*3*). For humans, the estimated probable lethal dose by ingestion of a "slightly toxic" compound is about 250 g (slightly more than ½ lb). Table 2 (*4*) presents LD_{50} values for a series of other compounds to compare the toxicity of CMA.

TABLE 1 ACUTE LETHAL DOSES FOR REPRESENTATIVE COMPOUNDS (*3*)

Example Compound	Acute LD_{50} (mg/kg)
Ethanol	10,000
Sodium chloride	3,750
Calcium magnesium acetate	3,150
Ferrous sulfate	1,500
Morphine sulfate	900
Phenobarbital	150
Strychnine sulfate	2
d-Tubocurarine	0.5
Tetrodotoxin	0.1
Dioxin	0.001
Botulinus toxin	0.00001

Clinical signs observed in this study indicated an effect on the lungs; signs of stress and general malaise were also noted. Effects on the lung appeared related to development of edema (fluid in the air spaces) and were confirmed by a pathology examination.

Sodium Chloride

The acute oral LD_{50} of sodium chloride in rats is 3,750 mg/kg (*5*), essentially the same as the LD_{50} for CMA. (Another widely cited value for sodium chloride is 3,000 mg/kg; however, documentation for this value was not found in a search of the literature.) Sodium chloride is therefore also a "slightly toxic" compound and is often cited as the prototype for this category (*3*).

Although sodium chloride is a common household chemical and is considered exceptionally "safe" by the public, it is not benign. Serious poisonings and even deaths have occurred following ingestion of large quantities or after its use to induce vomiting (*6–8*).

Calcium Chloride

Data are also available on the acute oral toxicity of calcium chloride, a frequently used low-temperature road deicing salt. The single dose oral LD_{50} is reported by Frank (*9*) to be between 1,000 and 2,000 mg/kg in rats. This places calcium chloride also in the "slightly toxic" category (*3*).

Subchronic Oral Toxicity

Subchronic oral toxicity testing indicates whether toxicity can develop from repeated exposures. Subchronic testing mimics human exposures of moderate duration or intermittent nature. A subchronic test is especially appropriate for a deicer that is used only seasonally, but on a daily basis. Another reason for this testing is that a few compounds exhibit greater toxicity from repeated versus single exposures.

The test compound is given by mouth for 28 consecutive days. Although the doses are lower than for the acute test (nonlethal doses are used), they are still high relative to anticipated human exposures. The animals are observed daily for any signs of illness. In addition, food consumption and body weight are monitored (decreases in either can indicate toxicity).

TABLE 2   TOXICITY CLASSIFICATION BASED ON LETHAL DOSE *(4)*

Category	Oral LD$_{50}$ (Rat) (mg/kg)	Dermal LD$_{50}$ (Rabbit) (mg/kg)	Probable Human Lethal Dose	Example
Extremely toxic	≤1	≤5	Taste	Nicotine
Highly toxic	1–5	5–45	Teaspoon	Parathion
Moderately toxic	50–500	45–350	Ounce	DDT
Slightly toxic	500–5,000	350–2,800	Pint	Salt
Practically nontoxic	5,000–15,000	2,800–22,600	Quart	Ethanol
Relatively harmless	>15,000	>22,600	>1 quart	Mineral oil

Calcium Magnesium Acetate

For subchronic oral testing, an upper "limit" dose of 1,000 mg/kg/day is recommended for compounds that exhibit low acute toxicity. This dose was used in the CMA study. For a human being this corresponds to ingestion of approximately 2½ oz of CMA per day.

No signs of toxicity developed in any of these animals. All of the animals maintained normal food consumption and growth patterns. Following the 28 days of CMA dosing, the animals were sacrificed and a complete autopsy was performed; no effect of CMA was observed.

Sodium Chloride

No subchronic oral toxicity studies on sodium chloride are available for comparison. A chronic toxicity study in rats, however, was performed by Boyd et al. *(10)*. This study identified the LD$_{50}$ for a 100-day repeated administration to be 2,690 mg/kg/day for sodium chloride.

It appears that sodium chloride and CMA are of comparable toxicity following repeated administration. Since no deaths resulted from administration of CMA at 100 mg/kg/day and the single dose LD$_{50}$ was 3,150 mg/kg, it is reasonable to project that a 100-day LD$_{50}$ would be in the range similar to that found for sodium chloride.

Acute Inhalation Toxicity

In the acute inhalation toxicity study, exposure to the test compound is through breathing rather than by mouth. Animals are exposed for 4 hours to very high airborne levels of the compound and then observed over 14 days for toxicity. Concentrations used in this test are often many times greater than the TLV for occupational exposure to nuisance dusts.

Calcium Magnesium Acetate

The 4-hour inhalation exposure to extremely high airborne levels of CMA produced no deaths in the exposed laboratory rats. The primary clinical sign observed following the exposure to CMA was respiratory difficulty; all affected animals returned to normal within 3 to 5 days. No other signs of toxicity attributable to CMA developed and all animals appeared normal until sacrifice at 14 days; no pathology was evident upon autopsy.

Sodium Chloride

Aerosolized saline (0.9 mg/100 ml sodium chloride in water) has been used for control exposures in some laboratory inhalation studies. There is some evidence from one of these studies to indicate that sodium chloride levels in the range of 90 to 100 mg/m^3 may produce minor lung irritation during an acute exposure (2 hours); all signs of irritation cleared within 2 days in these animals *(11)*.

Eye Irritation

The primary eye irritation test measures irritation or damage as a result of direct eye contact. The test compound is deposited directly onto the eye and any reactions occurring during the next 21 days are evaluated by a standard scoring system *(12)*. Both rinsed and unrinsed eyes were tested for their response to CMA.

Mechanical irritation, in addition to any chemical irritation, may occur when the compound is a solid. Therefore, granular or crystalline compounds often produce some irritation in this test.

Calcium Magnesium Acetate

Eyes treated with CMA and then washed developed only mild irritation, including moderate redness and discharge with some swelling of the iris. There was no effect on the clarity of the lens or its protective surface. By 24 hours only minor irritation remained, which cleared by 72 hours. Mild to moderate irritation occurred in the unwashed eyes. All showed slight redness and moderate to severe swelling or discharge initially, with some swelling of the iris. Slight clouding of the cornea was present initially, but cleared by 24 to 48 hours. This mild effect is not considered a "positive" response under the Federal Hazardous Substance Act guidelines *(13)*. No effect on the lens was noted. Most irritation cleared by 48 hours and all eyes were completely normal within 3 to 10 days.

The reactions to CMA yielded mean irritation scores of 11 (out of a possible 110) in the washed eyes and 23 in the unwashed eyes. These results classify CMA as a mild-to-moderate eye irritant. It is likely that at least part of the irritation observed was mechanical, due to the granular nature of the CMA. As expected for a granular material, this test demonstrated that prompt washing can reduce the mild irritation produced by CMA.

Sodium Chloride

In a similar test, granular sodium chloride was found to be slightly more irritating than CMA and was classified as a moderate eye irritant (*14*).

Skin Irritation

The skin irritation test assesses the test compound's ability to irritate or damage the skin upon direct contact. Irritation is due to a direct chemical reaction on the skin; it does not include activation of the immune system (allergic reactions).

A paste is made from the test compound and applied to the shaved skin of rabbits under an occlusive patch. Following an exposure of 4 to 6 hours, the paste is removed and any reactions are graded according to a standardized scale (*12*).

Calcium Magnesium Acetate

In the CMA study, the only sign of any reaction was mild redness, which was barely perceptible at 1 hour and cleared within 24 hours. These results classify CMA as nonirritating to the skin.

Sodium Chloride

Sodium chloride has been reported to be mildly irritating; this report is a Czechoslovakian publication and details are lacking (*15*).

Acute Dermal Toxicity

Acute dermal toxicity testing determines if the test compound can be absorbed across the skin in amounts sufficient to produce systemic effects. It is most relevant to a single, prolonged skin exposure.

A concentrated paste of the test compound is applied to the shaved skin of rabbits for 24 hours and the animals are observed for 14 days. The dermal exposure in this test is devised to maximize penetration of the compound through the skin for uptake into the body; it is not predictive of skin reactions.

Calcium Magnesium Acetate

In this study, a dose of 5,000 mg/kg CMA was tested for the ability to cross the skin and produce systemic toxicity. None of the test animals exhibited any systemic signs of toxicity. Some developed mild-to-moderate irritation of the exposed skin, which cleared after the first day. Therefore, following a single exposure, there is insufficient absorption of CMA across normal skin to be a health hazard.

Sodium Chloride

Although results on a similar study on sodium chloride are not available, it is unlikely that systemic toxicity would occur from dermal contact.

Dermal Sensitization

Dermal sensitization testing predicts the test compound's ability to elicit allergic skin reactions. Guinea pigs are the preferred animal for sensitization testing because they are the most sensitive laboratory animals (*16*).

Relatively large amounts of the test compound are repeatedly applied to the skin of guinea pigs over the course of 3 weeks; repeated exposure allows the animal sufficient opportunity to develop immunologic responsiveness. Following this induction phase, a single challenge dose is applied and any skin reaction is evaluated. Since the challenge dose is much smaller, the response is dictated by the animals' immunologic reactivity, not by any chemical irritancy of the test compound. The reaction, if any, is compared to that of a known sensitizer and the percentage of animals responding determines the strength of the sensitizer.

Calcium Magnesium Acetate

Calcium magnesium acetate produced no reaction in dermal sensitization testing. There was no evidence of any ability to elicit allergic responsiveness.

Sodium Chloride

Sodium chloride is not believed to have any sensitization potential.

Interpretation of CMA Toxicity Tests

The acute toxicities of CMA and sodium chloride are compared in Table 3. CMA exhibited a toxicity similar to that of sodium chloride for acute oral toxicity as well as skin and eye irritation potential. No inhalation or dermal toxicity data are available on sodium chloride for comparison; CMA exhibited low toxicity by both of these routes of exposure. In the subchronic oral toxicity test, CMA produced no toxicity at a "limit" testing dose, thus indicating low toxicity upon repeated exposure.

TABLE 3 COMPARATIVE ACUTE TOXICITY OF CALCIUM MAGNESIUM ACETATE AND SODIUM CHLORIDE

	Calcium Magnesium Acetate	Sodium Chloride
Rat oral LD_{50}	3,150 mg/kg[a]	3,750 mg/kg[a]
Eye irritation	11/110[b]	13/110[b]
Skin irritation	Nonirritating	Mildly irritating
Acute inhalation LC_{50}	>5,000 mg/m³	NA[c]
Acute dermal LD_{50}	>5,000 mg/kg	NA

[a] "Slightly toxic" category (*4*).
[b] "Nonirritating" (*11*).
[c] Not available.

The toxicity tests conducted (acute oral, acute inhalation, acute dermal, dermal irritation, ocular irritation, skin

sensitization, and subchronic oral toxicity) provide a good overall evaluation of the potential toxicity of CMA. These tests, as a whole, assess the local and systemic effects of the compound via a number of different routes of exposure. However, laboratory toxicity tests cannot guarantee that human exposure will always have the same results. Occasionally there are differences, mostly unexplained or incompletely defined, between the ways different species respond to chemicals. In addition, there may be more individual diversity in the human population than can be tested in laboratory animals. Therefore, laboratory tests may not completely predict the response of all individuals in the human population to all conceivable chemical exposures.

SITE INVESTIGATION

Some information is available on human exposure to CMA. Chevron Ice-B-Gon™ underwent field tests at a number of highway sites during the winters of 1986 and 1987: three sites were in the California Sierra Nevada Mountains and the others were Madison, Wisconsin; Neenah, Wisconsin; Charlotte, Michigan; and Ontario, Canada. With only one exception, there were no health-related complaints from workers at these sites.

The health complaints were received from a site testing CMA in 50-lb bags. This site normally handled deicing agents in bulk form; therefore, it neither had the dust control equipment nor followed the procedures typical of a facility accustomed to handling bags of this size. The use of CMA in bags was selected by this site because of concerns that they would be unable to store bulk material in a dry area. Six highway maintenance employees reported minor injuries—mainly skin, eye, and nasal irritation—while handling CMA. These complaints were unexpected, based on the laboratory animal data and the experience at the other field sites, and this site was investigated. A Chevron Chemical Company industrial hygienist visited the site during a February 1987 storm. Based on sampling results, observations, and discussions with employees, it appeared that dust levels during the bag dumping operation exceeded the TLV for occupational exposure to nuisance dusts (dust levels during road application were low). Thus the minor health effects appeared to be caused by overexposure to CMA as a result of the high dust levels during this operation. A recommendation was made to discontinue use of the 50-lb bags under the prevailing conditions; no further complaints were received from the workers.

Observations

Sand at this site was stored in bulk and CMA was stored on pallets in 50-lb bags. There were six employees in the crew, working a 12-hr shift; each wore coveralls, a dust mask, and goggles. During bag dumping, three employees moved bags from the pallets onto the floor; the other three cut through the middle of the bags and dumped them at their feet. The operation lasted 35 to 40 minutes and approximately two pallets of bags were cut. A dust haze was present in the room and the dust concentrations appeared to be higher near the floor where the bags were dumped. A slight acetic acid odor was noticeable and contact with the CMA left skin feeling sticky.

After the bags were dumped, a payloader was used to load sand and CMA into sanding trucks to produce a 20-percent-

CMA mixture. This operation lasted approximately 5 minutes. One employee then drove the sanding truck along a 3-mi section of the highway. It took approximately 2 hours to spread one truckload (5 tons) of the sand/CMA mixture. The truck had an enclosed cab and the employee did not wear respiratory protection. Because of heavy snowfall, the employee opened his window at times to check the load.

Sampling and Results

Seven total and respirable dust samples were collected at the site. Total dust includes all dust particles collected on the sampling filter; respirable dust includes only those particles that are small enough to penetrate to the gas exchange areas of the lung.

Samples were collected on preweighed polyvinylchloride filters using Gilian HFS 113A pumps at a rate of 1.7 l/min. Respirable dust samples were collected using a cyclone. Samples were collected in the breathing zone of the employees and were analyzed gravimetrically.

Results are shown in Tables 4 and 5. Six of the samples were collected during bag dumping: four samples for total dust and two for respirable dust. The results for the bag moving operation ranged from 26.2 to 32.2 mg/m^3 total dust and 0.75 mg/m^3 respirable dust. The results for the bag cutting operation were 72.5 mg/m^3 total dust and 1.68 mg/m^3 respirable dust. (A second total dust sample result was invalid because the pump became disconnected and the sampling time is unknown.)

TABLE 4   TOTAL DUST AIR SAMPLING RESULTS

Sample Number	Duration (min)	Total Dust (mg/m^3)	Operation
1	36	72.5	Cutting and dumping bags
2	36^a	32.3^a	Cutting and dumping bags
3	38	32.2	Moving bags to dumping area
4	38	26.2	Moving bags to dumping area
5	119	0.23	Driving sanding truck

^{a}Pump became disconnected—sampling duration may have been less, resulting in a proportionately higher concentration.

TABLE 5   RESPIRABLE DUST AIR SAMPLING RESULTS

Sample Number	Duration (min)	Respirable Dust (mg/m^3)	Operation
6	39	1.68	Cutting and dumping bags
7	36	0.75	Moving bags to dumping area

A total dust sample was also collected during the spreading of one load of sand/CMA mixture on the highway. The driver felt that he could not wear a pump while driving, so the industrial hygienist rode in the cab and wore the pump; exposure in the cab was 0.23 mg/m^3 total dust.

Samples were not collected on the payloader operator during loading of the sanding truck because the operator felt that he could not operate the payloader while wearing a pump.

Discussion of Site Investigation

Total dust results for bag dumping exceeded the TLV for occupational exposure to nuisance dusts of 10 mg/m^3.

However, a time-weighted average for the shift would not be expected to have exceeded the limit since dust exposures during the remainder of the shift appeared to be low. The low respirable dust level indicates that most of the dust does not reach the gas exchange areas of the lung, and therefore would not be expected to produce pulmonary symptoms.

The total dust result for road application using a sanding truck was below the TLV for occupational exposure to nuisance dusts. Current practices appear to be adequate to limit dust exposures over a full shift during this activity.

Dust levels were not measured during the payloader loading of the sanding truck. Loading generates dust but because the employee is in an enclosed cab, levels are not expected to be high. The operation takes 5 to 10 minutes per truck and could occur once an hour during a shift, for a maximum exposure time of 90 minutes. It appeared that the enclosed cab adequately controls the dust; however, industrial hygiene monitoring would be needed to verify this.

Recommendations

Appropriate industrial hygiene procedures for working with nuisance dusts should be instituted whenever working with CMA, sodium chloride, or sand; these include

- Approved respiratory protection if operating conditions create high airborne dust concentrations,
- Dust reduction techniques such as local exhaust ventilation and dumping material through chutes,
- Eye-wash units capable of providing 15 minutes of tempered water as a precaution against granular irritation of the eye, and
- Use of adequate bag-handling facilities when nuisance dusts packaged in 50-lb bags are used.

CONCLUSION

When a new chemical product is introduced, two concerns must be addressed: are there potential effects on (a) humans and (b) the environment? For a road deicing agent, the environmental question should consider both natural and man-made environments. Consideration of the man-made environment is made necessary by the negative impact that traditional road deicers have had on roads, bridges, and automobiles. CMA has a low environmental impact relative to water quality, aquatic toxicity, and terrestrial ecology (17); in these respects the effects of CMA are similar to or less severe than the main component of traditional road salt, sodium chloride. Corrosivity data show CMA to be less damaging to the man-made environment than traditional road salt; it is much less corrosive than salt to concrete, zinc, aluminum, and steel (18).

This report focused on the potential effects of CMA on humans. Two types of data were reviewed: (a) laboratory toxicity studies on the toxicity of CMA and (b) a report of an industrial hygiene investigation into complaints of minor injury from handling CMA.

The acute and subchronic toxicities of CMA are low, as are the skin and eye irritation potentials. In these respects, CMA is similar to sodium chloride. Inhalation exposure does not appear to pose a hazard greater than any nuisance dust. Dermal exposure appears also to present a low hazard of adverse effect.

CMA appears to have a low potential, if any, to induce allergic skin reactions.

Occupational experience with CMA during field testing bears out the conclusions from the laboratory animal studies. Health-related complaints were received from only one of the field test sites. An industrial hygiene investigation showed that exposure conditions at this site exceeded the TLV for occupational exposure to nuisance dusts. Although exposure levels were high, the complaints related only minor skin and eye irritation. Industrial hygiene practices appropriate for occupational exposure to any nuisance dust are expected to eliminate these health-related complaints.

In summary, the results reviewed in this report indicate that CMA's potential to adversely affect human health is no greater than that of sodium chloride.

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Effects of Calcium Magnesium Acetate on Pavements and Motor Vehicles

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The corrosion and deterioration of highway-related and automotive-related materials by chloride-containing deicing chemicals has become a major economic problem in the United States. The FHWA has proposed the use of calcium magnesium acetate (CMA) as an alternative to these chloride-containing chemicals (specifically, sodium chloride). This report describes the comparative effects of CMA and sodium chloride on various highway-related and automotive-related materials. The results of various exposure techniques, which were followed by extensive additional testing, indicate that CMA is much less deleterious to highway-related and automotive-related materials than sodium chloride.

Each year, millions of tax dollars are spent to reconstruct or repair damaged highways and associated highway structures, and millions of private dollars are spent to repair or replace corroded motor vehicles. Additionally, large amounts of money and time are used to assess and correct environmental problems that have resulted from the use of sodium chloride as a deicing chemical.

The FHWA has recognized this problem and has determined that calcium magnesium acetate (CMA) is a suitable alternative deicing chemical. CMA is a mixture of calcium acetate and magnesium acetate, manufactured by reacting acetic acid with dolomitic lime or limestone.

The FHWA wanted a deicing chemical that had deicing capabilities similar to sodium chloride but had less deleterious effects on highway-related and automotive-related materials. The FHWA also wanted to substantiate previous research indicating that CMA was less deleterious to highway-related and automotive-related materials than sodium chloride. This research might also indicate previously unknown effects of CMA on the aforementioned materials. This was the basis for the institution of this study.

At this time, there are no plans for CMA to replace sodium chloride as the United States' primary road deicing chemical. However, it is necessary to have a suitable, effective roadway deicing alternative that can be used in areas where sodium chloride may have significant effects on highway-related and automotive-related materials or great environmental impact.

DESCRIPTION OF THE STUDY

The purpose of this study was to determine the comparative effects of sodium chloride and calcium magnesium acetate on highway-related and automotive-related materials.

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Test material categories for this program were chosen because they include materials commonly used in highway-related and automotive-related applications and also are representative of other products made from similar materials. Specimens totaling 2,240 were tested from 81 categories, including portland cement concrete; asphalt; traffic-marking paint, plastic, and tape; reflective and ceramic pavement markers; pavement-marker adhesives; sign-reflective sheetings and paints; joint-sealant materials; plastic and wood stanchions; bridge-bearing materials; drainage pipe; automotive paints, primers, and undercoatings; automotive exterior adhesives; automotive plastics and elastomers; automotive tires and rubber; brake-lining materials; automotive steels; hydraulic brake-line tubings; automotive aluminum alloys and stainless steels; and automotive combined metals such as chrome, aluminized steel, galvanized steel, terne-coated steel, and nickel-zinc coated steel. The specimens were made from new materials to insure accuracy in testing and reproducibility. It must be noted that the purpose was not to evaluate the test materials' susceptibility to corrosion. Rather, the study sought to evaluate the comparative effects of sodium chloride and calcium magnesium acetate on the various materials tested.

The types of tests performed on the specimens were performed as specified by the ASTM. A total of 6,048 tests were performed on the aforementioned specimens, including salt fog exposure, concrete-compression, abrasion, and scaling-resistance testing; static-loading and impact testing; testing of rubber and light-related properties; paint evaluations; and shear, thickness, indentation/hardness, environmental, friction, adhesion, immersion, exfoliation, and electrochemical testing.

The specimens were exposed to a control solution and four test solutions. The control solution was deionized water and the test solutions were 4 percent by weight sodium chloride acquired from the Maryland State Highway Administration (4 percent NaCl), 1 percent by weight (1 percent $CMA_{(FHWA)}$) and 6.8 percent by weight (6.8 percent $CMA_{(FHWA)}$) calcium magnesium acetate (having a one-to-one molar ratio of calcium and magnesium ions) supplied by the FHWA, and 6.8 percent by weight calcium magnesium acetate made by the contractor by mixing pure calcium acetate and pure magnesium acetate, 4-hydrate (both purchased from American Hoechst Corporation) in a one-to-one molar ratio (6.8 percent $CMA_{(DAI)}$), all in aqueous solution.

Not all of the aforementioned tests were performed on each type of material specimen. Certain tests were performed on certain types of materials.

In the following sections, specimens are comparatively described as more or less affected by the aforementioned test

solutions. It would be unfair to attempt to be more specific about the test results, since each test was repeated only two, three, or four times.

TESTING OF HIGHWAY-RELATED MATERIALS

Pavement Materials

The compressive strengths of portland cement concrete and asphalt products were comparatively unaffected by sodium chloride or calcium magnesium acetate solutions. Additionally, scaling did not occur on any asphalt products.

However, some scaling did occur on portland cement concrete. In general, the scaling was severe on specimens exposed to sodium chloride solutions, moderate on specimens exposed to deionized water, and minimal on specimens exposed to calcium magnesium acetate solutions.

The same magnitudes of scaling occurred on joint-sealant-material specimens, but the joint-sealant materials themselves appeared to be comparatively unaffected.

Guidance Materials

Road-marking materials such as paints, plastic, and tape were affected by both sodium chloride and calcium magnesium acetate solutions. Road-marking paint specimens exposed to solutions of both compounds exhibited chalking, checking, erosion, and flaking. In all cases, the sodium chloride solutions were either more deleterious than the calcium magnesium acetate solutions, or so severely scaled the specimen substrates that no paint remained to be examined. Plastic and tape specimens were similarly affected. Hardness properties appeared to be unaffected, while whiteness of specimens exposed to deionized water and calcium magnesium acetate solutions appeared to be enhanced.

Similarly, hardness properties of pavement markers appeared to be unaffected. Light-related properties were difficult to analyze, since the specimen sizes and configurations inhibited consistent analyses. Although some pavement-marker adhesives exhibited increases or decreases in shear strength and impact resistance over exposure for one year, these were slight, and it appeared that neither solutions of sodium chloride nor solutions of calcium magnesium acetate affected the adhesives.

Sheetings and paints used in directional and informational highway signs that were exposed to sodium chloride and calcium magnesium acetate solutions all appeared to retain adhesion to their aluminum substrates. Light-related properties of the sign materials were either relatively unaffected or similarly affected. Physical degradation of sign paints did not occur.

The light-related properties of plastic road delineators, or stanchions, were either relatively unaffected or similarly affected by the sodium chloride or calcium magnesium acetate solutions. Again, specimen sizes and configurations inhibited consistent analyses. Likewise, hardness properties were also unaffected. Impact resistance of plastic stanchions and shear strengths of wood stanchions appeared to be unaffected.

Construction Materials

Hardness properties and impact resistance of bridge-bearing materials were unaffected by solutions of sodium chloride or calcium magnesium acetate.

Crushing strengths of concrete, bituminous-coated corrugated metal, and plastic pipes were also unaffected by solutions of sodium chloride or calcium magnesium acetate.

TESTING OF AUTOMOTIVE-RELATED MATERIALS

Automotive Paints, Coatings, and Adhesives

The adhesive, light-related, and hardness properties of automotive paints, primers, and undercoatings appeared to be relatively unaffected by solutions of sodium chloride or calcium magnesium acetate. Additionally, no blistering occurred on any of these specimens.

Some paint, primer, and undercoating breakdown and subsequent rusting occurred on both scribed and unscribed specimens. In all cases, however, sodium chloride caused more coating breakdown and more severe rusting than solutions of calcium magnesium acetate.

Some automotive exterior adhesives exhibited increases or decreases in shear strength over exposure for one year, but these were slight, and it appeared that neither solutions of sodium chloride nor solutions of calcium magnesium acetate affected the adhesives.

Automotive Plastics and Rubber

Solutions of sodium chloride and calcium magnesium acetate caused slight changes in the light-related properties of automotive hard plastics, elastomers, and transparent lens materials, but these changes usually occurred consistently for all materials. One exception was the haze exhibited by the Automotive Transparent Lens Material 1 specimen exposed to the solution of 6.8 percent $CMA_{(FHWA)}$. However, since the same respective specimens exposed to the other calcium magnesium acetate solutions appeared to be unaffected, it was determined that the subject specimen had most likely been damaged prior to the performance of the Test for Haze and Luminous Transmittance of Transparent Plastics (ASTM D1003). Additionally, with the exception of transparent lens materials, most automotive hard plastics and elastomers on automobiles are either painted or are not subjected to light. The specimens were, therefore, considered comparatively unaffected. Accordingly, the hardness properties and impact resistances of these specimens were also considered comparatively unaffected.

The hardness properties of automotive tire materials and rubber compounds exposed to solutions of sodium chloride and calcium magnesium acetate appeared to be unaffected. Compression sets of all specimens increased, although ultimate tensile strengths remained unaffected. The 300-percent moduli and tear resistances of the same specimens were only slightly affected. Some surface cracking appeared on these specimens, but remained consistent throughout the specimen type. Surface cracking, therefore, was not attributable to the exposure to solutions of sodium chloride or calcium magnesium acetate, but rather to the specimen composition.

Automotive Brake Systems

Solutions of sodium chloride and calcium magnesium acetate appeared to have no effect on the hardness properties of the automotive brake-lining materials. However, specimens exposed to solutions of sodium chloride consistently exhibited lower static and kinetic coefficients of friction.

In general, automotive hydraulic brake-line tubings exposed to solutions of sodium chloride exhibited greater weight losses as a result of corrosion and more rusting and deterioration than the same specimens exposed to solutions of calcium magnesium acetate. No pitting corrosion was observed on any specimens.

Automotive Metals

Automotive steels exposed to solutions of sodium chloride consistently exhibited greater weight losses as a result of corrosion, more pitting corrosion, and more general corrosion than the same respective specimens exposed to calcium magnesium acetate. Specimens exposed to solutions of sodium chloride were also susceptible to crevice corrosion, whereas the same respective specimens exposed to solutions of calcium magnesium acetate were not.

Automotive aluminum alloys exposed to solutions of sodium chloride consistently exhibited greater weight losses as a result of corrosion and more pitting corrosion than the same respective specimens exposed to calcium magnesium acetate. General corrosion of specimens was either minimal for all solutions or slightly enhanced by solutions of sodium chloride. Susceptibility to crevice corrosion varied from specimen to specimen and solution to solution.

Automotive stainless steels exposed to all solutions exhibited insignificant weight losses and minimal differences in general corrosion. Pitting corrosion was also minimal but did occur in some specimens exposed to solutions of sodium chloride. Specimens exposed to solutions of sodium chloride were also susceptible to crevice corrosion; the same respective specimens exposed to solutions of calcium magnesium acetate were not.

Automotive combined metals exposed to all solutions exhibited minimal pitting corrosion. However, greater resistances to pitting corrosion were prevalent in specimens exposed to the calcium magnesium acetate solutions than in specimens exposed to the sodium chloride solutions. Susceptibility to crevice corrosion varied from specimen to specimen and solution to solution. Chrome-plated steel and stainless steel alloys were only slightly affected by all solutions. Aluminized steel exposed to solutions of sodium chloride exhibited greater weight losses than the same respective specimens exposed to the calcium magnesium acetate solutions. Galvanized steel and terne-coated stainless steel were equally affected by all solutions. Results varied for exposures of nickel-zinc alloy coated steel.

It must be noted that the electrochemical tests were immersion-type tests, which were conducted in a nitrogen environment. Thus, the resulting susceptibilities to general corrosion and corrosion resistance were of limited importance because, under actual highway conditions, automotive metals are in contact with air-saturated environments. It must also be noted that in cases where no general corrosion was detected, as was the case for many metals exposed to deionized water and solutions of sodium chloride, the rate of corrosion would increase exponentially with the degree of aeration. The principal danger to automotive-related materials under actual highway conditions is their susceptibility to localized corrosion (pitting and crevice corrosion). As previously stated, pitting and crevice corrosion were generally more prevalent in specimens exposed to solutions of sodium chloride than in specimens exposed to solutions of calcium magnesium acetate.

CONCLUSIONS

Asphalts, plastics, elastomers, ceramics, wood, sign sheetings and paints, rubber compounds, sealers, and adhesives appeared to be either unaffected by solutions of sodium chloride or calcium magnesium acetate, or similarly affected.

Road marking paints were affected by both sodium chloride and calcium magnesium acetate solutions. However, it was obvious that sodium chloride solutions were much more deleterious. Road-marking plastics and tapes were affected by both solutions because of the solutions' effects on the portland cement concrete substrates. Again, specimens exposed to sodium chloride solutions were more severely damaged.

Portland cement concrete was affected by both sodium chloride and calcium magnesium acetate solutions. Although the calcium magnesium acetate solutions did minimally affect portland cement concrete, the sodium chloride solutions' effects were much more severe.

Automotive paints and coatings exposed to calcium magnesium acetate solutions exhibited some breakdown, but those same respective specimens exposed to sodium chloride solutions exhibited far greater breakdowns.

Automotive brake-lining materials exposed to sodium chloride solutions consistently exhibited slightly lower static and kinetic coefficients of friction than the same respective specimens exposed to calcium magnesium acetate solutions. However, automotive hydraulic brake-line tubings exposed to sodium chloride solutions consistently exhibited more severe corrosion than the same respective specimens exposed to calcium magnesium acetate solutions.

In general, solutions of sodium chloride cause more severe corrosion in automotive steels, aluminum alloys, stainless steels, and combined metals than solutions of calcium magnesium acetate. This is true for general corrosion, as well as localized corrosion.

Under nitrogen conditions, specimens exposed to solutions of sodium chloride exhibited no passivation, whereas specimens exposed to solutions of calcium magnesium acetate did. Because most sodium chloride solutions exhibit no passivation, in actual highway (aerated) exposures, general corrosion rates of metals caused by exposure to sodium chloride solutions will increase much more rapidly than general corrosion rates caused by solutions of calcium magnesium acetate.

It can also be concluded that in most metals, with the exception of aluminum, solutions of sodium chloride caused more localized corrosion, that is, pitting and crevice corrosion, than solutions of calcium magnesium acetate.

RECOMMENDATIONS

Results of testing of highway-related materials indicated that the effects of corrosion by salts of sodium chloride and calcium magnesium acetate could be relatively accurately predicted. This condition is probably not as true for automotive-related metallic materials, since new technology is constantly

providing new alloys with enhanced and varying properties. Periodic studies of the susceptibility to corrosion of these new alloys must be performed to ensure the use of the best corrosion-resistant products.

Additionally, further analyses of the effects of sodium chloride and calcium magnesium acetate on the light-reflectance properties of sign sheetings and paints are recommended.

Calcium magnesium acetate was never intended to replace sodium chloride as the United States' primary road deicing chemical. However, it must be noted that, in light of new manufacturing techniques of calcium magnesium acetate leading to lower production costs and its much lower corrosive tendencies, CMA has the potential for significant impact on the commercial and private consumer deicing markets.

The Effect of Deicing Chemicals on Reinforced Concrete

A. Nadezhdin, D. A. Mason, B. Malric, D. F. Lawless, and J. P. Fedosoff

The role played by deicing chemicals in the deterioration of reinforced concrete is addressed in this paper. Several newer and faster bench-scale methods of study and materials evaluation are described and compared to the ASTM recommended techniques. The difference in freezing temperatures between concrete pore solution and an outside deicer solution is shown to be one of the important factors in the spalling process. The importance of an anisotropic character of freezing zone is outlined. The macrocell corrosion mechanism of rebar deterioration has been studied in the laboratory environment using specially constructed mini slabs. The results were correlated with previously conducted microcell corrosion studies of small encapsulated rebar probes.

The use of rock salt as a deicing chemical has given rise in the last few years to important environmental concerns because of the potential damage to concrete pavements, to steel through corrosion, and to vegetation and soil. In 1983 Domtar Inc. launched a major R&D effort aimed at developing basic knowledge on salt's unfavorable side effects and how they could be minimized or eliminated. The major objectives were to (a) improve the understanding of the effects of rock salt and other deicing chemicals on metals, pavements, and the environment, (b) develop safer but still cost-effective deicers through additives to rock salt or new alternative products, and (c) devise methods for the evaluation of chemical deicer properties and their effect on various materials. Described in this article are several methods that were used in the laboratory to study the effects of deicer chemicals on reinforced concrete.

STUDIES OF CONCRETE SPALLING

The acceleration of freeze/thaw (f/t) deterioration of concrete as a result of the presence of deicing chemicals in solution has been known for over three decades. It has been shown in the past that scaling of the concrete surface is caused by physical processes, such as growth of crystals, rather than chemical reactions. The air entrainment in concrete formulations creates additional space for crystal growth to "cushion" the impact of physical change.

Standard methods exist for testing the performance of a given concrete formulation under f/t cycle conditions. These methods could be used for the evaluation and ranking of various deicing chemicals, as well as various road construction materials.

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Effect of Deicing Chemicals on Air-Entrained Concrete: The ASTM Test

A test program was carried out to compare the effects of various deicer formulations on concrete. Equipment included a walk-in freezer in a room with controlled climate and an abrasion test rig well described by Minsk (1) (Figure 1). A large number of concrete blocks were prepared by Canada Cement Lafarge in accordance with ASTM C672-84. The concrete blocks contained a built-in stainless steel dam to contain the deicing solution on the top surface of each block. The test procedure including f/t tests without abrasion and with abrasion using a steel blade under a specified load is well described elsewhere (1). The procedure basically consisted of ponding various solutions on top of the concrete slabs which were then subjected to f/t cycles. At the end of every five cycles the deicing solutions were poured through a filter. The material that came off the concrete surface as a result of f/t damage or abrasion in the tests was collected, rinsed with distilled water, and dried in an oven. The weight of the material was then used as a measure of the damage.
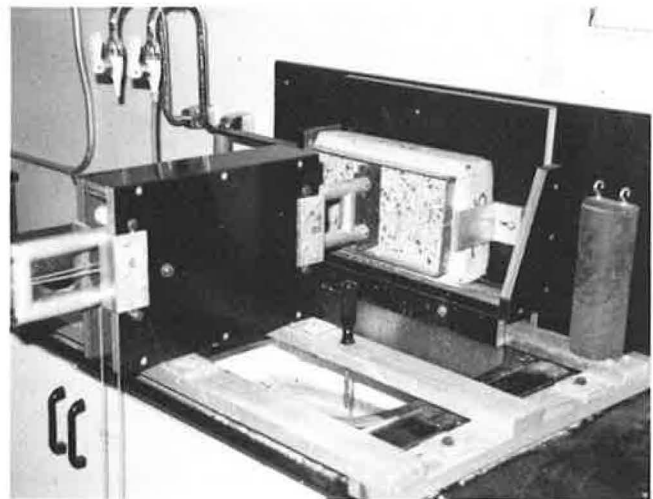

FIGURE 1 Abrasion of the concrete to supplement f/t spalling.

The rate of freezing and thawing was monitored using a thermocouple incorporated into one of the concrete blocks. A typical curve of temperature versus time during freezing is shown in Figure 2.

The f/t damage was compared to the air-entrained concrete caused by several deicer chemicals during 100 f/t cycles. All
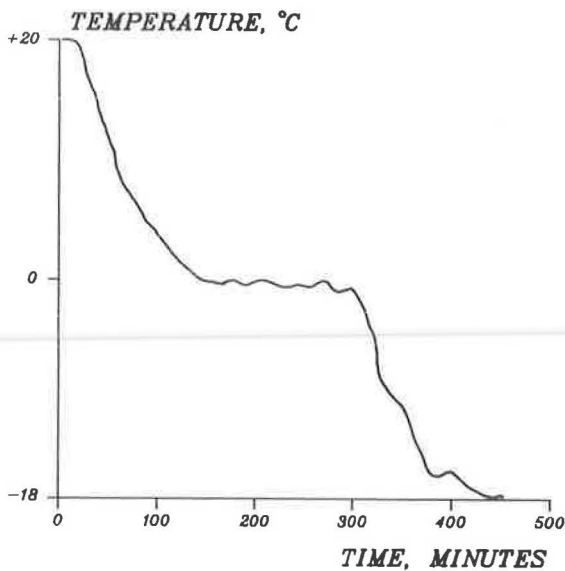
FIGURE 2 Temperature of a concrete slab in the freezer during the freezing cycle.
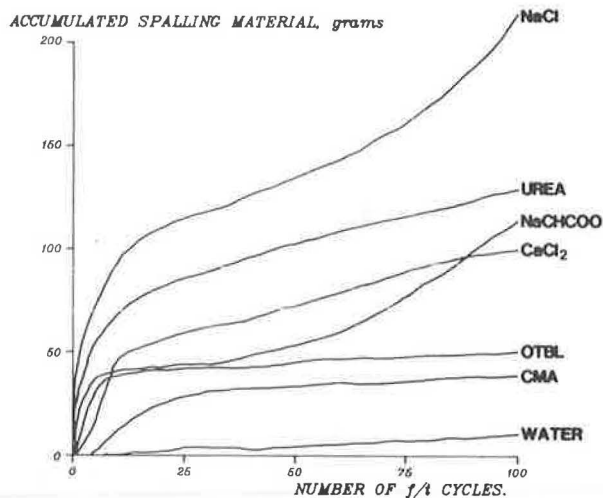

FIGURE 3 Air-entrained concrete spalling by various deicer solutions in the ASTM test. Concentration of all solutions was 4 percent. No abrasion.

subsequent concentrations are reported as w/w percent of solute. The degree of spalling without abrasion caused by 4-percent solutions of NaCl, urea, CaCl$_2$, sodium formate, and CMA (calcium magnesium acetate) is shown in Figure 3. Each point corresponds to the average value given by three identical specimens. The relatively large damage caused by urea and an accelerating destruction caused by sodium formate are quite evident.

Two deicer chemicals were less destructive toward concrete than the rest of the group not only in absolute level of spalling but also because the damage appeared to be levelling off with time, unlike the case of uninhibited salt, urea, or sodium formate. One of the chemicals, CMA, is a product well known to the transportation community for at least a decade. It has been shown to be less corrosive than rock salt while providing a comparable level of ice control. The other chemical, designated OTBL, is a Domtar proprietary, nonchloride product in

early development stage. Its deicing and corrosion characteristics are comparable to those of CMA.

The relative damage caused by different chemicals with abrasion of the exposed surface using a 10-kg load on the abrading blade (1) is shown in Figure 4. The surface area of the blade was ~5 cm^2. Although the abrasion accelerated scaling in the case of all four tested deicers, in the case of sodium formate the effect of abrasion was considerably greater than with the other tested chemicals, including NaCl.

Accelerated Tests Using Small Concrete Specimens

Although the data obtained according to ASTM 6672084, using air-entrained concrete, provide reliable information on the expected scaling action of various deicer formulations, two great disadvantages of the standard method are (a) the considerable length of time required and (b) the amount of labor involved.
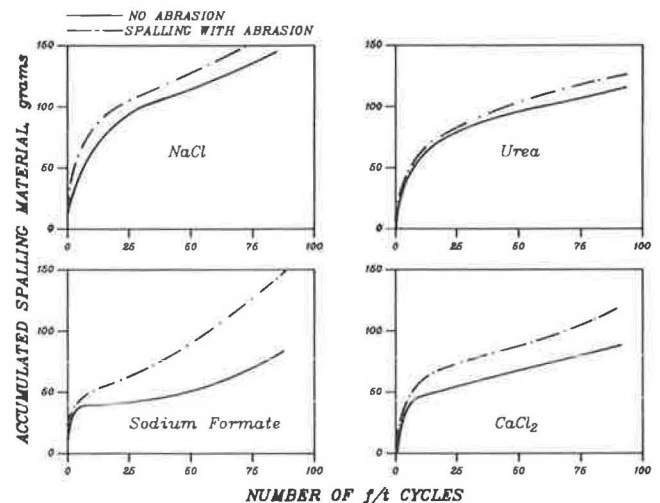

FIGURE 4 The effect of abrasion on the rate of spalling by various deicers. Four-percent solutions used in all cases. Abrasion was performed with 10-kg load on the blade (see text).

Following the example of a few researchers in recent years and, in particular, Peter Hudec of the University of Windsor (Windsor, Ontario, Canada), a quick-test method has been adopted using small concrete cubes without air entrainment. These cubes, if prepared with carefully screened aggregate and properly cured, can give reproducible data on the relative effects of deicer formulations or f/t conditions in a period of time as short as 5 days. Of course, subsequent verification of the observed effects using the standard ASTM procedure is recommended.

The specimens for the small scale tests were prepared as follows. Several kilograms of concrete mixture were made using the following composition of ingredients:

Component	Parts w/w
Portland cement, type 10	1.0
Water	0.7
Sand	2.25
Aggregate (−4 +20 mesh)	2.75

The concrete was cast into small cubes using plastic ice cube trays which were then covered with plastic sheet for 3 days. The solid cubes were subsequently cured in water for 28 days and then dried on the bench. The weight of an air dry cube was between 40 and 45 g.

Each individual test comprised four cubes placed in a shallow plastic Tupperware™ dish fitted with a lid. Prior to the beginning of f/t cycles the cubes were presoaked in a specified solution for 24 hours at room temperature (for most tests). If the presoak solution was the same as the one used for the f/t test then the cubes were simply lifted above its level in the same dish by using cellulose sponges as shown in Figure 5. When the presoak solution was different from the f/t test solution the cubes were transferred into another dish with new solution and placed on a sponge as just described. The dishes remained tightly closed with lids during the rest of the test period to prevent evaporation.
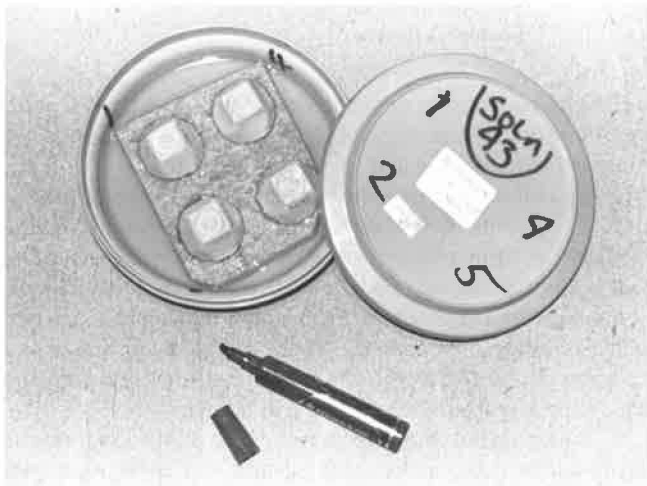

FIGURE 5   Small concrete cubes on a cellulose sponge placed in a 6-in. Tupperware™ dish.

After the predetermined number of cycles (from five to seven) the dishes were placed on the bench for complete thawing of their content, the cubes were rinsed in distilled water and all solids weakened by spalling so that they could be crushed by hand were discarded. The remaining solid pieces were dried overnight on a bench at a relative humidity of 50 percent. Each individual cube was weighed before and after the test and the dry weight loss that resulted from spalling was averaged over the four pieces per dish. It was found that the weight loss data are reproducible if all cubes are made from the same batch of concrete.

The small-scale f/t tests could at present be used only for relative ranking of various solution compositions. However, the results of recent studies have proven to be useful for the selection and refinement of antispalling additives and their combinations, which subsequently have been tested using the standard ASTM method for confirmation of the findings.

Discussion of Accelerated Test Results

The results of the small-cube tests can be related to the data obtained using air-entrained concrete. In Table 1 the percent of

TABLE 1   WEIGHT LOSS OF SMALL CONCRETE CUBES AFTER FIVE F/T CYCLES IN 4-PERCENT DEICER SOLUTION

Deicer Material[a]	Weight Loss (%)
NaCl	40 ± 3
Sodium formate	37 ± 2
Urea	27 ± 2
$CaCl_2$	26 ± 1
OTBL	0.6 ± 0.3
CMA	0.1 ± 0.1

[a]4-percent solution.

small-cube weight loss is shown after five f/t cycles with 4-percent solutions of the same deicers as in the standard ASTM tests illustrated in Figure 3. It is apparent that the relative ranking of the deicer chemicals with respect to spalling is similar for both series of tests. Another comparison of the two methods is shown in Figure 6, in which the effect of NaCl concentration in solution on the rate of f/t damage is shown for (a) standard tests with entrained concrete (200 f/t cycles) (2) and (b) small cube tests (5 f/t cycles). In both cases the degree of spalling versus the percentage of NaCl in solution passes through a maximum in the 3- to 4-percent interval.
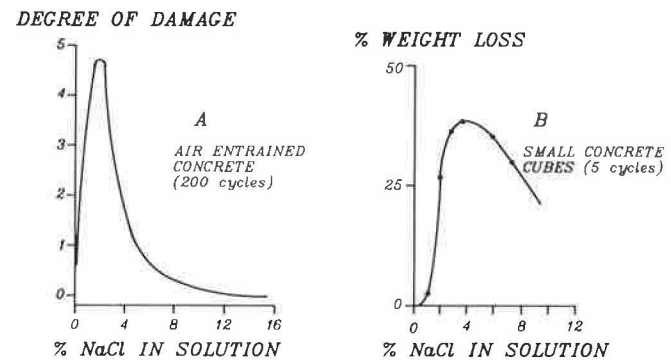
FIGURE 6   The effect of salt concentration on the degree of spalling: air entrained concrete, 200 cycles (A) (2); small concrete cubes (no air entrainment), 5 cycles (B).

With that degree of confidence in the fast method, work could cautiously proceed on the preliminary selection of antispalling compounds in order to reduce damage to concrete associated with the use of rock salt. It was found that a number of chemicals when added to salt solution would considerably reduce the degree of spalling as, for example, is shown in Figure 7. The weight loss sustained by concrete cubes immersed in a pure salt solution (curve 1) and into salt solution containing an additive (curve 2) is plotted versus the number of f/t cycles. The additive in that case was a soluble salt of phosphoric acid added at the level of 5 percent on the basis of total dry solids. It is hoped that the research conducted in this area will result in the early development of a cost-effective and environmentally acceptable additive that could greatly reduce f/t spalling of concrete structures where rock salt is used for ice control.

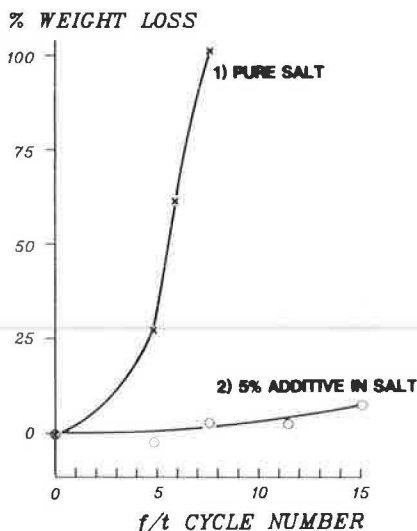FIGURE 7 The effect of antispalling additive in 4-percent NaCl solution on the f/t resistance of small concrete cubes: *1*, no additive, *2*, antispalling agent added to salt solution.

FIGURE 9 The percentage of weight loss of small cubes after five f/t cycles versus NaCl concentration in the deicing solution at three different levels of NaCl in the presoak solution.

In addition to the practically oriented additive selection work, a more fundamental study on the salt-assisted spalling mechanism has recently been initiated. In all previously mentioned small-cube tests the concrete specimens were presoaked and tested in f/t cycles using the same solution composition. The question was posed as to what would happen if the presoak and f/t test solution were of different concentrations or different compositions in general.

The effect of NaCl concentration in the presoak solution on the f/t spalling caused by 4-percent NaCl solution is shown in Figure 8. The series of graphs in Figure 9 represents the spalling effect of NaCl solutions at various concentrations, from 0 to 8 percent at a given presoak solution concentration. Both figures clearly demonstrate that there is a sharp reduction in the f/t damage when the presoak solution concentration equals or exceeds the deicing solution concentration. It should be noted that the specimen presoaked in salt solution was not damaged by f/t action of pure water. The conclusion was drawn from these observations that it was not the salt per se but the
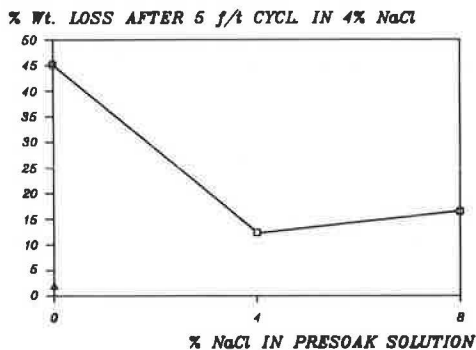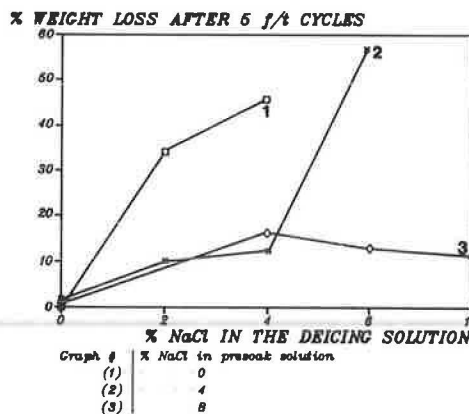
difference between the salt concentrations in the concrete pores and those in the outside deicing solution that was primarily responsible for accelerated spalling in these tests.

It is possible to go one step further and relate the difference in NaCl concentrations to the subsequent difference in freezing temperatues of liquids under and on concrete surface. In other words the working hypothesis could be formulated as follows: if the freezing temperature of the solution inside the concrete pores is lower than or equal to the freezing temperature of solution on the surface of concrete, the f/t damage generally should be less than when the reverse is true.

The next series of tests represented in Table 2 appears to confirm that observation. In these tests the cubes were presoaked in various deicing solutions—such as 5 percent sodium acetate, 7 percent calcium nitrate, and 7 percent ethylene glycol—and 4 percent NaCl and subsequently subjected to f/t action in 4 percent NaCl. The concentrations of the deicer components in presoak solution were chosen to give the same reduction in freezing temperature of water as does 4 percent NaCl. The data in Table 2 show that all tested presoak solutions with a notable exception of calcium nitrate have considerably reduced the subsequent f/t spalling as compared to the control test with deionized water used for presoaking.

FIGURE 8 The effect of salt concentration in the presoak solution on the f/t spalling of small cubes in 4-percent NaCl solution.

TABLE 2 EFFECT OF PRESOAK SOLUTION COMPOSITION ON THE F/T CONCRETE SPALLING CAUSED BY SALT SOLUTION

Presoak Solution Composition	Weight Loss (%)
Distilled water	30
4 percent NaCl	17
5 percent sodium acetate	14
7 percent ethylene glycol	13
7 percent $Ca(NO_3)_2$	22

NOTES: Used small cubes and five f/t cycles, with presoaking for 24 hours before freezing. Freeze/thaw test was conducted using 4 percent NaCl solution in all cases.

At this point the results obtained with the small cubes should be considered preliminary because the experimental techniques are still being refined.

It has been noted in the past [see e.g., (2), (3)] that the essentially anisotropic character of freezing in concrete-deicer solution systems is a major factor in the f/t spalling process. The data described here indicate the same thing. A properly designed experiment should take into account the mutual orientation of heat flow versus gradients of solution concentration and moisture content of concrete. This is one of the areas where more work is anticipated.

STUDY OF A MACROCELL REBAR CORROSION ON A MINI SCALE

Concrete, a porous material containing a pore solution, the chemical composition of which depends on the concrete parameters, the surrounding environment, and exposure time (4), normally provides reinforcing steel with excellent corrosion protection. This is a result of the formation, in the presence of sufficient O_2, of a stable passive layer of gamma Fe_2O_3 on the steel surface in the high-pH (12 to 13) concrete environment. The corrosion of steel in concrete, shown in Figure 10, is a naturally occurring phenomenon driven by the tendency of iron to seek the lowest possible energy state, which is the oxide (rust) form.
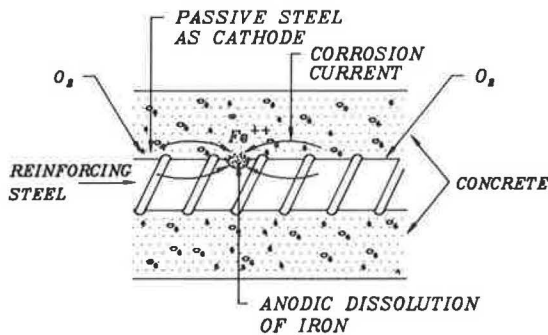

FIGURE 10 Schematic illustration of the corrosion of reinforcement steel in concrete (5).

Initially the passive film inhibits the corrosion process. However, once this film is damaged or removed, the steel continues to corrode. As the steel rusts (formation of Fe_2O_3), its oxidation products build up in the concrete and, because of their greater volume, exert tensile stress on the concrete (up to 10,000 psi) (6). This rapidly exceeds the low tensile strength of the concrete (500 psi) resulting in stress cracks which in turn allow for more rapid diffusion of corrosion-accelerating substances such as CO_2, leading to further deterioration of the structure.

An inhibitor is a substance that, when added in small concentrations to an environment, effectively decreases the corrosion rate. The evaluation of the effectiveness of any inhibited NaCl mixture, as compared to salt alone, follows a natural procession of tests. Preliminary screening methods, such as weight-loss corrosion-rate determinations via total coupon-immersion (various metals) tests or aqueous (simulated concrete pore water) electrochemical investigations of steel probes using such techniques as linear polarization or a.c. impedance,

allow for the initial selection of suitable chemicals. The next stage in any good evaluation program involves a closer simulation of the actual concrete environment through the construction of rebar concrete probes. This yields a greater wealth of information concerning such system characteristics as the corrosion resistance (Rp) (proportional to the inverse of the corrosion rate), the double layer capacitance, film resistance, and so on. Finally, the construction of small (laboratory-controlled environment) and large (subjected to external exposure) reinforced concrete slabs allows for evaluation of inhibitor performance under macrocell current conditions. The focus of the remainder of this section of the paper is on the small-scale laboratory slabs.

In existing reinforced-concrete structures exposed to deicing salts, a macrocell corrosion effect is believed to be of major importance in the structure deterioration process. Macrocell corrosion is indicated where significantly different environments (chloride, O_2, moisture levels, pH, etc.) exist at various sites on the rebar mat. Areas of adjacent concrete having higher levels of chloride become anodic (iron oxidation), whereas areas with low chloride or high O_2 levels become cathodic (oxygen reduction). Anodic and cathodic sites may be widely spearated in real life, but generally steel close to concrete upper surfaces will be primarily anodic and steel in lower mats or shielded from chloride will be cathodic.

Based on research performed by FHWA and other agencies (7), small-scale reinforced concrete prisms were designed, fabricated, and treated in order to enhance a macrocell effect, and the macrocell corrosion current was measured as a function of deicer/inhibitor application. The present test design is also being considered by ASTM as a standard method for admixed corrosion inhibitor evaluation in reinforced concrete.

Figure 11 is a schematic of the prism used in the lab scale macrocell tests. Two mats or rebars were cast in concrete prisms using average quality air-entrained concrete. Various levels of sodium chloride were admixed into several of the top mat layers to accelerate corrosion and simulate the environment present in old bridge decks. A dam was placed on top of each slab and 6-percent NaCl/inhibitor solutions of deicer product ponded to a depth of $^3/_4$ in. Solutions were replenished every 2 weeks.
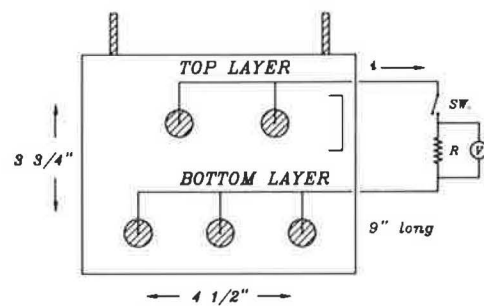
SMALL SCALE SLABS

Portland Cement	*1.0*
Water	*0.53*
Sand	*1.76*
Aggregate	*2.36*

FIGURE 11 Schematic of small-scale prism.

The top and bottom sets of rebars were electrically connected and a momentary off/on switch in series with a 1.0-ohm resistor installed between the two mats. Initially the corrosion current ($I = E/R$) was determined from the voltage drop across the resistor. Later a direct corrosion current was obtained by using a zero-resistance (Hokuto Denko Corp.) ammeter. Measurements were taken at weekly or biweekly intervals and plotted versus time of exposure in days.

The macrocell current data, followed over a period of 231 days, for one of the proprietary inhibitor formulations (patent pending) of salt and water, are shown in Figures 12–15. The slabs contained 0, 5, 10, and 15 lb/yd^3 sodium chloride mixed into the top layer. These conditions were chosen to simulate both fresh uncontaminated concrete and existing contaminated bridge surfaces.

Several conclusions can be reached. First, as might be expected, water does not initiate corrosion, suggesting that other factors (availability of O_2, differences in rebar potential, pH, etc.) are responsible. As can be seen from Figures 12–15, the inhibited salt mixture not only passivates the steel surface but appears to be nonaggressive to rebar in fresh concrete. It can be speculated that the inhibitor is diffusing through the concrete

FIGURE 14   Macrocell current data: 10 lb/yd^3 chloride top layer.
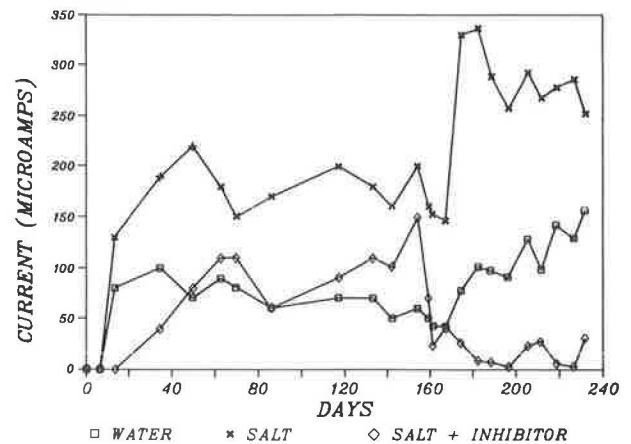
FIGURE 15   Macrocell current data: 15 lb/yd^3 chloride top layer.

FIGURE 12   Macrocell current data: 0 lb/yd^3 chloride top layer.

FIGURE 13   Macrocell current data: 5 lb/yd^3 chloride top layer.

and forming a passivating film on the steel surface. Verification of these encouraging preliminary results under conditions that more closely approximate existing bridge decks and surfaces is in progress using larger (6- × 14½- × 24-in.) slabs under environmental exposure.

The search for an inhibitor to add to salt that would preserve the effectiveness of the deicer without damaging the environment covered a wide array of known inhibitor classes. An extensive list of chemicals was reduced to a select few using techniques previously listed. The data obtained from macrocell current measurements correlate fairly well with data obtained from the more reliable screening and rebar probe tests. A comparison of the performance of the inhibited salt with salt alone in immersion tests and through studies on a steel probe is shown in Table 3. Experiments on rebar concrete probes, which attempt to measure inhibitor performance under microcell conditions, confirm that the inhibitor functions well in this environment. This can be seen in Figure 16, which illustrates the time dependence of Rp (inversely proportional to the corrosion rate) which was obtained from a.c. impedance measurements. However, rebar probes can only simulate and provide information on microcell corrosion; problems associated with variations in the environment found within macrocells, which better

TABLE 3 COMPARISON OF CORROSION RATES OBTAINED IN SALT AND INHIBITED SALT SOLUTIONS

	214.5-hr Imersion Tests Rate of Corrosion (mpy)		Linear Polarization Rate of Corrosion[a] (mpy)	ac Impedance Corrosion Rates of Steel Electrodes[b]
	Mild Steel C1010	Gal- vanized Steel		
NaCl	2.32	0.98	2.0	8.01
NaCl + inhibitor	0.56[c]	0.11[c]	0.849	2.09

[a]As measured in 10 percent NaCl and 10 percent NaCl + 0.33 percent inhibitor solution saturated with $Ca(OH)_2$.
[b]As measured in 1 m NaCl; pH 8.2; C1018 steel.
[c]4 percent solution of 95:5 salt:inhibitor mixture.
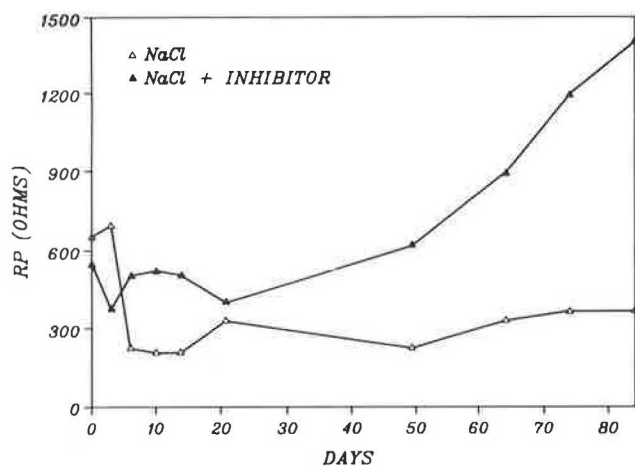
FIGURE 16 ac impedance time dependence.

approximate real life, are not addressed. The construction of small-scale slabs is an attempt to simulate macrocell conditions (in the controlled laboratory environment) currently found in bridge decks. The results indicate that the inhibitive salt mixture continues to perform well confirming earlier observations.

ACKNOWLEDGMENTS

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Study on Wetting Salt and Sand Stockpiles with Liquid Calcium Chloride

A. D. McElroy, Robert R. Blackburn, Jules Hagymassy, and Henry W. Kirchner

Highway and city maintenance departments began wetting rock salt and abrasives with liquid calcium chloride more than 20 years ago to enhance the deicing performance of these materials on highways and streets. The newest method for combining rock salt or abrasives with liquid calcium chloride is called stockpile wetting. Stockpile wetting of rock salt consists of the injection of solutions of calcium chloride into the upper sections of piles of rock salt stored for use in highway ice and snow control. In this study, stockpile wetting was simulated by injection of calcium chloride solutions into 6-in.-diameter by 9-ft-tall columns of salt at temperatures of 50°F, 45°F, 40°F, 35°F, and 30°F. Concentrations of calcium chloride in the injected solutions ranged from 32 to 42 percent. The following characteristics of stockpile wetting were determined: (a) the extent and rate of movement of liquid downward through the simulated stockpile; (b) the quantity of liquid exiting the bottom of the stockpile as a function of temperature, solution concentration, and time; (c) the distribution of calcium chloride within the stockpile and quantities of calcium chloride in leachates; and (d) the ice melting capacity of stockpile-wetted rock salt compared to that of unwetted rock salt. Test results at temperatures 50°F or lower indicate that the preferred wetting parameters consist of injecting 42 percent $CaCl_2$ at a rate of 8 gal per ton. At 50°F and lower, wetting with 32 percent, 35 percent, and 38 percent $CaCl_2$ yielded leachates. Quantity of leachates is primarily a function of $CaCl_2$ concentrations. Wetted salt that remains in storage during hot summer months may produce leachate based upon test temperature rise to 85°F. Stockpile wetted rock salt out-performed dry rock salt in total ice melt at all temperatures and almost all time intervals.

To enhance the deicing performance of rock salt and abrasives on streets and highways, road officials began wetting these materials with liquid calcium chloride more than 20 years ago. The newest method for combining rock salt or abrasives with liquid calcium chloride is called stockpile wetting. This involves the injection of a calcium chloride solution throughout a stockpile at various space intervals.

Because no guidelines had been established for wetting stockpiled salt or sand, a series of tests to determine the percent brine concentration, leachate, and solution distribution was undertaken. These tests revealed that a 42 percent calcium chloride concentration by weight solution would be best for this application because it (a) provides relatively uniform distribution of the calcium chloride solution from top to bottom in salt and sand stockpiles, and (b) generated no leachate at the

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test temperatures, which would occur during expected use conditions.

In an auxiliary test, however, it was determined that 42 percent liquid calcium chloride began to leach from the bottom of the four test salt stockpiles after 2 days when the temperature was raised to 85°F, simulating hot, summer weather. However, under normal field conditions it could be expected that only the surface of a stockpile would reach this high temperature as it equilibrates with the ambient temperature. Therefore, $CaCl_2$ leachate from the warm outer layer could be expected to re-crystallize as the leachate contacts material that is at 69°F and below.

Over the past 20 years, road officials have been wetting rock salt and abrasives such as sand with liquid calcium chloride primarily by two means. The first involved the use of an overhead spraybar system whereby a loaded truck drove under the spraybar and the entire load was wetted with liquid calcium chloride. The other method involved mounting the spray equipment directly on spreader trucks. The salt or sand was then treated with liquid calcium chloride as it was dispensed from the truck's hopper.

In an effort to cut the capital equipment costs involved with those two methods, road officials began looking for different ways to apply liquid calcium chloride to salt and sand. During the mid-1980s, this led to the practice of wetting the materials while in stockpiles.

While many road officials were experienced in treating rock salt and sand with liquid calcium chloride using spraybar or truck-mounted systems, no guidelines had been established for treating stockpiled salt and sand. Therefore, 40 tests were conducted during an 8-month period starting in mid-1986 to provide potential users with guidelines for applying liquid calcium chloride to each stockpiled material and an indication of the results they could expect when treating icy streets and highways with this deicing combination.

Specifically, tests were conducted on 32, 35, 38, and 42 liquid calcium chloride weight percent solution concentrations at five different stockpile temperatures: 30°F, 35°F, 40°F, 45°F, and 50°F. These temperatures represent a typical range that could be found in the interiors of stockpiles during winter storage. The objective was to determine (a) the amount of liquid that leached out the bottom of the stockpiles over a specified period of time, and (b) the distribution of calcium chloride solutions on a 100 percent dry weight basis from top to bottom of the salt stockpiles.

A secondary test consisted of wetting sand stockpiles with each calcium chloride concentration at a stockpile temperature

of 35°F. The purpose of this test was the same as described in (a) in the previous paragraph.

In one auxiliary test, the salt was injected with 42 percent liquid calcium chloride at a stockpile temperature of 35°F, held at this temperature for 6 days, then warmed to 85°F and held at that temperature for 12¼ days. This test was to determine if leachate would be generated when stockpiles were wetted in cold weather then kept in storage until the summer-like temperatures occurred.

In another auxiliary test, the deicing performance of stockpiled rock salt wetted with 42 percent liquid calcium chloride was compared to untreated rock salt in terms of the total ice-melting rate and volume of each material.

BACKGROUND

Stockpile wetting is accomplished by injecting a calcium chloride solution at a specified rate into stockpiled salt to a depth of 2 to 3 ft and at 1- to 2-ft intervals throughout the surface of the stockpile. The solution then percolates downward and outward from the areas of injection. Ideally, wetting results in uniform distribution of the calcium chloride solution throughout the stockpile, with none of the solution leaching out the bottom.
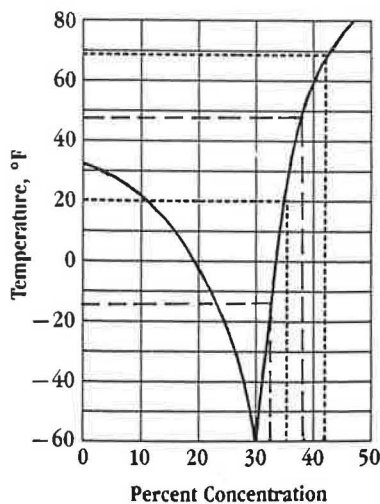

FIGURE 1 Crystallization points of solutions of liquid calcium chloride.

Liquid calcium chloride is available in concentrations of 32 percent, 35 percent, 38 percent, and 42 percent. Theoretically, 42 percent liquid calcium chloride heated to 80°F to 90°F would be expected to perform best for stockpile wetting applications. As shown in Figure 1, 42 percent liquid calcium chloride crystallizes at 69°F. Because application of the liquid calcium chloride to a stockpile would likely occur in late fall or early winter when stockpile temperatures are typically 30°F to 40°F, it would be necessary to heat a 42 percent solution to a temperature safely above its crystallization point to keep it in a free-flowing state.

When the 42 percent material is injected into the cooler salt stockpile, its temperature begins to drop rapidly. At 69°F, crystallization would begin to occur. Deeper into the pile,

crystal growth continues. As long as the temperature remains below 69°F, runoff should not be expected.

Although application would normally take place in late fall when the stockpile's temperature has stabilized near 35°F, there may be instances with large stockpiles when the internal temperature is greater than 35°F. The higher brine concentration is then more important to prevent leaching.

Under those conditions, liquid calcium chloride concentrations of 32 percent, 35 percent, and 38 percent will leach out the bottom of the stockpile and possibly create environmental problems. This is because these brines crystallize at temperatures of −17°F for a 32 percent concentrate, 20°F for a 35 percent concentrate, and 48°F for a 38 percent concentrate as shown in Figure 1. For that reason, the 42 percent concentration of liquid calcium chloride theoretically should be used to produce the best results.

TESTING METHODOLOGY

The rock salt used in the tests met the Standard Specification for Sodium Chloride (ASTM D632), which specifies a sodium chloride product of 95 percent or higher purity and a distribution of particle sizes. As delivered, the salt contained about 0.1 percent moisture, according to supplier specifications and as verified by drying. The moisture content was increased to 0.5 percent prior to testing by adding the calculated quantity of water slowly to 150-lb batches of salt in a cement mixer and tumbling for at least 10 minutes. The purpose of increasing the moisture content of the rock salt to 0.5 percent was to simulate the conditions state and county highway departments experience when storing rock salt under cover.

Test sand conformed to Kansas Department of Transportation (KDOT) ice-control specifictions for particle size as follows:

Size	Percent Passing
³/₈ in.	100
4 mesh	85–100
16 mesh	50–90
30 mesh	5–50
100 mesh	0–5
200 mesh	2 (max)

No moisture specification was reported by KDOT. When received, the sand contained 4 to 5 percent moisture and was dried to an average of 0.95 percent moisture. The calcium chloride used in the tests met ASTM D98 specifications. To conduct the tests, four Plexiglas™ columns were constructed, each measuring 9 ft 4 in. high, 6 in. I.D., and ⅛ in. thick. Four columns were built so that tests for each calcium chloride concentration could be carried out simultaneously at the various test temperatures.

Fastened to the bottom of each column was a sheet metal plate with a ¼-in. hole drilled into its center. A tube was placed over the hole for draining, collecting leachate in plastic bottles.

All columns were placed in a refrigerated enclosure which consisted of an insulated double-walled plywood box, 10 ft high × 5 ft wide × 4 ft deep. The front of the box consisted of a double walled 4 ft × 8 ft Plexiglas™ door to provide insulation and permit observation and photography without entering the test chamber.

The columns were loaded with rock salt to within 4 in. of the top. As the columns were filled, they were vibrated slightly to allow settling of the salt.

The temperature within the salt stockpile columns was measured by insertion of a thermometer to a depth of approximately 10 in. All salt stockpiles in the refrigerated enclosure were cooled overnight (16 to 18 hours) until the temperature was within 0.5°F of the test temperature.

To assure visual observation of the calcium chloride solution as it penetrated through the stockpile columns, all solutions were treated with a blue dye, Bull's Eye (Milliken Chemical), at the rate of 1 part dye:500 parts calcium chloride solution.

Injection of the calcium chloride solutions was by a metal probe, consisting of $1/2$-in. diameter copper tubing 30 in. long which contained four sets of $1/8$-in. holes at 6-in. spacings and 90-degree intervals. The injection pressure apparatus consisted of a 2-gal Freon™ tank fitted on the bottom with a $1/2$-in. pipe and a lever-type quick-open valve. The top was fitted with a pressure gauge, a quick-connect fitting for attachment of an air hose, and a screw cap which was removed to introduce the calcium chloride solutions to the tank.

The calcium chloride solutions were injected at 40 psig and at a depth of 2 ft. The quantity of 100 percent dry weight calcium chloride per ton of rock salt was 40.15 lb for all tests (1.91 percent) (Table 1). Therefore, the liquid volume injected into the piles was at the following application rates: 32 percent solution, 11.45 gal per ton of salt; 35 percent solution, 10.19 gal per ton of salt; 38 percent solution, 9.10 gal per ton of salt; and 42 percent solution, 8.0 gal per ton of salt.

TABLE 1   APPLICATION RATES

	Percent			
	42	38	35	32
100 percent dry CaCl$_2$/ column (g)	1.130	1,139	1,139	1,139
Solution/column (g)	2.814	2,998	3,255	3,560
Solution/column (ml)	1,892.5	2.157.5	3,410.3	2,710.8
100 percent dry CaCl$_2$/ ton (lb)	40.15	40.15	40.15	40.15
Solution/ton (gal)	8.0	9.1	10.19	11.45

To ensure that each calcium chloride solution was above its crystallization point at the time of injection, the temperature of each was as follows:

1. At 32 percent: 35°F (crystallization temp. −17°F),
2. At 35 percent: 35°F (crystallization temp. +20°F),
3. At 38 percent: 60°F (crystallization temp. +48°F),
4. At 42 percent: 80°F (crystallization temp. +69°F).

The Plexiglas™ columns were charged sequentially with 42, 38, 35, and 32 liquid calcium chloride weight percent solution concentrations over a 30 to 40 minute period. Total test time was 120 hours.

TEST RESULTS

In the primary tests, studies were conducted on 32, 35, 38, and 42 liquid calcium chloride weight percent solution concentrations at stockpile temperatures of 30°F, 35°F, 40°, 45°F, and 50°F. In the first part of these tests, the objective was to determine the amount of calcium chloride that leached out the bottom of these stockpiles over a 1-week period.

Because of the significant amount of data that was generated by these tests, it is impractical to reproduce all results in this paper and allow for comparisons between the different concentrations of liquid calcium chloride. Therefore, Tables 2–4 summarize the relevant results of this test. These are the results of two tests for each concentration. It is interesting to note that leachate quantities exhibited no significant trend with temperature. Also, on average, leachate breakthrough times decreased as the calcium chloride concentration used increased. For example, the average breakthrough time on all tests for the 32-percent solution was 0.9 hours; the 35-percent solution was 3.4 hours; and the 38-percent solution was 6.0 hours (Table 5).

TABLE 2   LEACHATE QUANTITY (GALLONS PER TON ROCK SALT)

Percent CaCl$_2$ Solution	Temperature (°F)					
	50	45	40	35	30	Avg
32	4.55	4.94	4.60	4.45	4.77	4.7
35	2.32	4.00	2.83	2.88	2.97	3.0
38	1.86	1.70	1.76	1.82	1.66	1.8
42	0	0	0	0	0	0

TABLE 3   LEACHATE QUANTITY (PERCENT OF INJECTED VOLUME)

Percent CaCl$_2$ Solution	Temperature (°F)					
	50	45	40	35	30	Avg
32	40	43	40	38	42	41
35	23	39	28	29	29	30
38	20	19	19	20	18	19
42	0	0	0	0	0	0

TABLE 4   CONCENTRATION OF CaCl$_2$, IN LEACHATE, WEIGHT PERCENT

Temperature (Replicate) (°F)	Percent CaCl$_2$ Solution		
	32	35	38
50 (1)	28.5	28.4	32.0
50 (2)	25.9	29.4	32.1
Avg	27.2	28.9	32.15
45 (1)	27.2	31.8	34.2
45 (2)	27.9	31.9	29.4
Avg	27.6	31.85	31.8
40 (1)	27.5	31.5	27.8
40 (2)	29.7	33.5	32.6
Avg	28.6	32.5	30.2
35 (1)	29.1	31.0	32.6
35 (2)	27.6	29.7	32.3
Avg	28.4	30.4	32.5
30 (1)	28.0	31.4	33.3
30 (2)	25.1	30.2	31.9
Avg	25.6	30.8	32.6
Composite Avg	27.7	30.9	31.9

NOTE: No leachate was observed from any test for the 42 percent solution.

TABLE 5 LEACHATE BREAKTHROUGH TIMES OF STOCKPILE ROCK SALT WETTING

Temperature (°F)	Percent CaCl$_2$ Solution										
	32			35			38			42	
	No. 1	No. 2	Avg	No. 1	No. 2	Avg	No. 1	No. 2	Avg	No. 1[b]	No. 2[b]
50	0.5	0.5	0.5	4	2	3	1.0	1.0	1.0		
45	0.5	0.5	0.5	0.2	0.2	0.2	5.0	10[a]	7.5		
40	0.2	4	2.1	0.2	4	2.0	15[a]	2	8.5		
35	0.5	0.7	0.6	7.5	15[a]	11	20[a]	2	11		
30	1.0	0.8	0.9	1.5	0.4	1.0	3	1.3	2.1		
Avg			0.9			3.4			6.0		

[a]Extrapolated breakthrough times.
[b]No leachate breakthrough.

The second part of the primary testing was to determine the distribution of calcium chloride solutions on a 100 percent dry weight basis from top to bottom of the stockpiles over a specified period of time.

This was achieved by removing the salt from the columns in four equal sections from bottom to top; each column was marked by quarters 27 in. long. Each column was then placed over a 5-gal pail and the bottom sheet metal plate was removed and replaced with a metal shim. Each quarter of salt was then evenly discharged by gravity into separate pails. Salt from each pail was mixed for 3 to 4 minutes in a cement mixer to promote even liquid distribution. Samples of 1 to 2 lb were removed from the overall mixture and placed in glass jars for testing. These were analyzed for calcium chloride according to procedures specified in ASTM E449.

Interpretations of analytical data on calcium chloride contents of each of the four sections of the salt columns were slightly hindered by the presence of calcium sulfate in the rock salt in variable concentrations (from 0.5 percent CaSO$_4$ to 3 percent CaSO$_4$). Reported data contain obvious anomalies attributable to this problem. The data generally indicate, however, reasonably uniform distribution of calcium chloride in rock salt stockpiles wetted with 32 percent, 35 percent, and 38 percent calcium chloride concentrations. With the 42 percent solution, CaCl$_2$ concentrations in upper sections tend to be higher than the average concentration, and in the lower sections lower than the average concentrations, especially at lower temperatures. Table 6 provides data on calcium chloride retained in each of the forty test stockpiles.

In the secondary testing, sand stockpiles at 35°F were wetted with the calcium chloride concentrations. The purpose of this test was the same as Part a of the primary test, that is, to determine the amount of calcium chloride leachate out the bottom of each stockpile over a specified time period. The calcium chloride application rate for sand stockpiles was the same as it was for rock salt: 40.15 lb (100 percent dry weight basis) per ton of sand for each concentration.

Tables 7 and 8 summarizes the relevant results of this test regarding leachate produced. In general, permeation of sand breakthrough occurred much more slowly than with rock salt, as follows:

Percent CaCl$_2$ Solution	Breakthrough Time
32	Approximately 30 hr
35	Approximately 50 hr
38	Approximately 72 hr
42	None

The average percent CaCl$_2$ (dry weight basis) in wetted sand compared with that in wetted rock salt is as follows:

Percent CaCl$_2$ Solution	Percent in Rock Salt	Percent in Sand
32	1.27	1.44
35	1.47	1.50
38	1.67	1.80
42	1.91	1.91

In the first auxiliary test (the dual-temperature test) a rock salt stockpile was injected with 42 percent liquid calcium chloride after the stockpile stabilized at a temperature of 35°F. This temperature was maintained for a 6-day time period. The temperature was then increased to 85°F and held there for a period of 12¼ days. The purpose of this test was to simulate wetting salt stockpiles in cold weather and allowing the material to remain in storage into the summer season.

Leachate breakthroughs occured at times ranging from about 45 to 100 hours after warmup. The end-of-test (12¼ days) leachates averaged 2.03 gal of the 8 gal of 42 percent liquid calcium chloride concentration per ton injected into the rock salt, or 25 percent of the injected quantity.

In the other auxiliary test, the deicing performance of stockpile rock salt wetted with liquid calcium chloride was compared to untreated rock salt by measuring the volumes of ice melted as a function of time and temperature. Rock salt containing 0.5 percent moisture was stored in stockpiles at 40°F. Portions of this salt were wetted with 38 percent and 42 percent liquid calcium chloride solutions. These materials were tested at temperatures of 5°F, 15°F, and 25°F, and at time intervals of 10, 20, 30, 45, and 60 min. The equipment needed was as follows.

Ice-Melting Test

The apparatus used in the ice-melting test consisted of two pieces of Plexiglas TM, one ¼ in. thick, one ½ in. thick, and both 11 in. square. A hole 9 in. in diameter was cut through the ½-in.-thick piece. The two pieces were then glued together under pressure, thereby producing a hole 9 in. in diameter and ½ in. deep. (See another paper by McElroy et al. in this Record, Figure 4.) Ten dishes were constructed in this manner in order to carry out simultaneous testing.

For each test, the dishes were charged with 130 ml of deionized water and placed in a level freezer compartment of a refrigerator overnight. This volume of water corresponded to an ice thickness of ⅛ in. Before each test, it was necessary to

TABLE 6   CALCIUM CHLORIDE RETAINED IN WETTED ROCK SALT: PERCENT OF 100-PERCENT-DRY-WEIGHT-BASIS CaCl$_2$

Percent CaCl$_2$ Solution	Quadrant (4 = top quadrant)	Temperature (°F)														
		50			45			40			35			30		
		No. 1	No. 2	Avg	No. 1	No. 2	Avg	No. 1	No. 2	Avg	No. 1	No. 2[a]	Avg	No. 1	No. 2[a]	Avg
42	1	1.41	2.19	1.8	1.66	1.69	1.67	0.84	1.35	1.10	0.73		–	1.36		–
	2	2.42	1.65	2.04	1.97	1.81	1.89	1.73	1.90	1.82	1.78		–	1.75		–
	3	1.63	2.02	1.82	1.95	2.26	2.10	1.87	1.85	1.86	1.80		–	1.68		–
	4	2.17	1.77	1.97	2.06	1.87	1.97	3.20	2.52	2.86	3.33		–	2.85		–
	1–4 composite	1.91	1.91	1.91	1.91	1.91	1.91	1.91	1.91	1.91	1.91	1.91	1.91	1.91	1.91	1.91
38	1	1.87	1.91	1.89	–[a]	1.87	–	1.62	1.20	1.45	1.32		–	2.49		–
	2	1.94	1.71	1.83	–[a]	1.56	–	1.55	1.80	1.68	1.40		–	1.27		–
	3	1.40	1.36	1.38	–[a]	1.66	–	1.85	1.62	1.73	1.07		–	1.50		–
	4	1.28	1.11	1.20	–[a]	1.57	–	1.60	1.78	1.69	2.68		–	1.34		–
	1–4 composite	1.62	1.53	1.58	1.62	1.66	1.64	1.66	1.62	1.64	1.62	1.61	1.61	1.65	1.63	1.64
35	1	1.18	1.43	1.31	1.08	1.18	1.13	1.29	1.71	1.50	1.33		–	1.87		–
	2	1.82	1.27	1.55	1.08	1.38	1.23	1.30	1.50	1.40	1.56		–	1.17		–
	3	2.54	1.94	2.24	0.92	1.14	1.03	1.26	1.54	1.40	1.03		–	1.42		–
	4	0.86	1.44	1.15	2.24	1.25	1.74	1.35	1.15	1.25	1.67		–	1.49		–
	1–4 composite	1.60	1.52	1.54	1.33	1.24	1.28	1.30	1.47	1.39	1.40	1.55	1.47	1.49	1.43	1.46
32	1	1.28	1.11	1.20	1.15	1.42	1.29	1.35	1.46	1.40	1.23		–	0.61		–
	2	1.39	0.95	1.17	1.42	1.05	1.24	1.46	0.98	1.22	1.40		–	0.99		–
	3	1.05	1.06	1.05	1.14	1.16	1.15	1.19	1.24	1.21	0.89		–	1.49		–
	4	1.20	2.04	1.62	1.26	1.19	1.22	1.20	0.94	1.07	1.16		–	1.57		–
	1–4 composite	1.23	1.29	1.26	1.24	1.20	1.22	1.30	1.16	1.23	1.17	1.37	1.27	1.17	1.31	1.24

[a]Not analyzed.

TABLE 7   LEACHATE VOLUMES IN WETTED SAND AT 35°F

	Percent CaCl$_2$ Solution			
Hours	32	35	38	42
21	0	0	0	0
44	1.75	0	0	0
68	2.71	1.25	0	0
75	2.89	1.50	0.016	0
92	3.25	1.92	0.033	0
99	3.39	2.11	0.18	0
116	3.65	2.44	0.53	0
121	3.73	2.56	0.64	0

NOTE: Volumes represent gal per ton.

TABLE 8   CaCl$_2$ DISTRIBUTION IN WETTED SAND AT 35°F

	Percent CaCl$_2$ Solution			
	32	35	38	42
CaCl$_2$ charged, 100 percent dry weight basis, per ton sand (lb)	40.15	40.15	40.15	40.15
Leachate				
Gal per ton	3.73	2.56	0.64	0
Percent CaCl$_2$	25.86	32.33	33.53	–
lb dry weight CaCl$_2$ per ton	10.0	8.82	2.13	–
CaCl$_2$ retained by sand lb dry weight per ton	30.15	31.33	38.02	40.15
Percent by weight, dry weight basis	1.44	1.50	1.81	1.91

smooth the ice surface. Therefore, a thick aluminum plate was placed on the ice surface and rotated by hand for several seconds until the surface ice was melted. The dishes were then placed on a level surface inside the testing cold room until melted water was refrozen. The deicers to be used for the day's operation were also placed inside the temperature control box bedore testing and allowed to equilibrate in order to simulate actual winter conditions.

To ensure accurate and consistent test results, a minimum of three runs was recorded for each time period and temperature level, and the average of those results was taken. Test equipment was thoroughly flushed and rinsed with distilled water after each test to avoid contamination.

Melting application rate was 3 oz/yd^2 for dry rock salt and 3.14 oz/yd^2 for stockpile wetted salt. The addition of 0.14 oz/yd^2 represents the amount of calcium chloride associated with the salt. These deicer rates created amounts of brine for each test series that were both measurable and manageable at all test temperatures and within the test time limitations.

To measure the amount of melt after a specified time period, each dish was tipped so that the brine flowed to the perimeter of the dish. Using a syringe and needle, the brine was quickly withdrawn and measured; the amount was recorded and then replaced in the deicer bore holes using the same syringe and needle.

As no CaCl$_2$ leachate was collected in a winter simulation, the 42 percent appears to be the ideal material for wetting stockpile rock salt, based on the test results. Tables 9 and 10

summarize the melting results of tests with plain rock salt androck salt treated with 42 percent liquid calcium chloride at 8.0 gal per ton.

In addition to greater melt volume when dry rock salt is wetted with calcium chloride, the liquid itself assists the salt to

TABLE 9 MELTING RESULTS OF TESTS WITH PLAIN ROCK SALT

| Temperature (°F) | Time (min) | Melt Volume (ml) | |
		Three-Test Avg	Standard Error
25	10	5.50	0.794
	20	11.53	0.897
	30	16.57	0.940
	45	21.80	0.586
	60	25.77	0.536
15	10	2.13	0.088
	20	5.20	0.058
	30	7.97	0.088
	45	10.37	0.167
	60	12.53	0.088
5	10	0.45	0.050
	20	1.40	0.082
	30	2.45	0.155
	45	3.65	0.296
	60	4.93	0.217

NOTE: Application rate is 3 oz/yd^2.

TABLE 10 MELTING RESULTS OF TESTS WITH STOCKPILE WETTED ROCK SALT

| Temperature (°F) | Time (min) | Melt Volume (ml) | |
		Three-Test Avg	Standard Error
25	10	6.50	0.361
	20	12.90	0.153
	30	18.30	0.058
	45	22.87	0.348
	60	27.87	0.581
15	10	1.97	0.145
	20	5.90	0.058
	30	8.87	0.088
	45	11.10	0.115
	60	13.67	0.240
5	10	0.48	0.085
	20	1.78	0.075
	30	3.15	0.144
	45	4.63	0.193
	60	5.98	0.165

NOTE: Application rate is 3.14 oz/yd^2.

remain upon the pavement surface. This retention was demonstrated in a study by the Michigan Department of State Highways and Transportation (*1*) which showed that only 46 percent of dry salt remained in the center third of a 24-ft pavement (location where it was placed) to 73 percent for the wetted material. Total percent lost from this pavement (not retrieved) was 30 percent for dry salt to 4 percent for wetted salt.

A third consideration to evaluate, in addition to retention and melt, is the strong possibility of dry rock salt being blown away with traffic. This consideration has yet to be scientifically measured.

CONCLUSIONS

Test results of stockpile wetting on rock salt at temperatures 50°F or lower indicate that the preferred wetting parameters consist of injection of 42 percent $CaCl_2$ at a rate of 8 gal per ton. These conditions result in relatively uniform distribution of calcium chloride throughout the stockpile, without generation of leachate from the bottom of stockpiles. At 50°F and lower, wetting with 32 percent, 35 percent, and 38 percent $CaCl_2$ yielded leachates ranging from 7 to 41 percent of the material injected. The quantity of leachates is primarily a function of calcium chloride concentrations.

In actual field conditions, these leachates could present a hazard to the environment. All salt stockpiles, dry or wetted with calcium chloride, should be stored under cover on impervious floors with proper drainage and diking for environmental reasons.

Since about 25 percent of the 42 percent liquid calcium chloride leached out of the test stockpiles when these piles achieved 85°F, environmental precautions should be taken when stockpile wetted salt remains in storage during hot summer months. However, under normal field conditions only the surface material in the rock salt stockpiles would be expected to remain at 85°F. Therefore, the $CaCl_2$ leachate from the warm, outer stockpile layer could be expected to recrystallize as it penetrates the pile.

Results of these deicing performance tests indicated that stockpile wetted rock salt outperformed dry rock salt. In total ice melt, stockpile wetted rock salt significantly outperformed plain salt at all temperatures and almost all time intervals.

REFERENCE

1. *Prewetted Salt Report*. Michigan Department of State Highways and Transportation, June 1, 1975.

Investigation of the Ice-Retardant Characteristics of Verglimit-Modified Asphalt

JOHN M. RAINIERO

This project involved the design, application, and evaluation of an asphalt concrete mix, made ice retardant by the addition of encapsulated calcium chloride pellets (Verglimit). This deicing asphalt was placed along an $^8/_{10}$-mi section of Route 173 in Clinton, New Jersey. The agent was effective in retarding icing of the pavement and made snow removal easier. Skid-resistance values taken over a 10-month period are as good as those of other Mix I-4 asphalt concrete pavements.

One of the hazards confronting motorists is slippery conditions caused by snow and ice. In an effort to investigate the potential of maintaining roadway safety during these conditions, the New Jersey Department of Transportation's Bureau of Maintenance has installed a deicing asphalt. The deicing material, Verglimit, derived from the French expression "limité le verglas" or "end slippery ice," was developed in Switzerland in 1973 and has been in use for ice control for 14 years in Europe, 10 in Canada, and 9 in the United States. This deicing material is essentially calcium chloride flakes, to which approximately 5 percent sodium hydroxide is added. The flakes are coated with linseed oil, which is polymerized to protect the flakes from water. This material is introduced into the asphalt concrete mix as part of the aggregates during the mix cycle. The treated mix is laid and compacted using conventional paving equipment. Thus, Verglimit flakes are exposed as traffic wears away the pavement surface. This abrasion should amount to approximately 1 mm per year, creating a continuous ice-free surface for the life of the overlay.

TEST SITE

A single test site was selected for the introduction of Verglimit. This site is located along an $^8/_{10}$-mi section of Route 173 in the rural town of Clinton, New Jersey. This site receives an AADT of 5,000 and is situated in the northwestern part of the state, known as Region I (Figure 1). It is important to note that the AADT of 5,000 occurs during morning and evening rush hours; other times of the day, the AADT drops to 1,000 or less. The Route-173 site was selected because of the potential microclimate that would exist in a small area of roadway. There is a culvert, overhanging trees, a lake (acting as a solar collector), several side streets entering, and a stop light, creating various traffic conditions (Figure 2).

New Jersey Department of Transportation, Bureau of Maintenance, 1035 Parkway Avenue, E&O Building, CN600, Trenton, N.J. 08625.
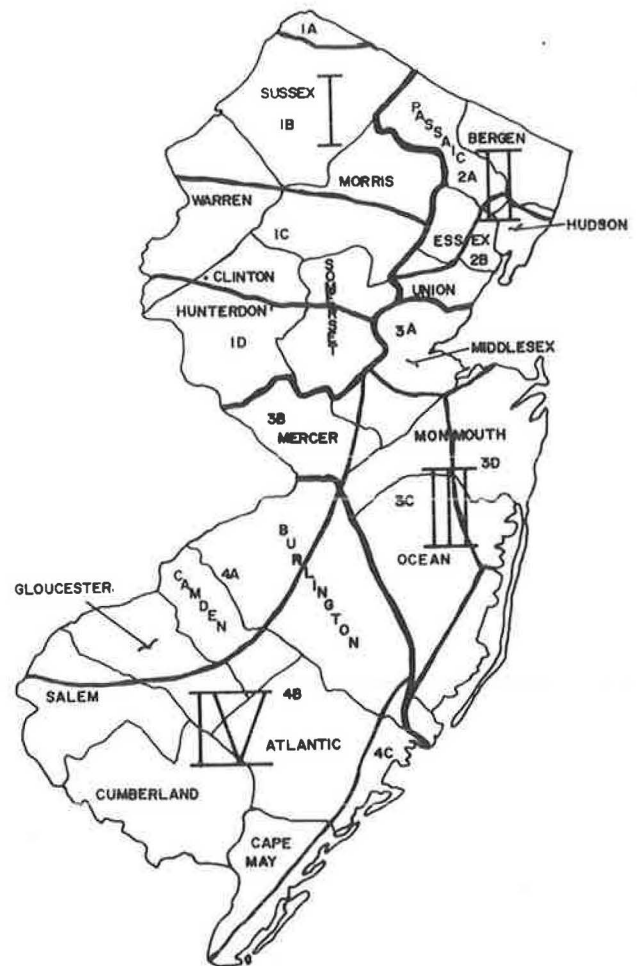
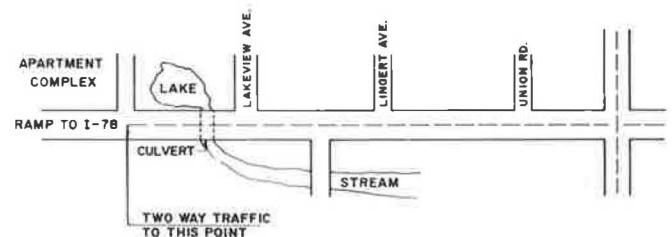FIGURE 1 Weather map showing Clinton, New Jersey, test site.

FIGURE 2 Section of Route 173 chosen for Verglimit testing.

MONITORING CRITERIA

1. At what temperature does Verglimit cease to be hygroscopic at the Route 173 test site?

2. How does snow accumulation affect the ice retardant pavement?

3. Does AADT affect the ice retardant pavement? If so, how?

4. What effect, if any, do changes in weather (i.e., rain to snow, or snow to rain) have on the deicing pavement?

5. What effect does the presence of a year-round deicing chemical have on appurtenances?

6. What are the monthly skid data?

7. How do sample cores taken periodically compare to original ones taken at the test site?

MIX DESIGN

The mix design chosen is shown in Tables 1 and 2.

MIX PREPARATION AT THE PLANT

Handling of Verglimit

It is important to handle Verglimit with care, so as not to crush the particles. The least amount of mixing necessary should be used in ensuring that all particles are totally coated with asphalt cement. To avoid undesirable absorption of moisture, the sacks of Verglimit should not be opened before they are placed in the mix. To eliminate occasional lumps, the sacks should be dumped over a sieve with openings of $^3/_4$ in. $\times$ $^3/_4$ in.

Protection of Personnel

Since Verglimit is an irritant, workers in direct contact with the Verglimit particles must wear goggles and gloves. Depending on other conditions, protective breathing masks should be considered. Contact with the skin must be avoided.

Verglimit Addition

Verglimit must be added continuously and loosely into the pug-mill. The apparatus for the addition must be constructed in such a way that each batch can be added in no less than 5 (to ensure homogeneous distribution in the mix) and no more than 10 (to avoid cracking) sec. If a batch mixer is used the following procedures have proven successful:

• Adding directly into the pug-mill through a hopper or via a conveyor belt. Whenever possible, Verglimit should be added in complete sack units only, which means that the batch weight must be adjusted accordingly. When using a hopper, a lock-gate is appropriate so that the hopper can be filled while the mixing process takes place.

• Adding directly over the filler scale. This method is favorable when there are two filler scales at the pug-mill. When using this process, it is particularly important to make sure that Verglimit is added gradually (minimum 5 sec) and is not exposed to the air for a long period of time.

Auger systems are to be avoided because they might lead to a considerable amount of cracking of the Verglimit particles. If

they must be used, the auger should be no longer than 2.2 yards and should only be used for horizontal transportation. Under no circumstances should it be heated with the aggregate.

Time for Verglimit Addition

All aggregates, including the fines, must be in the pug-mill first. Then the addition of the asphalt cement is started. After a minimum of one-third of the asphalt cement is added, the Verglimit addition can be started; it should be finished at approximately the same time as the asphalt cement addition is completed.

Final Mixing Time

The mixing time, after all components including Verglimit have been added, should only be long enough for the Verglimit particles to be adequately coated with asphalt cement. This can be checked easily by looking at the mixed batch. No white particles should be visible after mixing. It has been found that the total mixing time usually remains unchanged from normal procedures. If the asphalt cement and Verglimit cannot be added at the same time because of plant constraints, the basic mix including the asphalt cement is mixed properly first. Then the Verglimit is added while the mixing continues. Once all the Verglimit is in the mix, the additional mixing time should not exceed 15 sec.

Mixing and Storage Temperatures

The mixing temperature depends on the type of asphalt cement. The respective norms must be observed. A mixing temperature of 329°F to 338°F should not be exceeded at any time in order to keep the mix from becoming like a mastic asphalt (bituminous mastic concrete) in character. This temperature also must not be exceeded if the mix is stored in heated or insulated silos. (It should be noted that the temperature in silos with a capacity above 50 tons can increase due to exothermic oxidation processes without any further heat being supplied to the mix from the outside.)

PLACEMENT OF THE OVERLAY

Supporting Pavement Surface

Surfaces being paved over must fulfill the usual requirements for smoothness, freedom from cracks, and impermeability. Wide cracks will reflect through (as they do when normal mixes are used) when a thin overlay of 1 to 1.5 in. thickness is applied. Therefore, the surface being paved over should be given a proper cleaning and preparation, or even a new profile if necessary. The supporting pavement surface must be dry and free of dirt and dust. The surface being paved over should be precoated with 10 oz to 1 lb/yd^2 of a suitable cationic emulsion or 5 to 10 oz/yd^2 of a water-free tack coat to obtain a proper bond between the old and new layers.

Weather

Verglimit surfaces should be placed in dry and warm weather only. The air temperature should not be lower than 50°F and

TABLE 1 MIX DESIGN

Mix: I-4 Verglimit
Producer: Trap Rock Industries, Inc. - Pennington, New Jersey
Type of Plant: Batch

Job Mix Formula

(Total Percent Passing Each Sieve)

Sieve Size	Verglimit Formula	Verglimit AVG. of 5
2"		
1 1/2"		
1"	100	100
3/4"	100	98 - 100
1/2"	93	88 - 98
3/8"	76	65 - 88
No. 4	52	35 - 65
No. 8	44.0	40.0 - 48.0
No. 16		
No. 30		
No. 50	16.0	13.0 - 19.0
No. 100		
No. 200	6.5	5.1 - 7.9
ASPH. CONT.	5.8	5.35- 6.25

*Percent Asphalt Cement Based on the Total Weight of Mixture

Bin Pulls

	PER CENT	APPARENT SPEC. GRAVITY	COMPONENTS - PRODUCER & LOCATION
Bin No. 5			
Bin No. 4	10.8	2.955	Trap Rock Ind., Inc.; Pennington, NJ
Bin No. 3	30.6	2.945	Trap Rock Ind., Inc.; Pennington, NJ
Bin No. 2	13.7	2.938	Trap Rock Ind., Inc.; Pennington, NJ
Bin No. 1	33.6	2.736	Trap Rock Ind., Inc.; Pennington, NJ
*VERGLIMIT ..	5.5		Verglimit -L & R Dist., Stanhope, NJ
Asphalt Cont. AC-20	5.8	1.025	West Bank Oil

Maximum Theoretical Specific Gravity: 2.597
Approximate Cold Feed Proportions: #67 Stone 30%,#8 Stone 25%,
#10 Stone 39.5%, Verglimit 5.5%

Criteria - Original Mix Design

Stability - Lbs.	3010
Flow Value - 0.01"	16
Air Voids - Percent	2.7
VMA - Percent	16.8
Wt./Sq. Yd. Inch Thick	119

Mixture samples, Marshall Specimens and asphalt cement samples taken at Trap Rock Industries, Pennington, New Jersey. Tested at the plant and the Bureau of Materials Central Laboratory.

TABLE 1 *continued*

		A	B	C	D	E	AVG.	RANGE	MIN	MAX	RANGE
LOT PORTION							2 SAMPLES		JOB MIX REQUIREMENTS FOR 2 SAMPLES		
Date Sampled		9-23	9-23						MIN	MAX	RANGE

SIEVE SIZE PASSING — COMPOSITION ANALYSIS

SIEVE SIZE PASSING		A	B	C	D	E	AVG.	RANGE	MIN	MAX	RANGE
2"	%	100									
1 1/2"	%	100									
1"	%	100	100						100		
3/4"	%	100	100						98	100	
1/2"	%	92	94						88	98	
3/8"	%	83	86						65	88	
No. 4	%	56	57						35	65	
No. 8	%	40.5	39.5				40.0	1.0	37.5	50.5	13.0
No. 16	%										
No. 30	%										
No. 50	%	18.5	17.0				18.0		11.5	20.5	
No. 100	%										
No. 200	%	10.8	9.8				10.3	1.0	4.3	8.7	4.8
Asphalt	%	5.75	5.75				5.75	−	5.10	6.50	1.5

TEST PROPERTY	MARSHALL TEST RESULTS								MIN.		MAX.
Stab. lbs.	3500	2050					2775		1000		
Flow, .01	18	13					16		6		16
Air Voids %	3.9	4.5					4.2				

PROJECT: ROUTE 173 – CLINTON, NJ   TYPE OF MIX: I-4, VERGLIMIT

SAMPLE	1	2	3	4	5	6	AVE.	TARGET
LOAD TEMP. (F)	280	285	285	280	285	290		

SIEVE	% PASSING							
1"	100	100	100	100	100	100	100	100
3/4"	100	100	100	100	100	100	100	100
1/2"	94	95	95	90	87	92	92	93
3/8"	78	85	82	78	77	79	80	76
#4	52	59	55	54	52	51	54	52
#8	38.0	39.0	36.5	35.5	34.5	33.5	36.0	44.0
#50	14.5	16.0	15.0	15.0	16.0	14.0	15.0	16.0
#200	7.2	8.1	8.1	8.2	8.9	6.7	7.9	6.5
AC	5.85	6.00	5.85	5.65	5.70	5.60	5.80	5.8

MARSHALL SPECIMENS

	1	2	3	4	5	6	AVE.	
Stability	2260	2220	2600	2370	2360	2460	2380	
Flow	17	19	17	16	18	16	17	
% Voids	2.2	3.2	2.8	3.0	2.4	3.5	2.8	

NOTE: From Evaluation of I-4 Modified with Verglimit, E. Connolly, S. Seabridge, and J. Smith, unpublished data.
*See Table 2.

TABLE 2 PERCENT VERGLIMIT ADDITION

Average Speed of Vehicles Between 30-55 m.p.h.		
AADT Based on 2 Lane Roadway		
Number of Vehicles	Verglimit Addition	Minimum Number of Vehicles Per Lane
20,000 –	5.0%	10,000
5,000 – 19,999	5.5%	2,500
2,500 – 4,999	6.0%	1,250
1,000 – 2,499	6.5%	500
500 – 999	7.0%	250
100 – 499	7.5%	50
AADT Based on 4 Lane Roadway		
Number of Vehicles	Verglimit Addition	Minimum Number of Vehicles Per Lane
20,000 –	5.0%	5,000
7,000 – 19,999	5.5%	1,750
3,500 – 6,999	6.0%	875
875 – 3,499	6.5%	219
400 – 874	7.0%	100
100 – 399	7.5%	25
AADT Based on 6 Lane Roadway		
Number of Vehicles	Verglimit Addition	Minimum Number of Vehicles Per Lane
20,000 –	5.0%	3,333
10,000 – 19,999	5.5%	1,666
4,500 – 9,999	6.0%	750
1,000 – 4,499	6.5%	166
500 – 999	7.0%	83

*Percentages are based on 100% total weight of mix (e.g. aggregate + asphalt asphalt cement + Verglimit = 100%)

*Above 7.5% recommended only when used with a modified asphalt cement.

the supporting pavement surface should be dry. All placing should be avoided during rain.

Pavers

The same general conditions and specifications for placing a regular mix are applicable. Use only pavers with high precompaction screed capabilities operated at the highest compaction settings to obtain a smooth, closed surface. If there are still some porous spots visible behind the paver, they should be filled with some additional mix before the first roller passes. Inclines should always be paved uphill. If the width of the road varies, the use of pavers with hydraulically movable extensions is recommended.

Hand Work

Hand work must be kept to an absolute minimum and must be avoided in the wheelpaths. Porous areas and those being placed by hand must be sealed with a suitable emulsion-filler sealant before they are opened to traffic.

Longitudinal Joints

If possible, the whole width of the road should be placed in one pass with a single paver. Otherwise, two pavers should be operated in tandem to avoid cold longitudinal joints. When this is impossible, careful longitudinal joint compaction is necessary. If the longitudinal joint is placed cold (edge of first paver path—cold, new path—hot), the necessary uncompacted height of the mix has to be calculated (screed must be elevated sufficiently above the surface of the first paver path). A tack coat or infrared heating (or both) of the cold joint is required. (Alternatively, a melting joint tape can be used.) It is strongly recommended that the joint be sealed to a width of 6 in. the same day. This is mandatory if the joint is at all porous.

Construction Joints and Edges

Verglimit pavements must not be feathered down during construction. A full, sawn joint is required. The edges and the sawn joint must be clean and treated with tack coat. (If feathering must be adopted because of construction constraints, this must

be done with a regular mix.) The most suitable working method is to start and end placing with a plain mix (minimum of one truckload) and to continue with Verglimit mix without a transition. This way not only are the construction joints safe but an opportunity is provided to run the pneumatic-tired roller hot before it is operated (as the first roller) on the Verglimit mix.

Sealing of Critical Parts

All construction joints, contacts, porous parts, sides, and edges are to be sealed the same day to keep water from penetrating the surface. This will prevent potential ravelling of those areas.

Pavement Thickness

The thickness of a Verglimit pavement should at no point be less than 2.5 times the size of the coarsest aggregate.

Air Voids

Compaction of the mix is the governing performance factor for the pavement, in terms of stability and durability. (Suitable calibrated nuclear gauges can be used for overall compaction control.) The voids content of the pavement or drilled cores must under no circumstances exceed an average of 4 percent and an individual value of 5 percent.

A voids content between 3 and 4 percent should be the goal (while water can be used during core drilling, the use of special, denatured alcohol minimizes any water influences). For any Verglimit addition rate lower than 5.5 percent, the voids content of the pavement should not be much lower than 3 percent; otherwise the effectiveness during winter might be affected. On the other hand, the voids content of the pavement must not exceed 4 percent; otherwise water might penetrate into the pavement resulting in pavement damage. Local destruction always indicates an insufficient compaction.

Compaction Techniques

To avoid unwanted cooling of the mix, but more importantly, to keep water from penetrating the uncompacted surface, no water should be used on rollers (i.e., rolling should be hot and dry). If unavoidable, steel-wheeled rollers may be moistened but not wetted. Pneumatic-tired rollers should be driven dry; if absolutely necessary to avoid sticking, a very light oiling may be used.

Recommended Rollers

A pneumatic-tired roller (minimum of 2-ton wheel load; hot and dry) is recommended to obtain a quick closing of the surface. Next best is a steel-wheeled roller (minimum 12 tons). If a vibratory roller is used, the surface should be closed by a static steel-wheeled pneumatic-tired roller afterwards.

On-Site Placement of Overlay

With the test case, the average load temperature leaving the asphalt batch plant did not exceed 290°F. On-site temperatures were not recorded, but based on temperature versus time in transit measurements, the temperature of the mix at the paver was 275°F (using grand average) (Table 3) (*1*). The temperature range for Verglimit is 284°F to 338°F. In addition to this borderline temperature, there was a delay between the time of placement by the paver and compaction. Both of these contributed to the 7 percent voids, determined by cores taken at the job site (Table 4).

Verglimit should have between 3 and 4 percent voids. To improve skid resistance, angular concrete sand was rolled into the hot surface with the last roller pass (2 lb/yd^2), per manufacturer's suggestion. This was done to compensate for the slipperiness caused by the crushing of the calcium chloride pellets by the rollers during compaction, not the release of linseed oil. Additional sand was hand broadcast several times to soak up the "oil." This additional sand did not work well; in fact, it caused a roller-bearing effect. One accident—the only one on the Verglimit paved area—is attributed to this roller-bearing effect. It was found that flushing with water was the better method.

PERFORMANCE OF THE TEST SITE

Winter 1986–1987

In order to observe and control the amount of salt spreading of the test section, evaluators were present on site during all snow storms. The intent of Verglimit is not to terminate entirely the need to spread deicing chemicals. But because evaluators would be present during snow storms, spreading would not be allowed unless the integrity of safety was in question. Integrity of safety criterion was Verglimit failure (e.g., snow padding, vehicles sliding, etc.). Based on this decision, the test site was spread a total of 8 times, as compared to the 40 times for adjacent areas. Before each snow storm the presence of Verglimit on the surface was verified by the silver nitrate test; if silver nitrate was present, it would produce a blue color.

Since Verglimit is hygroscopic it is transformed immediately after its release into solution and adheres to the pores of the road surface. Once in solution it is distributed by passing traffic, creating a thin layer of solution on the roadway. This was evident during ice storms and light snow accumulations, when either the entire roadway was ice free, or in the case of light snow accumulations, the wheelpaths were clear. Snow pads (snow adhering to the surface) for the most part were nonexistent except when the AADT was low and snow accumulations heavy.

COST

To say that the Verglimit modified asphalt reduced labor, equipment, and material usage by 86.4 percent is misleading. Verglimit, in 1986, cost $101.00 per ton for materials. The Route-173 project took 846 tons for a cost of $85,446.00. The data in Table 5 indicate a savings of $647.00 for labor, equipment, and materials as compared to the control section. If the life of the Verglimit-modified asphalt pavement is 10 years, then viewed in terms of manpower, equipment, and materials savings, Verglimit is not cost-effective. Therefore, cost should not be the only consideration; reduction in ice- and snow-related accidents should be the principal reason for placement.

TABLE 3 RATING EFFECTIVENESS OF HOT MIX TARPS (1)

			Tarped			Untarped		
Load (Tons)	Transit Time (Minutes)	Air Temp Degrees F.	Mix Temp Plant* Degrees F.	Mix Temp Paver Degrees F.	Paver Temp Mix Temp	Mix Temp Plant* Degrees F.	Mix Temp Paver Degrees F.	Paver Temp Mix Temp

PLANT AND PAVER TEMPERATURES – 25 INDIVIDUAL TESTS

Woodworth and Company, Inc.

–	25	51**	345	310	89.8%	338	300	88.7%
14	30	50**	365	353	96.7	355	338	95.2
13	35	–	323	328	102.0	330	328	99.4
15	18	41	395	347	87.8	360	318	88.3
9	17	48	348	328	94.2	345	338	97.8
15	30	55	355	332	93.5	358	320	89.4
15	35	–	373	358	96.0	375	348	92.8
8.5	30	65	370	343	92.7	350	328	93.7
15	60	48	363	333	91.7	355	332	93.5
				Avg.	93.8			93.2

Michigan Dept. Highways and Transportation

40–15	20	48	300	298	99.3	300	298	99.3
55	45	55	310	303	97.7	310	303	97.7
21	50	42	350	338	96.6	350	315	90.0
–	40	34	350	348	99.4	350	340	97.1
–	30	40	348	348	100.0	348	345	99.1
				Avg.	98.6			96.6

Central Paving Company

15	60	51	320	288	90.0	315	288	91.4
15	60	57	273	220	80.6	260	208	80.0
15	60	51	323	303	93.8	345	300	86.9
15	60	54	340	300	88.2	330	290	87.9
26–30	45	48	310	297	95.8	310	293	94.5
36	58	53	283	275	97.2	320	308	96.2
26–30	45	55	305	285	93.4	298	288	96.6
32	45	68	320	300	93.8	313	290	93.5
26–30	60	73	290	270	93.1	298	272	91.2
30	65	38	345	338	98.0	348	307	88.2
30	65	34	323	295	91.3	353	315	89.2
				Avg.	92.3			90.5
				***GRAND AVG.	94.9			93.4

* Average Temperature 4" Below Surface of Truck Load
** Rain
*** Used Grand Average

Verglimit has other positive benefits. Because there is a reduction in manpower usage (Figure 3), other problem areas can be covered, thus further reducing possible accidents caused by ice and snow.

SKID DATA

Skid resistance values were determined (in accordance with ASTM E274) the day after placement and are on a monthly monitoring schedule. These values indicate that the Verglimit added asphalt is as good as other Mix I-4 areas (Figure 4).

DISCUSSION OF RESULTS

Visual inspections indicate that Verglimit, during the first winter of operation, performed as indicated by the manufacturer. There was a reduction of icing during ice storms, and in light snow accumulations, the wheelpaths were clear. In heavier accumulations the wheelpaths were mealy in appearance and snow did not adhere to the pavement. Nonadherence to the pavement was true except when conditions of rain to snow existed. This condition has a tendency to flush the surface, causing temporary padding. This is temporary because Verglimit in solution is present in the pores of the roadway and is redistributed by the action of rolling tires. The fact that the

TABLE 4 PERCENT VOIDS

ROUTE 173   MAINTENANCE CONTRACT A-70895   I-4 MODIFIED WITH 5.5% VERGLIMIT
PRODUCER (A) TRAP ROCK IND.-PENNINGTON, NJ   ICE RETARDANT ASPHALT CONCRETE
DATE COMPLETED: MIX NO. I-4   MIX NO.

CORE NO.	LOCATION (POLE)	STATION W.O.S	LANE	OFF SET	DATE CUT	THICK-NESS	BULK SP.GR.	S.I.	AIR 2&3 VOIDS %
1	209	610'	R	9'	10-9-86	2.0"	2.347	2.587	9.3
2	214	1025'	R	6'	10-9-86	1.2"	2.457	2.597	5.4
3	415	1743'	R	8'	10-9-86	1.6"	2.335	2.547	8.3
4	419	1607'	L	5'	10-9-86	1.7"	2.364	2.555	7.5
5	217	1175'	L	4'	10-9-86	1.3"	2.454	2.578	4.8
						B5=			
6	244	531	L	5'	10-9-86	1.8"	2.411	2.604	7.4
					% VOID		AVERAGE		7.1

TABLE 5 COMPARISON OF COSTS OF SPREADING DEICING CHEMICALS

Verglimit (Mix Mod. I-4)	Control Section (Mix I-4)

Labor and Equipment $33.00 Per Hour
                         $ 8.25 Per 15
                                 Minutes
	Labor and Equipment $33.00 Per Hour
	                         $ 8.25 Per 15
	                                 Minutes

Materials (Salt) $30.00 Per Ton
                      $ .015 Per Lb.
	Materials (Salt) $30.00 Per Ton
	                      $ .015 Per Lb.

Spread Rate (Material):
        150 Lbs. Per Lane Mile
2 Lane Miles = 300 Lbs. of Material
	Spread Rate (Material):
	        350 Lbs. Per Lane Mile
	2 Lane Miles = 700 Lbs. of Material

Cost: $ 4.50 in Materials Per Spread
       $12.75 Per Spread (Labor,
              Equipment & Materials)
   For 2 Lanes -
       $12.75 (8 Spread) = $102.00
	Cost: $10.50 in Materials Per Spread
	       $18.75 Per Spread (Labor,
	              Equipment & Materials)
	   For 2 Lanes -
	       $18.75 (40 Spreads) = $749.60

SAVINGS: $647.60 (1986-87 Snow Season) 86.4% Reduction in Cost	
NOTE: Time to Spread 2 Lane Miles: 15 Minutes	

solution tends to stay in the pores can be explained by the specific gravity of the solution, which comes to 1.3 in contrast to 1 for water. Padding also occurred when the AADT became low, but as the AADT increased, traffic broke up this padding. When snow accumulation is light, the AADT can be low and Verglimit will be effective. As the storm intensifies, the AADT must increase. Verglimit requires a minimum of 5,000 AADT to release the additive properly and knead any frozen precipitation on the pavement. On the Route-173 site the necessary

AADT occurred during the morning and evening rush hours; other times of the day the AADT dropped to 1,000 or less. If a storm arrived in between the rush hours, spreading became necessary.

CONCLUSIONS AND RECOMMENDATIONS

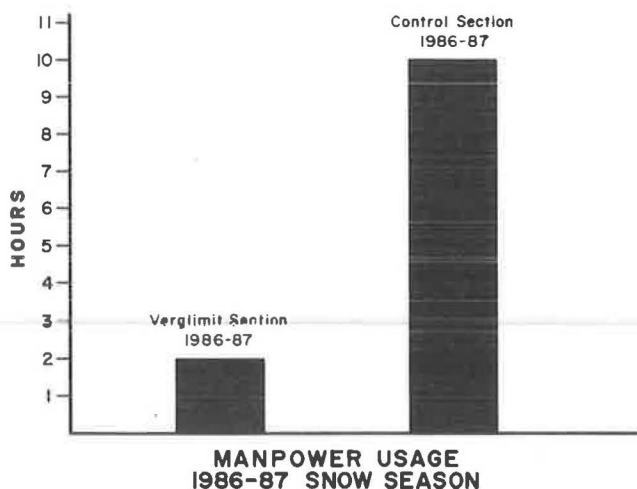• Since Verglimit is hygroscopic, problems with effectiveness occur at or below 27°F. On occasion, ambient

FIGURE 3 Comparison of manpower/equipment usage in spreading operations, 1986–1987 snow season.
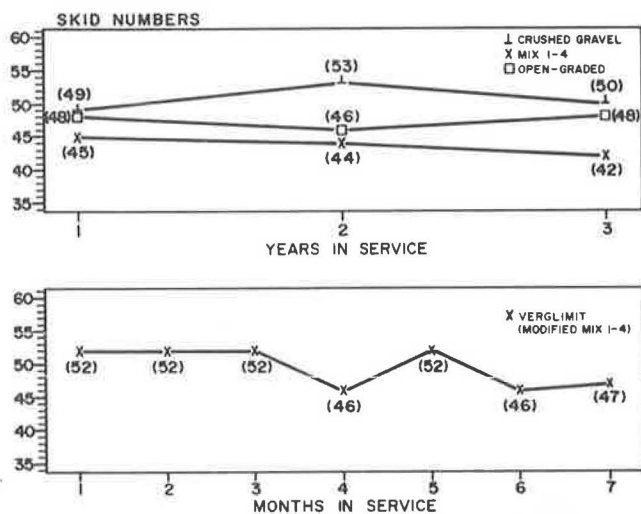

FIGURE 4 Comparison of skid data [average skid number (SN40)].

temperature dropped to 24°F and still functioned. This may have occurred because a brine solution existed on the surface. Another factor was depth of snow (accumulation). Provided there was sufficient AADT, wheelpaths were clear with accumulation up to 1 in. Again, with sufficient AADT, wheelpaths were mealy (offered good traction) in accumulations up to 2 in. It was advantageous to plow at this point, thus reducing the depth of snow on the roadway surface and allowing vehicles to redistribute the Verglimit additive and knead frozen precipitation on the pavement.

• Skid resistance is as good as other Mix I-4 areas (Figure 4).

• Verglimit overlays should be placed in dry and warm weather only. Before paving, the roadway should be dry; placement during rain should be avoided.

• During compaction, the Verglimit flakes at the surface are broken. Since they are hygroscopic, they tend to expand and, along with the linseed oil, create a potentially slippery condition. Skid testing was not done at this point, but on-site evaluation indicates a possible problem. After flushing with

water, skid data taken the day after placement show excellent results (average 50).

At this time, any environmental problems associated by flushing have not been evaluated. According to the producer, however, only 0.5 g/m^2/day is released. This small amount should not pose a problem. Future test sites will be monitored to address this question.

• Angular sand should be rolled into the hot surface with the last roller pass (2 lb/yd^2), and not hand broadcast after compaction. In addition, the pavement should be flushed with water for several days after placement.

• Mixing and placing temperature range is 284°F to 338°F. Because batch plant tests indicate temperatures to 290°F leaving the plant, arrival on the job site 30 minutes later suggests a borderline temperature range placement (Table 3). This may have contributed to the 7 percent voids (Table 4). Verglimit should be in the 3 to 4 percent void range.

• Future monitoring should include
   – Skid testing immediately after compaction, to see if observations of a potentially slippery condition are true (on new installations of Verglimit). Continue to skid test every month.
   – Measuring the ambient temperature to determine the temperature at which Verglimit ceases to be hygroscopic.
   – Measuring snow accumulation to determine how it affects road conditions.
   – Checking AADT on nonpeak hours.
   – Taking core samples to check voids and thickness and comparing with initial samples.

• Though the Verglimit paved area initially received adverse publicity of traffic accidents, after placement only one accident occurred on the Verglimit paved area. This accident may have been caused by the sand which was broadcasted to prevent accidents but acted as rollers instead.

• A Verglimit modified asphalt overlay should not be restricted to the bridge deck parameters; it should be extended to the approaches or beyond. This will eliminate tracking of conventional deicing chemicals onto the deck.

• The placement of Verglimit on bridge decks should reduce corrosion since salting is minimized. Verglimit itself is released at a rate of 0.5 g/m^2/day. Future test sites should include bridge decks to determine if this is true.

• Durability of the pavement is excellent to date, but this pavement has 7 percent voids and is less than 1 year old. Because there is a full-time presence of chloride, the effect on appurtenances, if any, will be monitored.

SUMMARY

Because of the cost, Verglimit is not meant to be used to keep hundreds of miles of roadway free of ice and snow; nor is it meant to replace the regular ice control material, but rather to supplement it. Verglimit should be placed in points of danger, where ice and snow conditions cause accidents. These areas are usually a result of a combination of geographic and climatic conditions (places where there are structures, forested areas, swampy areas, river and stream valleys, steep inclines and declines, mountain cuts, etc.). It should be kept in mind that Verglimit is a continuous ice control; it prevents ice-ups,

thereby buying time to respond to call-outs, and to concentrate on other sections of snow-covered roadways.

ACKNOWLEDGMENTS

REFERENCE

1. Carl E. Minor. Are Hot Mix Tarps Effective? *Information Series 77*, National Asphalt Pavement Association, Riverdale, Md., pp. 3–5.