Laboratory Comparison of Calcium Chloride and Rock Salt as Ice Removal Agents

G. C. Sinke and E. H. Mossner, Chemical Engineering Laboratory, Dow Chemical Company, Midland, Michigan

For ecological as well as economic optimization of highway deicing operations, one must know the relative efficiencies of the two agents most commonly used—calcium chloride and rock salt. Because data on this subject are in conflict, new measurements have been made of the extent to which anhydrous calcium chloride pellets and typical Michigan rock salt undercut a sheet of 0.3175-cm-thick (1/8-in-thick) ice bonded to a concrete block. The extent to which undercutting (the breaking of the bond between ice and concrete) occurred as a function of time and temperature was followed by adding a dye to the chemical, which caused the brine formed by melting ice to fluoresce under ultraviolet light. Commercial anhydrous calcium chloride pellets have a relatively narrow particle size distribution and are very uniform in action; reproducible data could be obtained. However, the action of rock salt was found to be strongly affected by wide variability in size and purity of individual particles. After the action of two particle sizes of pure fused sodium chloride was measured, a reasonable estimate could be made of the average action of a typical commercial Michigan rock salt. The results are presented as a table of the quantity of chemical per unit area required to completely undercut the ice sheet as a function of time and temperature. Rock salt is about equal to calcium chloride above -3.89°C (25°F) for 1 h. As temperatures are lowered and times are shortened, increasingly larger relative quantities of rock salt are required. This must be considered an ecological concern.

A recent comprehensive review of the state of the art of deicing highways by chemicals reported that "calcium chloride, sodium chloride, and their mixtures offer, within certain limitations, the best combinations of useful physical properties and reasonable cost" (1). Sodium chloride (as rock salt) finds the largest use because of its low cost; calcium chloride ($CaCl_2$) is employed for low temperature conditions where its greater effectiveness justifies its higher price. A recent concern is the relative ecological impact of use of the two chlorides (2). Quantitative comparison of the ice-melting properties of the two chlorides is essential for the overall optimization of deicing operations.

Although calcium chloride is generally rocognized to be more effective than rock salt as a deicer at low temperatures, the exact extent of this advantage is not clear from previous laboratory studies. For example, at -6.67°C (20°F) 30 min after application, Toddie (3) found that anhydrous calcium chloride pellets melted about four times as much ice as rock salt. Under the same conditions, Brohm and Edwards (4) found that calcium chloride melted only 1.5 times as much ice as did rock salt. Dickinson (5) reported that calcium chloride melted only 20 percent more ice than rock salt did. The difference therefore ranges from severalfold to insignificant. These previous studies were carried out by spreading the chemical on a tray full of ice, allowing an interval of time to elapse, and pouring off and weighing the brine produced or determining the loss in weight of the ice. This procedure yields only a single data point per experiment and appears to be difficult to carry out accurately.

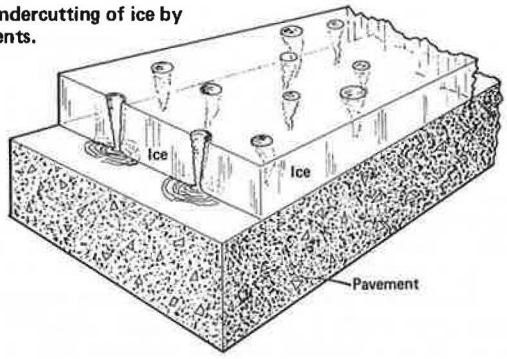
ICE REMOVAL STUDIES

New Technique

In this study, a laboratory method for continuous observation of ice-melting action in a situation simulating an ice-covered concrete highway was used. A particle of chemical when dropped on the ice will melt down through the ice, and the brine will then spread out underneath the ice as shown in Figure 1. This bond-breaking action is the most significant effect of deicing chemicals because calculations show that it would be prohibitively expensive to melt all the ice. In these experiments, a 0.3175-cm (1/8-in) layer of clear ice was built up on a concrete block and the block was placed in a commercial deep freeze unit held at the desired temperature. A small fan in the freezer circulated the cold air to eliminate temperature gradients. Weighed particles of chemical were lightly dusted with a dye, the sodium salt of fluorescein, and loaded into a dispenser in which the particles were isolated in individual compartments. The dispenser was placed over the ice-covered concrete block, and the system was allowed to come to a uniform temperature as measured by thermocouples or thermometers. The dispenser was then actuated by pulling cords passing through the freezer lid. The particles were dropped on the ice, and the dispenser was drawn

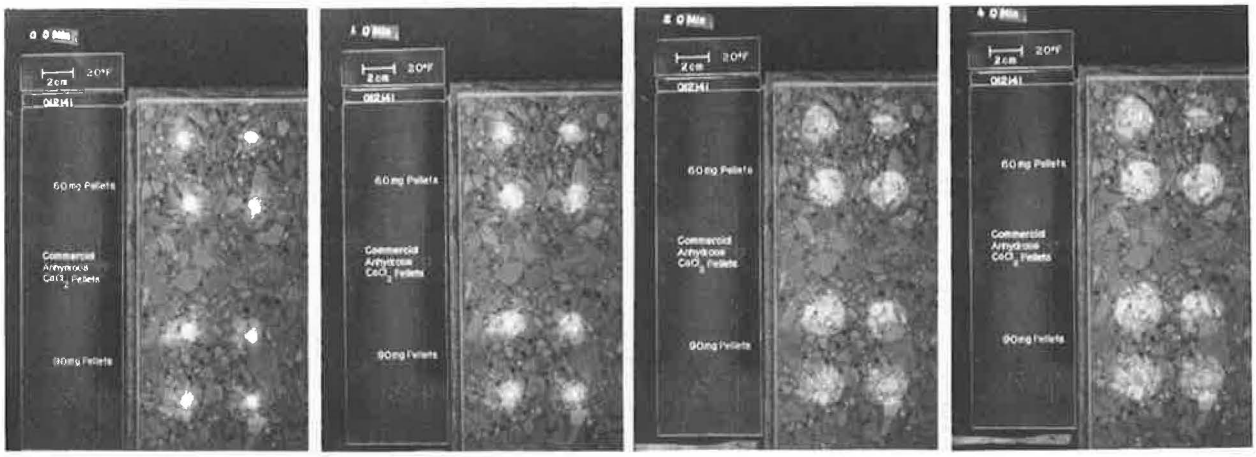
Publication of this paper sponsored by Committee on Winter Maintenance.

Figure 1. Undercutting of ice by chemical agents.



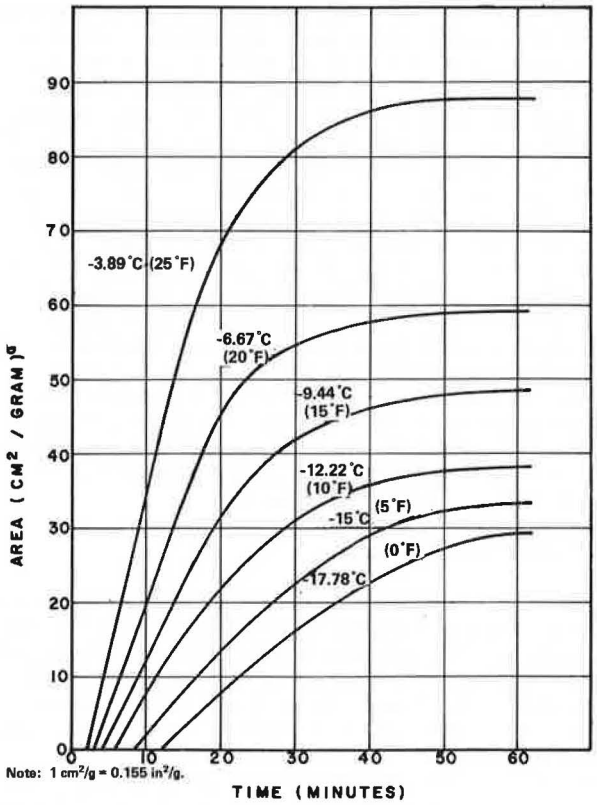
out of the way. As melting action began, the dye dissolved and fluoresced because of an interior ultraviolet light source. The fluorescent brine clearly outlined the extent to which the bond between the ice and the concrete was dissolved. Color photographs of the melting action were taken through a plastic window in the freezer lid at appropriate intervals. Selected photographs from an experiment with anhydrous calcium chloride pellets at -6.67°C (20°F) are shown in Figure 2. Unfortunately, the distinctiveness in melting and undercutting action evidenced is not clearly shown in black and white photographs. The initial hole melted through the ice becomes surrounded by a lighter colored area, which is the thin layer of brine between the ice and concrete. The area

Figure 2. Fluorescent dye technique for measuring undercutting of ice by chemical agents.



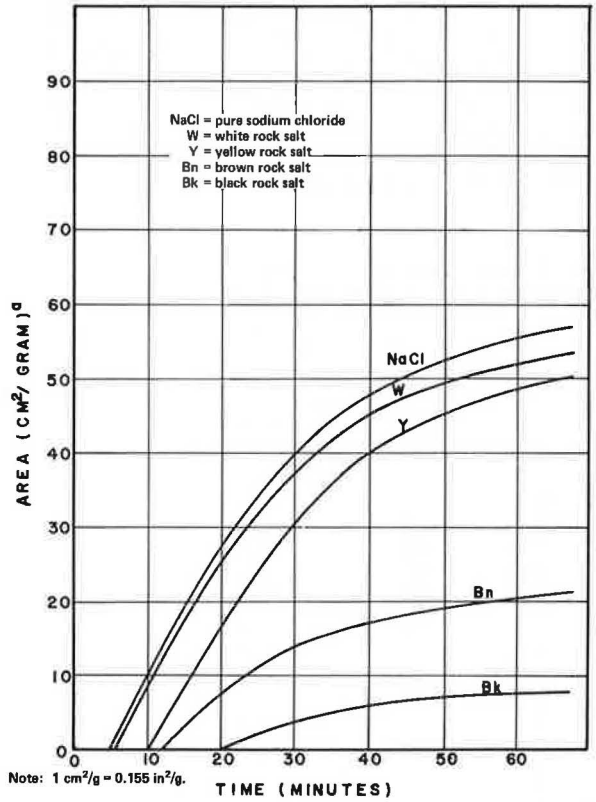
Note: 1 cm = 0.394 in. 1°C = (1°F - 32)/1.8.

Figure 3. Area of ice undercut by anhydrous $CaCl_2$ pellets as a function of time and temperature.



Note: 1 cm²/g = 0.155 in²/g.

Figure 4. Area of ice undercut by 90-mg particles of sodium chloride.



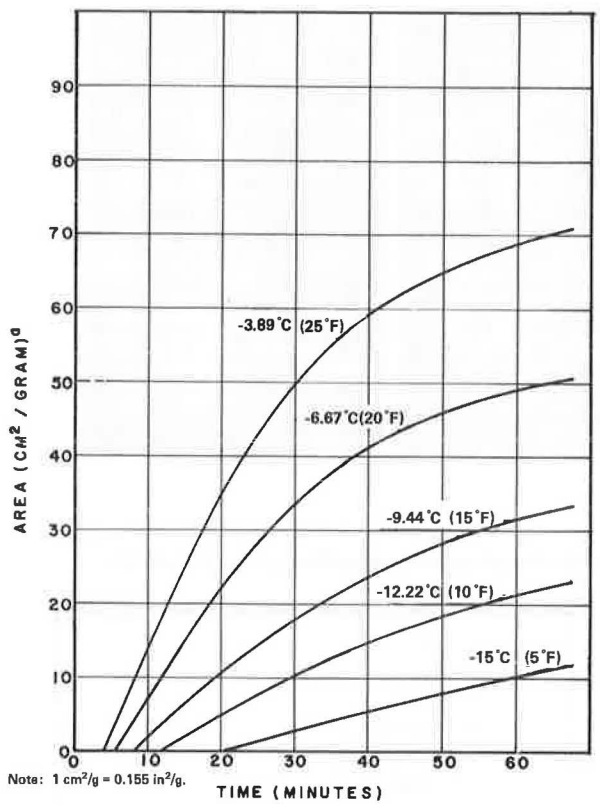
Note: 1 cm²/g = 0.155 in²/g.

undercut by each chemical particle is determined by comparison with the 2-cm (0.79-in) standard length in each picture. The rate at which the ice melts as well as the ultimate area of undercutting can be determined in one experiment at a given temperature.

Calcium Chloride

Experiments on calcium chloride were limited to commercially available anhydrous pellets. The pellets met specifications of ASTM D98 for chemical analysis and grading. Calcium chloride content of various samples was between 94 and 95 percent, and alkali chloride content was between 4 and 5 percent. Particle size was nearly 100 percent passing the 4.75-mm (No. 4) sieve and retained on the 850-μm (No. 20) sieve. About 70 percent was passing the 4.75-mm (No. 4) sieve and being retained on the 2.36-mm (No. 8) sieve. Particles weighing 60 mg were selected as typical and were used to determine the extent of ice melting as a function of time and temperature. The results are shown in Figure 3. After a short period required to melt through the ice, the area undercut increases rapidly and then levels off at a maximum characteristic for each temperature. The maximums relate to each other approximately as expected from solubility data for calcium chloride. The time required to achieve 90 percent of the ultimate action varies from about 30 min at -3.89°C (25°F) to about 1 h at -17.78°C (0°F).

Figure 5. Area of ice undercut by Michigan rock salt as a function of time and temperature.



Note: 1 cm²/g = 0.155 in²/g.

Table 1. Quantity of chemical required for complete undercutting of 0.3175-cm-thick ice.

Time (min)	Temperature (°C)	Quantity (kg/m²)	
		$CaCl_2$ Pellets	Rock Salt
15	-3.89	0.18	0.40
15	-6.67	0.29	0.66
15	-9.44	0.44	1.54
15	-12.22	0.65	4.76
15	15	1.25	—[a]
15	-17.78	3.12	—[a]
30	-3.89	0.12	0.20
30	-6.67	0.18	0.30
30	-9.44	0.24	0.55
30	-12.22	0.32	0.97
30	-15	0.44	3.63
30	-17.78	0.61	—[a]
60	-3.89	0.11	0.15
60	-6.67	0.17	0.21
60	-9.44	0.21	0.31
60	-12.22	0.27	0.47
60	-15	0.30	0.98
60	-17.78	0.34	—[a]

Note: 1°C = (1°F - 32)/1.8. 1 kg/m² = 0.205 lb/ft².
[a]No undercutting by rock salt under these conditions.

Rock Salt

Difficulty was encountered as soon as an attempt was made to develop similar data for rock salt. Particles of Michigan rock salt contain calcium sulfate (anhydrite) in a concentration that, according to Kaufmann (6, p. 322), correlates roughly with particle color. Calcium sulfate dissolves very slowly and greatly inhibits the melting action of the colored particles as shown in Figure 4. Colored particles constitute from 5 to 15 percent of typical samples of Michigan rock salt. Many white particles contain enough calcium sulfate to noticeably slow up their melting action relative to a fused reagent grade sodium chloride that was used as a standard. Because this technique involves only a few particles per experiment, a truly representative sample could not be selected. For the study, measurements were made on a uniformly pure fused reagent grade sodium chloride, and the action of typical Michigan rock salt was estimated to be 90 percent of this standard.

A second difficulty was the selection of a typical particle size for rock salt. Wide variations are allowed by the ASTM specifications for highway deicing salt, and attrition in handling may cause an appreciable change in size distribution. A sample of Michigan rock salt was obtained from a 23-kg (50-lb) bag selected at random from a local supply used for deicing purposes. A screen analysis showed 60 percent passing the 4.75-mm (No. 4) sieve and retained on the 600-μm (No. 30) sieve and 40 percent passing the 9.5-mm (3/8-in) sieve and retained on the 4.75-mm (No. 4) sieve. To correspond with the calcium chloride pellet range, 60-mg particles were selected as typical of the 60 percent fraction and 240-mg particles were selected as typical of the 40 percent fraction. The average action of this sample of Michigan rock salt was taken as 90 percent of the weighted average of 60-mg and 240-mg particles of pure fused sodium chloride. The results for various times and temperatures are shown in Figure 5. At low temperatures, rock salt does not reach its maximum effect in an hour, and at -17.78°C (0°F) no appreciable undercutting occurs in less than an hour.

DISCUSSION OF RESULTS

From this research, one can conclude that at least part of the variation in the data reported in previous studies is due to the inhomogeneity of rock salt. Small samples of rock salt would be expected to vary considerably in purity and particle size. Meaningful comparisons of deicing salts will require careful definition of the actual materials used.

A second factor greatly affecting previous data is the rate of application of chemical. At -6.67°C (20°F), these

data indicate that complete undercutting of the ice sheet will be achieved by optimum distribution of about 0.16 kg/m^2 (0.3 lb/yd^2) of calcium chloride pellets. However, Toddie (3) used a loading of about 0.54 kg/m^2 (1 lb/yd^2), and the Brohm and Edwards (4) loadings ranged from 0.39 to 3.9 kg/m^2 (0.72 to 7.20 lb/yd^2). These high loadings imply that many particles were too close together for maximum efficiency and that, in some cases, the amount of ice rather than the amount of chemical was the limiting factor. At temperatures above about -9.44°C (15°F), differences between calcium chloride and rock salt were overwhelmed by the high load factor.

For example, to undercut 70 cm^2 (10.85 in^2) of ice at -3.89°C (25°F) with 1 g of chemical, calcium chloride pellets would require about 20 min and rock salt would require about 60 min. If 3 g of chemical were used, calcium chloride pellets would require about 8 min and rock salt would require about 14 min. Because the first determination made by Toddie (3) and Brohm and Edwards (4) was at 15 min, the 3-g loading would show little difference between the two chemicals; both would have completely loosened the ice in 15 min.

The current concern over the ecological damage done by highway deicing operations demands that minimum quantities of chlorides be used. The current data permit one to calculate the amount of chloride needed to completely undercut 0.3175 cm (1/8 in) of ice as a function of time and temperature. The data given in Table 1 show that in 1 h at -3.89°C (25°F), only slightly more rock salt is needed than calcium chloride pellets. However, the difference increases rapidly if a shorter time is required or if lower temperatures are involved. Thus, if it is desired to clear the ice in 15 min at -3.89°C (25°F), about twice as much rock salt will be needed as calcium chloride pellets. If plowing or scraping is done at 15 min, much of the excess salt will be thrown to the roadside. Similarly, if an hour is allowed but the temperature is -12.22°C (10°F), about twice as much salt is needed. Although the price differential makes rock salt the cheaper agent even at the two to one ratio, the excess chloride charged to the environment should not be dismissed lightly. The data of Table 1 and Figures 3 and 5 should be very helpful in optimizing deicing operations.

CONCLUSIONS

On the basis of the data obtained in this research, two conclusions can be drawn.

1. Wide variations in previous comparisons of calcium chloride and rock salt are probably due to variations in the purity and particle size of the rock salt. Comparisons are meaningless without careful specification of the rock salt sample.
2. Commercial anhydrous calcium chloride pellets and a commercial Michigan rock salt were found to be about equal in undercutting ice at temperatures above -3.89°C (25°F) and a time of 1 h. For more rapid action or for lower temperatures, the quantity of rock salt required is greater than the quantity required for calcium chloride, ranging to severalfold at -9.44°C (15°F) and 15 min. The data are of value in assessing the ecological impact of the excess rock salt required.

REFERENCES

1. J. Hode Keyser. De-Icing Chemicals and Abrasives: State of the Art. HRB, Highway Research Record 425, 1973, pp. 36-51.
2. G. H. Brandt. Potential Impact of Sodium Chloride and Calcium Chloride De-Icing Mixtures on Roadside Soils and Plants. HRB, Highway Research Record 425, 1973, pp. 52-66.
3. A. J. Toddie, Jr. A Laboratory Study of Ice Removal Utilizing a Circular Track. Univ. of Minnesota, Minneapolis, MS thesis, 1958.
4. D. R. Brohm and H. M. Edwards. Use of Chemicals and Abrasives in Snow and Ice Removal From Highways. HRB, Bulletin 252, 1960, pp. 9-30.
5. W. E. Dickinson. Ice-Melting Properties and Storage Characteristics of Chemical Mixtures for Winter Maintenance. HRB, Bulletin 220, 1959, pp. 14-24.
6. D. W. Kaufmann. Sodium Chloride. American Chemical Society, Monograph 145, 1960.