

Time, Temperature, and Relative Humidity in Deicing of Highways Using Sodium Chloride or Magnesium Chloride with a Metal Corrosion Inhibitor

GOPAL GOYAL, JADE LIN, AND JOSEPH L. MCCARTHY

The ice-melting effectiveness of sodium chloride (SC), "Qwiksalt® + PCI® Granular Reduced Corrosion Road Deicer" (Qwiksalt or QS) and "Freezgard® + PCI® Liquid Reduced Corrosion Road Deicer" (Freezgard or FG) with respect to the removal of ice from highways was studied by laboratory experimentation. QS is a solid consisting of a mixture of SC, magnesium chloride, water, and a lignin-based biodegradable corrosion inhibitor called PCI corrosion control polymer. FG is a concentrated aqueous solution of magnesium chloride and PCI. The rate of melting of ice by salts was investigated by two variants of a "blotter" method in which the aqueous saline solution generated by the melting of ice and dissolving of salt is absorbed onto a tared blotter paper and weighed. The effects of several different conditions of relative humidity, temperature, treatment time, and extent of application of the deicers were studied. Results are reported as grams of saline solution generated per square meter of ice surface and also as estimated net pounds of water generated per lane-mile (63,360 ft²). Some preliminary experiments were conducted to estimate the effectiveness of the preparations with respect to penetration of ice and debonding of the ice-concrete interface. Relative to SC, Qwiksalt generates brine more rapidly during treatment times up to 30 min. Differences are observed especially under conditions of low temperature and low relative humidity, for example, at -18°C and about 5 to 20 percent relative humidity. Freezgard forms brine very rapidly, although less extensively than QS or SC. These new deicers should find many important applications.

For the effective functioning of modern society, reliable and rapid transportation is an essential need. During winter, the highways in some parts of the United States are heavily covered with snow and ice, which may substantially impede travel. Sodium chloride (SC) is often applied to melt ice on highways and thereby to facilitate movement of automobiles and other vehicles. However, this salt is limited in effectiveness at low temperatures and corrodes metal parts of automobiles and bridges, including reinforcing steel members embedded in concrete.

Published literature reporting controlled experimentation designed to determine the effects of variables on the rate and extent of melting of compacted snow and ice by use of salts is small. Detailed methodology has been nearly nonexistent. Keyser has presented reviews of ice melting by salts (1, 2).

Earlier experiments by Kersten et al. (3) and by Brohm and Edwards (4) were conducted at levels of deicer application that were considerably higher than present field practice. Additional investigations were reported by Grant in 1974 (5).

In a 1986 study (6), Schenk evaluated the rates of ice melting by calcium magnesium acetate (CMA) preparations, calcium chloride, and SC by measuring the rates at which pellets penetrate into ice at various temperatures. This might be called the penetration method. In most cases, calcium chloride penetrated more rapidly than did the SC, and both acted more rapidly than any of the several CMA preparations tested.

In 1988, McElroy and Blackburn of the Midwest Research Institute and Hagymassy and Kirchner of the Dow Chemical Company reported the results of three investigations relating to deicers (7-9). One described comparative studies of CMA and rock salt (7). To evaluate extent of melting, a deicer salt was placed on the surface of ice and, at the end a selected treatment time, the sample container was tilted. The solution that formed was collected in a syringe, its volume was determined, and the solution was reintroduced into the melt holes. This might be called the pour-off method.

In a study of effects of wetting rocksalt (8), experimentation was conducted at -4°, -10°, and -15°C (25°, 14°, and 5°F) with rocksalt and with samples of the same rocksalt after wetting with solutions of calcium chloride. The preparations were apparently applied at a rate of 3 oz of rocksalt per square yard of ice surface (about 102 g/m² of ice surface), or about 1,378 lb of deicer per lane-mile (lb/lm) of 63,360 ft². The amounts of solution generated increased progressively with time. The amounts formed were substantially less at lower temperatures. Wetting with calcium chloride solutions caused the sodium chloride to act 10 to 20 percent more rapidly.

In another important paper (9), the authors commented that there were no standard methods available for testing deicer penetration and ice melting capacity when their study was initiated. Using the pour-off method, they found that

- At all temperatures studied, calcium chloride penetrates ice at about twice the rate of the other deicers studied (SC, potassium chloride, and urea);

- SC does not work well at -15°C (5°F), penetrates more slowly than does calcium chloride up to about 45 min, and penetrates at about the same rate thereafter;

TABLE 1 CHEMICAL COMPOSITION OF DEICERS STUDIED^a

Component	SC	QS	FG
NaCl	99.70	80.	0.
MgCl ₂	0.	2.3	25.
PCI	0.	15.	5.
H ₂ O	0.08	2.7	68.1
Other	(b).	(c).	(d).

(a) Analyses were provided by scientists of the the Great Salt Lake Minerals and Chemicals Corp, Ogden, Utah. (b) "Other" consisted of insolubles = 0.03; SO_4^{2-} = 0.10; K^+ = 0.04; Na^+ = 0.02 and Ca^{++} = 0.03; (c) "Other" consisted of the several components of SC which were used to prepare the QS. (d) "Other" consisted of SO_4^{2-} = 1.4, K^+ = 0.2, Na^+ = 0.2 and Ca^{++} = 0.01.

- Urea and potassium chloride are substantially less active than sodium and calcium chloride;

- For ice debonding, the order of preference is calcium chloride, SC, potassium chloride, and urea; and

- Sharp-edged deicers, such as crystals of SC, behave differently than spherical deicers.

The paper included the results of extensive penetration experiments.

In this context, and before the studies of McElroy et al. (7–9) were published, the present investigation was undertaken to compare the behavior of SC with two commercially available deicing preparations. One is a solid called Qwiksalt (QS) that consists of a mixture of SC, magnesium chloride, and water. The other is a liquid called Freezgard (FG) that is a nearly saturated aqueous solution of magnesium chloride. Both preparations contain a lignin sulfonate-type biodegradable metal corrosion inhibitor called PCI corrosion control polymer; the methods used for its preparation and evidence of its effectiveness have been described elsewhere (10). Table 1 gives the composition of each deicer studied.

In view of the difficulty of securing reproducible results in laboratory experimentation with compacted snow, the authors studied the melting of ice only. Experimentation using two variants of the blotter method was conducted to estimate the rates at which the deicers generated aqueous saline solutions under a number of experimental conditions.

EXPERIMENTAL

Materials

The preparations studied were provided by the Great Salt Lake Minerals and Chemicals Corporation of Ogden, Utah.

As soon as they were received in the laboratory, they were stored in closed containers at room temperature. The SC sample originated from the Great Salt Lake and was separated by a process of solar evaporation. The magnesium chloride sample was obtained from the same source by further evaporation and crystallization from the brine. PCI is a product of the Georgia Pacific Corporation and is produced from lignin sulfonates by a process described by Neal (10). QS is made by pressing its components into the form of approximately spherical pellets. The densities of SC and QS were determined experimentally and found to be about 2.17 and 1.97 g/cm³, respectively. The density of FG is 1.28 g/cm³.

In terms of cumulative weight percentages, the distribution in size of particles for the SC sample studied was found to be 1, 84, and 97 for retention on 8, 14, and 20 mesh screens, respectively. For the industrial QS sample, the retentions were 4, 72, and 85. Thus the through-20-mesh fractions amounted to 3 and 15 percent for the SC and QS samples, respectively. A separate QS-2 sample was screened in the laboratory to provide uniform particles within the range of 12 to 14 mesh.

The ice studied was prepared using Seattle city tap water.

Blotter-S and Blotter-Z Procedures

Generally, ice was made by placing water in cylindrical plastic containers, usually 11.5 cm in diameter, which could be covered if desired, and then allowing the open containers to stand overnight in a -10°C cold room. Cold room temperature varied about $\pm 2^\circ\text{C}$. If an ice surface was not substantially smooth, the preparation was rejected.

To carry out the blotter-S or blotter-Z method for estimating the rate and extent of melting of ice, already formed ice samples within their containers, along with previously

weighed masses of the deicers to be studied, were equilibrated, usually overnight, at the temperature and relative humidity (RH) of interest. A test was begun by scattering the deicer uniformly over the surface.

In the "high" RH experiments, the plastic containers were tightly covered immediately after adding the deicer to the surface of the ice and the cover was removed only at the end of the treatment time. By this procedure, the equilibrium vapor pressure of the ice at the experimental temperature (i.e., RH = 100 percent) should have been attained or closely approached soon after starting the experiment.

The "low" RH experiments were carried out in a 61- × 42- × 46-cm "dry box" constructed from sheets of a transparent plastic material about 0.64 cm thick. The front (42 × 46 cm) of the box was penetrated by two circular holes and the ends of the sleeves of two rubber gloves were attached to the periphery of these holes. "Drierite" pellets (anhydrous calcium sulfate containing a blue-pink dye to signify its extent of conversion to the useless dihydrate from Hammond Chemical Company) were spread over the bottom of the dry box and served to create and maintain a low RH level within the box. Humidity was measured by a dial-indicating Cole-Parmer Model 3310-20 hygrometer calibrated by the supplier. Levels of about 10 percent RH (5 to 20 percent) were indicated during the subject experiments. The supplier of the hygrometer was uncertain of the reliability of the instrument at -20°C. However, freshly dried Drierite pellets (3 days' drying at 160°C) were used in the dry box and should have created and maintained the desired low RH levels.

In conducting experiments at low RH, an uncovered sample container, upside down with its exposed surface of ice located close to but not touching the Drierite, was equilibrated, usually overnight, inside the dry box. The weighed deicer, in an uncovered container, and tared blotters stored inside a moisture-impermeable plastic bag (Ziploc; Dow Chemical Company) were also equilibrated overnight inside the dry box at the desired temperature.

An experiment was begun, without opening the dry box, when the experimenter placed his hands within the gloves and scattered the deicer upon the surface of the ice. The experiment was terminated, always inside the dry box, by removing the blotter from the plastic bag, placing it on the surface of the treated ice, letting it absorb the available brine, and then replacing the wet blotter inside the plastic bag. The dry box was then opened for the minimum possible time (20 to 30 sec), the plastic bag and wet blotters were removed, and the box was reclosed. The wet blotters were weighed and the mass of brine collected was calculated in terms of grams of solution generated per square meter of ice surface.

Two variants of the blotter method were used. The blotter-S (for surface) procedure was completed by placing the blotter in contact with the horizontal and upward-facing surface of the ice and maintaining contact for about 10 sec while the brine solution was absorbed on the paper. In a few cases, two or three blotters were used in sequence. The wet blotter was then weighed to evaluate the mass of solution collected.

In the blotter-Z method, the blotter was placed in contact with the ice surface and the container was turned upside down. Then the system was shaken 5 to 10 times with vigorous motion in the vertical plane in an attempt to expel all of the brine through the created pores and onto the surface of the blotter.

Nonvolatile solids present in the solutions studied were determined by drying a weighed sample overnight at 105°C and then reweighing it.

RESULTS AND DISCUSSION

The objective of the present experiment was to evaluate the effects of variables upon the performance of SC and two commercially available deicers, Qwiksalt (QS) and Freezgard (FG). A laboratory-prepared sample identified as QS-2 was also studied. The chemical compositions of these materials are shown in Table 1. The main criteria of performance were taken to be the rate and extent of melting of ice per unit mass of deicer applied.

Variables of interest have been the particular deicer studied, its particle size distribution, the mass of deicer applied, the temperature and relative humidity of the gas phase over the deicer and surface of the ice, and the time of treatment. The effects of heat on melting and dissolving of ice and of heat transfer rates were not taken into special account. Some preliminary experiments were carried out relative to the penetration of ice by the deicer and to the debonding of ice-concrete interfaces.

Estimation of the Extent of Melting of Ice by Salts

At the time this investigation was undertaken, no standardized procedure for measuring the amounts of melting of ice by deicer salts could be found in the literature.

Initially, attempts were made to measure the brine that formed by simply tilting the ice sample container, pouring off the contents, and then weighing the mass of brine generated. When the authors read the papers of McElroy et al. (7-9), they learned that this pour-off method had been used in their experimentation. In the text below, some of their results are compared with those obtained in present work using the blotter methods.

In these experiments, after as much brine as possible had been poured off, it was observed that significant amounts of liquid were still associated with the ice surface. In an attempt to recover this brine, and thus to estimate the extent of the melting accompanied by the deicer, two variants of the blotting paper procedure were devised, blotter-S and blotter-Z. These schemes are discussed below and details are given in the experiment section.

Experiments usually were replicated three or more times. The standard deviation varied with the experimental conditions used. It is estimated that one standard deviation usually was equivalent to about ± 5 percent of the mean value reported.

In the following tabulations, the level of deicer application is stated in terms of grams of deicer per square meter of ice surface and as pounds of deicer applied per lane-mile. Results of ice-melting experiments are reported in terms of the arithmetic mean of the number of grams of saline solution collected per square meter of ice surface. Estimates of the net water generated also are reported in parentheses in terms of pounds of water formed per lane-mile.

Experiments with FG

Because FG is a liquid, its behavior may be discussed advantageously before considering the solid deicers. The blotter-S method was tested as a means for characterizing FG and was found to give results that were reproducible within the range of about 10 percent. The net mass of ice melted was estimated by subtracting the mass of deicer added from the mass of the brine collected.

The effect of time of treatment was considered first (Table 2, Figure 1). Experiments were conducted using a deicer application level of 63 g/m² of ice surface or 818 lb/lm. At -5°C (23°F), the masses of formed solution and water were measured after treatment times of 4, 8, 15, and 30 min. Melting took place rapidly and was mostly completed within about 4 min.

When the temperature was lowered to -10°C (14°F) and then to -18°C (0°F), experimentation showed that the mass

TABLE 2 MELTING OF ICE IN THE PRESENCE OF FG^a

Temp.	Applic.	GSSM/(PWLM) at Time (min)			
		4.	8.	15.	30.
C	GDSM(PDLM)				
R. H. = High					
- 5	63.2 (818)	187. (1598)	200.(1774)	218. (2009)	(b).
- 10 (c)	"	133. (908)	133. (907)	142. (1018)	148.(1096)
- 18 "		96.0 (425)	104. (528)	104. (528)	107. (568)
- 18	126. (1637)	194. (875)	196. (901)	200. (947)	198. (925)
- 18	253. (3273)	391.(1783)	378. (1621)	(b).	(b).
R. H. = Low					
- 10 (d)	63.2(818)	126.(813)	143.(1033)	(b).	(b).

(a) Abbreviations are defined as follows: GDSM = grams of deicer applied square meter of ice surface; PDLM = pounds of deicer applied per lane mile; GSSM = grams of brine solution collected per square meter; PWLM = net pounds of water collected per lane mile; RH = relative humidity; (b) means not determined; (c) For 0.5, 1, 2 and 3 minutes treatment time, GSSM = 98.0, 103.0, 123.0 and 122.0, resp.; (d) For 1, 2 and 3 minutes treatment time, GSSM = 98.0, 123.5 and 124.0, resp..

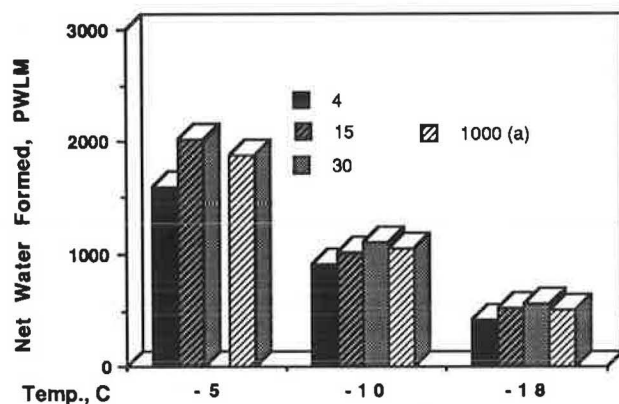


FIGURE 1 Ice melted by FG at 818 lg/lm and high RH versus time and temperature. (a) = estimated maximum PWLM (lb water/lane-mile).

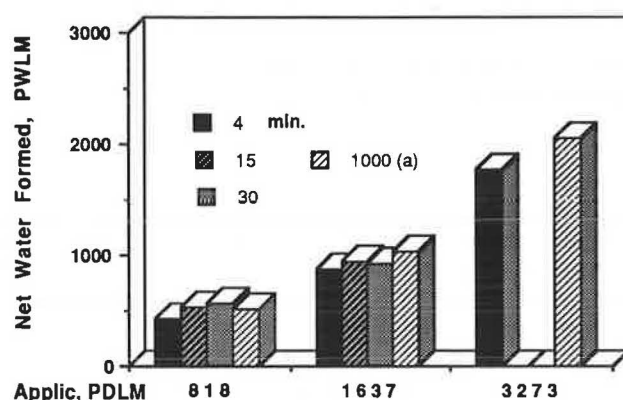


FIGURE 2 Ice melted by FG at -18°C and high RH versus time and application rate. (a) = estimated maximum PWLM. (PDLM = lb deicer/lane-mile.)

of water formed became progressively smaller, about one-half and then one-fourth of that formed at -5°C . At -10°C , about two-thirds of the total melting was completed in 1 or 2 min. Even at -18°C , most melting took place within the first 4 min after the treatment had been started.

When the mass of deicer applied at -18°C was doubled to about 1,637 lb/lm and then doubled again to 3,273 lb/lm (Table 2 and Figure 2), the masses of water produced increased in a similar manner, roughly doubling and then redoubling.

The effect of the RH prevailing in the gas phase above the ice was studied at two levels, "high" (about 90 to 100 percent RH) and "low" (about 5 to 20 percent RH), as described above (Table 2). At an application level of about 818 lb/lm and -10°C , the mass of melted ice was found to be about the same at the low and high RH levels.

Based on the assumption that, during the melting of ice by salts, equilibrium or near-equilibrium conditions exist with respect to the ice and the brine phases, estimates were made of the maximum brine yields attainable. In FG, magnesium chloride, PCI, and water are present to the extent of about 25, 5, and 70 percent by weight, respectively. From the phase diagram (11), it is known that aqueous solutions will contain about 7.8, 13, and 18 percent by weight of magnesium chloride when in equilibrium with ice at -5° , -10° , and -18°C . Assuming that the presence of PCI does not substantially change the solubility relations in the magnesium chloride-water system, the concentrations of nonvolatile solids present in FG solutions have been estimated to be 9.2, 15, and 21 mg per 100 mg of solution, respectively. These values yield multiplying factors of 0.908, 0.85, and 0.79 to provide for calculation of the mass of water present in the brines collected.

From these concentrations, the "theoretical" or maximum yields of brine were calculated. The results are shown in Figures 1 and 2 under the arbitrary designation of treatment time as 1,000 min. It is evident that each calculated result is in approximate agreement with the corresponding experimental finding. Since the latter were evaluated simply by subtracting the mass of deicer added from the mass of the brine collected, the agreement supports the proposition that phase equilibrium prevails, at least approximately, during the melting process and also that the blotter-S method is useful to evaluate the effects of variables with FG.

The authors conclude that FG acts rapidly to complete its full potential, as might be expected to occur with a liquid that comes into immediate and intimate contact with the ice surface. However, the ultimate extent of melting of ice by FG (compared, for example, with that of solid magnesium chloride or sodium chloride) will be considerably lower because FG and similar liquid preparations already contain water as their major component and thus have a correspondingly decreased capability to generate additional water.

Finally, it is important to note that the main concern here is with the magnesium chloride-water chemical system, for which the eutectic temperature is about -31°C . Assuming addition of 818 lb/lm of FG, the above-described calculation procedure was used to estimate the maximum amounts of net water formed at certain low temperatures, 426, 290, and 219 lb/lm at -20 , -25 , and -30°C , respectively. Thus FG can be used to melt ice at temperature levels much lower than is possible with sodium chloride, for which the corresponding and limiting eutectic temperature is about -21°C .

Experiments with SC and QS Using Blotter-S Method

Because QS is composed predominantly of SC, the ultimate ice-melting capability of the two deicers may be expected to be similar. However, it was believed that the rates of melting might differ somewhat as a result of the presence of a coating of magnesium chloride around the QS particles, which is known to be strongly hygroscopic (12) and to provide a low eutectic temperature with water. Also, the PCI added to incorporate its metal corrosion inhibition properties is a good surfactant (10).

In view of the utility found for the blotter-S method in evaluating the effects of variables on the functioning of FG, this procedure was applied in experiments conducted with SC and QS.

With these solid deicers, under most conditions studied, substantially all of the deicer solids rapidly became attached to the surface of the ice and were not taken up by the blotter. However, at low temperature, and especially at low RH and for treatment times less than about 8 min, it was observed that some deicer particles did not immediately form a bond with the ice but became attached to the blotting paper and introduced possible error into the results. These crystals could be observed visually and, as much as possible, were brushed off the blotting paper before it was weighed.

A commercial sample, identified as Qwiksalt or QS, was tested. The particle size distributions found for SC and QS (see experimental section) showed that the crystals or pellets fell mainly in the range of 8 to 14 mesh Tyler screens, although the QS consisted of about 15 percent fines, compared with about 3 percent for SC.

To permit the results to be compared on the same basis, the masses of net water formed were estimated by calculations based on the amount of saline solution collected. The existence of phase equilibrium was assumed and, in a few cases, this proposition was approximately confirmed. The concentrations of the subject salts in aqueous solutions in equilibrium with ice at the temperatures of interest are known from phase diagrams that are available for sodium chloride (13) and magnesium chloride (11).

For SC, neglecting impurities, the concentrations of the solute at equilibrium should be about 8.2, 14, and 21 g of solids per 100 g of solution at -5° , -10° , and -18°C . Thus the net amounts of water generated were estimated by multiplying the masses of brine collected by the factors 0.918, 0.86, and 0.79 for the three temperatures of interest.

QS consists of about 80, 2.5, 2.5, and 15 percent by weight of sodium chloride, magnesium chloride, water, and PCI, respectively. Because magnesium chloride is present in small proportion and because the equilibrium solubilities of sodium and magnesium chlorides are similar, the calculations were made by considering that the total mass of the two salts [i.e., $(100)(0.80 + 0.025) = 82.5$ mg/100 mg QS] behaves as does NaCl. On this basis and at -5°C , 100 mg of QS would generate $(100)(0.825)/0.082 = 1006$ mg solution. PCI, which is a polyelectrolyte with a number average molecular weight of around 3000, is assumed to dissolve in the formed brine without causing a major change in the solubility relationships. Because the PCI mass is $(100)(0.15) = 15$ mg, the mass of the total solution becomes $1006 + 15 = 1021$ mg per 100 mg QS applied at -5°C . The total nonvolatile solids amounts to $82.5 + 15 = 97.5$ mg/100 mg QS. Thus the estimated con-

TABLE 3 MELTING OF ICE IN THE PRESENCE OF SC AND QS^a

Time (min)	SC GSSM(PWLM)	QS GSSM(PWLM)
<u>Temperature = - 5 C (23 F)</u>		
4	148. (1763)	206. (2406)
8	153. (1825)	237. (2762)
15	197. (2341)	266. (3107)
30	296. (3513)	406. (4742)
<u>Temperature = - 10 C (15 F)</u>		
4	111. (1240)	111. (1211)
8	115. (1278)	147. (1602)
15	146. (1626)	185. (2010)
30	159. (1765)	224. (2431)
<u>Temperature = - 18 (0 F)</u>		
4	31.3 (320)	34.2 (337)
8	68.2 (698)	49.9 (491)
15	92.7 (948)	98.3 (967)
30	113. (1160)	120. (1181)

(a) Abbreviations are explained in footnotes to Table 2.

High RH: Application = 57.3 GDSM (745 PDLM)

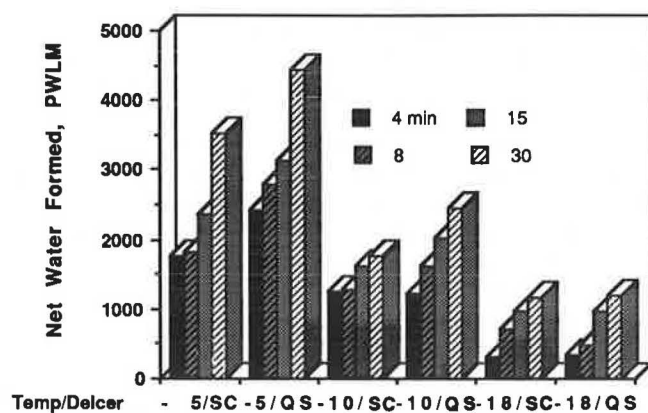


FIGURE 3 Ice melted by SC and QS at 745 PDLM and high RH versus time and temperature.

centration of solids at equilibrium is about $97.5/1021 = 9.8$ mg/100 mg solution. Similarly, for equilibrium conditions at -10° and -18°C , the concentrations of nonvolatile solids in the generated solutions are estimated to be about 16 and 24 mg/100 mg solution, respectively. The multiplying factors for the three subject temperatures are 0.902, 0.84, and 0.76, respectively.

By the use of the blotter-S method, estimates were made of the net water formed after several different treatment times at -5° , -10° , or -18°C (Table 3 and Figure 3) and at high RH with an application rate of about 745 lb/lm. Generally, the water generated by QS was considerably greater than that

generated by SC. With applications at levels of 573, 1,146, and 2,292 lb/lm and otherwise similar conditions (Tables 3 and 4 and Figure 4), the estimated differences are smaller. However, comparisons made at low RH at temperatures of -10° and -20°C (Table 4 and Figure 5) indicated a substantially greater brine-generating capability for QS than for SC.

Reducing SC and QS to a fine powder by grinding them with a mortar and pestle gave deicers that in 30 min generated relatively large masses of water.

Comparison of Results from Blotter-S Versus Blotter-Z Methods

In the course of a preliminary study of debonding of the ice-concrete interface with deicers, it was observed that crystals of SC and pellets of QS may penetrate a significant distance into the mass of ice (see below). Active deicer particles, viewed through the side wall of a transparent plastic container, were observed to form roughly conical or bullet-nose-shaped passages or wells as a result of penetration of the deicer particles downward into the ice. In many cases, the shape of these wells departed substantially from that of a simple cone. Thin, irregularly shaped streamers of brine (made visible by the presence of a red dye with an SC crystal or by the brown color of the PCI in the QS pellet) could be seen extending downward (sometimes 5 to 10 mm or more) from the remaining solid deicer particle, probably as a result of rapid movement of brine downward through the quasi-amorphous regions between the ice crystals.

TABLE 4 MELTING OF ICE IN THE PRESENCE OF SC AND QS: EFFECTS OF APPLICATION LEVEL AND RELATIVE HUMIDITY^a

Time (min)	SC GSSM(PWLM)	QS GSSM(PWLM)
115 GDSM (126 PDLM); High RH; T = -18 C (0 F):		
4	65.5(670)	70.3 (692)
8	137.(1400)	159. (1565)
15	171. (1747)	206. (2027)
30	186. (1898)	259. (2549)
2292 MDSC (2528 PDLM); High RH; T = -18 C (0 F):		
4	137.(1402)	152. (1496)
8	223.(2276)	238. (2342)
Low RH; T = -10 C (0 F); 57.3 GDSM (745 PDLM)		
1	17.0 (189)	33.0(359)
2	30.5 (340)	60.0 (653)
3	71.5 (796)	92.5 (1006)
4	86.5 (963)	117.(1272)
8	109. (1214)	158.(1722)
15	128. (1427)	181.(1969)
30	132. (1466)	198.(2158)
Low RH; T = -20 C (0 F); 573 MDSC (745 PDLM)		
8	17.0 (171)	26.0 (253)
15	27.5 (276)	46.0 (447)
30	42.5 (427)	73.0 (709)

(a) Abbreviations are explained in footnotes to Table 2.

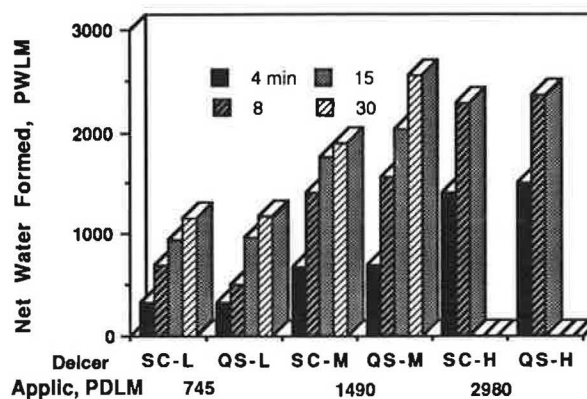


FIGURE 4 Ice melted by SC and QS at -18°C and high RH versus time and application rate.

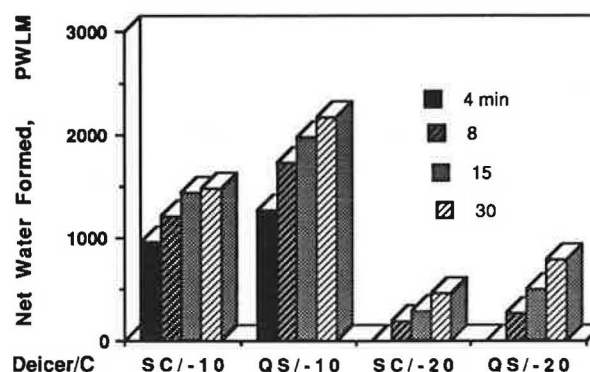


FIGURE 5 Ice melted by SC and QS at 745 PDLM and low RH.

Although the blotter-S method was found to function adequately in the experiments with FG, in which nearly all brine was generated near the surface of the ice, it appeared that the modified procedure, the blotter-Z method, was needed in order to collect the brine generated by the solid deicers, including both the surface and the imbedded liquids.

To complete the blotter-Z method, an ice container was turned upside down and shaken vigorously with a vertical motion to expel the brine from the ice mass "wells" onto a blotter paper for subsequent weighing.

Experimentation showed that significantly more brine was recovered using the blotter-Z instead of the blotter-S method. For example, in quintuplicate experiments with SC at -10°C, 750 lb/lm, and high RH for 30 min treatment time, the S method yielded 175, 190, 196, 188, and 182 g/m² (mean = 186 g/m²); the Z method yielded 284, 290, 322, 314, and 356 g/m² (mean = 313 g/m²).

The authors conclude that the blotter-S method [and very probably the pour-off procedure of McElroy (8) as well] provides mainly for measurement of brine generated on or near the surface of the ice. With SC, a substantial fraction of the brine that forms appears to remain imbedded in the ice and is collected by the Z but not by the S method.

The results obtained by the S method with the particular QS sample studied are believed to be valid relative represen-

tations of the effects of variables on the performance of this deicer. However, the QS results probably cannot be compared directly with the results found for SC, mainly because of the 15 percent fines in QS (versus 3 percent in SC) and the resultant deeper penetration into ice by SC.

Experiments with SC and QS Using Blotter-Z Method

The blotter-Z method was utilized to study the ice-melting characteristics of SC and a Qwiksalt sample identified as QS-2. This sample was narrowly screened in the laboratory to provide particles sized as 12 to 14 mesh. The SC crystals studied were the same as those used in the above-reported experiments, and these particles were sized mainly within the range of 8- to 14-mesh Tyler screens.

Experiments were carried out at -10°C and at both high and low RH conditions using SC and QS-2 applications at a rate of about 745 lb/lm. Measurements were made after treating times of 10, 15, 30, and 60 min. Results (Table 5 and Figure 6) indicate that the extent of melting provided by the two deicers is similar and probably the same within experimental error. If anything, ice melting is slightly higher for SC at high RH but a little lower for SC at low RH.

Both deicers show less melting at low RH than at high RH. These differences are believed to be significant and probably arise because the deicer surfaces interact more slowly at lower levels of RH.

Additional experimentation was conducted at -18° and -20°C and low RH. The masses of ice melted (Table 5, Figure 7) are much less than those found at -10°C .

At these low temperatures and at low RH, the QS-2 sample yielded significantly more melting than did the SC. The authors believe that this difference arises mainly because of the hygroscopic and surfactant properties imparted to QS as a result of its surface layer of magnesium chloride and also of its content of PCI.

In the course of this experimentation at low temperatures, it was found that reproducible results were very difficult to obtain. Two main causes were identified. The ability to maintain experimental temperatures at a sufficiently constant level was inadequate—unavoidable changes in temperature up to $\pm 2^{\circ}\text{C}$ took place in the cold rooms, whereas (as is evident

from the phase equilibrium data) variations of 1° or 2°C may give rise to substantial shifts in the maximum extent of melting, especially at temperatures near the eutectic. The authors also suspect that major variations took place in the characteristics of the ice preparations studied in terms of the form, size, and orientation of the crystals (as judged by viewing untreated ice samples under polarized light) formed under the conditions of rapid freezing (14) that were utilized. In such crystals, quasi-amorphous regions appeared to exist to differing degrees in samples prepared under similar conditions, with the result that imbedded brines were difficult to recover reproducibly.

Generally, the authors conclude that QS brings about rapid melting of ice, especially under conditions of low temperature and low humidity where its rate of action appears to be significantly faster than that of the SC sample studied.

Penetration of Ice by Salts

For salt preparations to be used successfully to debond the interface between ice and a roadway surface such as concrete, the salt must first penetrate through the layer of ice covering the roadway. To examine the rate and extent of penetration of ice by the preparations of interest, preliminary experiments were conducted in which the progress of the salt downward through ice was measured by observing horizontally through the transparent ice the position of the lowest boundary of the

TABLE 5 MELTING OF ICE IN THE PRESENCE OF SC AND QS AT LOW AND HIGH RH USING BLOTTER-Z METHOD^a

Temperature = -10°C (15 F)			
RH	Time (min)	SC	QS-2
GSSM (PDL M)			
High.	15.	284.(3162)	272.(2963)
	30.	306.(3403)	284.(3087)
	60.	326.(3635)	302.(3288)
Low.	10.	216.(2407)	229.(2491)
	15.	224.(2495)	226.(2453)
	30.	226.(2540)	256.(2783)
	60.	253.(2821)	271.(2969)
Temperature = -18°C (0 F)			
High.	15	81.3(837)	74.5(733)
Low.	20.	65.8(673)	97.8(963)
	30.	75.1(768)	97.5(960)
	40.	84.0(859)	122.(1200)
	50.	90.8(929)	126.(1244)
	60.	95.1(973)	134.(1323)
Temperature = -20°C (-4°F)			
Low.	15.	23.7(238)	28.2(274)
	30.	48.8(490)	68.0(660)

(a) Abbreviations are explained in footnote to Table 2.

Application = 57.3 GDSM (745 PDL M)

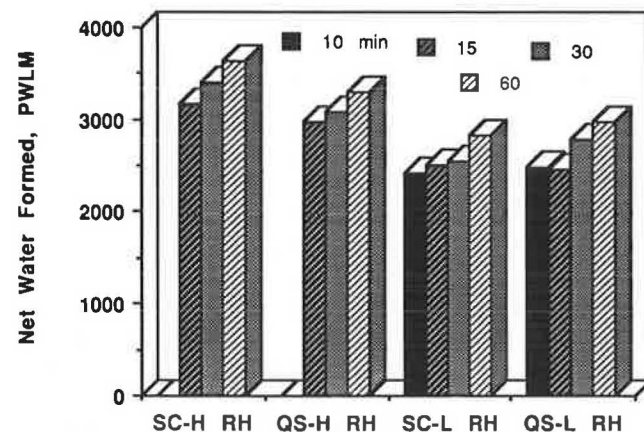


FIGURE 6 Ice melted by SC and QS at -10°C versus time and RH: Z method.

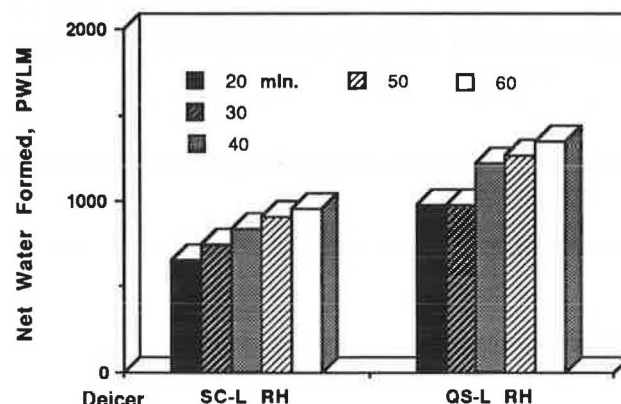


FIGURE 7 Ice melted by SC and QS at -18°C and low RH: Z method.

ice solution that formed with respect to the surface of the ice. The authors later learned that McElroy et al. applied this type of procedure in an extensive study of penetration (8).

The results were useful but not of high precision. For example, at -10°C and high RH with deicer application at a single spot at a level of 57 g/m^2 (745 lb/lm), the depths of penetration after 5, 30, and 60 min were found for SC and QS to be 5 and 4, 28 and 30, and 34 and 36 mm, respectively. Thus the behavior of the two preparations was similar. In general, the extent of penetration should be greater as the size of a deicer particle is increased. Assuming that ice-brine equilibrium conditions prevail and that a perfect cone-shaped well is formed as a particle penetrates into the ice, the following relationship can be derived to model the maximum depth of the penetration:

$$h = (2.165)(4)(r)(R)/(D) \quad (1)$$

where

h = maximum depth in millimeters,

r = radius of a spherical particle,

R = mass of brine generated per mass of deicer applied, and

D = density of formed brine.

Applications of this equation for a sodium chloride particle with $R = 0.77\text{ mm}$ gives depths of 76, 43, and 27 mm for maximum penetration of ice at -5° , -10° , and -18°C . The depth of penetration observed in the experiments was only 10 to 30 percent of these calculated maximum values. This result is probably to be expected in view of heat transfer effects, partial horizontal spreading, and the complex patterns observed as a particle penetrates downward into ice.

Debonding of an Ice-Concrete Interface by Use of Salts

Debonding was measured by observing visually from above the surface and through a transparent layer of ice formed over a concrete surface the extent to which a colored deicing solution spread approximately horizontally over the surface of a concrete slab. QS is already brown by virtue of the presence of PCI; for SC, one small particle of a red dye was added. Experiments showed that the debonded areas closely approached perfect circles in shape. The authors therefore measured mean diameters and calculated the debonded areas assuming perfect circles.

In preliminary experiments, individual particles of SC and QS were placed on ice surfaces. Their rates of penetration downward through the ice and subsequent spreading and debonding of the ice-concrete interface were observed visually as functions of temperature and time. At a rate of 57.3 g/m^2 (745 lb/lm) and at -10°C (14°F), QS and SC penetrated a 2-mm layer of ice and debonded ice-concrete interfaces at nearly the same rates. The areas debonded increased nearly linearly with increases in the mass of the deicer applied.

CONCLUSIONS

The effectiveness of two commercially available deicing preparations was studied and significant characteristics were identified. Relative to SC, the results suggest that QS has an

enhanced capability to accomplish rapid melting of ice, especially at low temperatures and low levels of relative humidity. FG acts rapidly. The challenge now ahead is to determine how best to apply these findings.

ACKNOWLEDGMENTS

The authors are grateful for the financial support provided by the Great Salt Lake Minerals and Chemical Corporation, for the very helpful advice contributed by Grant Braun and Peter Behrens of that corporation and for the helpful suggestions and comments given by John A. Neal and Richard Buchholz of the Georgia Pacific Corporation, Chemicals Division.

REFERENCES

1. M. S. Keyser. De-icing Chemicals and Abrasives; State of the Art. In *Highway Research Record* 425, HRB, National Research Council, Washington, D.C., 1973, pp. 36–51.
2. M. S. Keyser. Chemicals and Abrasives for Snow and Ice Control. In *Handbook of Snow: Principles, Process, Management and Use* (Dx. M. Gray and D. H. Male, eds.), Pergamon Press, Toronto, Ontario, Canada, 1981, pp. 580–612.
3. M. S. Kersten, L. P. Pederson, and A. J. Toddie, Jr. Laboratory Study of Ice Removal by Various Chloride Salt Mixtures. *Bulletin* 220, HRB, National Research Council, Washington, D.C., 1959, pp. 1–13.
4. H. G. Brohm and H. M. Edwards. Use of Chemicals and Abrasives in Snow and Ice Removal from Highways. *Bulletin* 252, HRB, National Research Council, Washington, D.C. 1960, pp. 9–30.
5. C. L. Grant. Some Comparisons of Solar and Rock Salt for Ice Melting. In *Transportation Research Record* 506, TRB, National Research Council, Washington, D.C., 1974, pp. 47–55.
6. R. W. Schenk. *Ice Melting Characteristics of Calcium Magnesium Acetate*. Report FHWA/RD-86/005. FHWA, U.S. Department of Transportation, 1986.
7. A. D. McElroy, R. R. Blackburn, H. Kirchner, J. Hagymassy, and D. Stevens. Comparative Evaluation of Calcium Magnesium Acetate and Rock Salt. In *Transportation Research Record* 1157, TRB, National Research Council, Washington, D.C., 1988, pp. 12–19.
8. A. D. McElroy, R. R. Blackburn, J. Hagymassy, and H. Kirchner. Study on Wetting Salt and Sand Stockpiles with Liquid Calcium Chloride. In *Transportation Research Record* 1157, TRB, National Research Council, Washington, D.C., pp. 38–43.
9. A. D. McElroy, R. R. Blackburn, H. Kirchner, and J. Hagymassy. Comparative Studies of Chemical Deicers. In *Transportation Research Record* 1157, TRB, National Research Council, Washington, D.C., 1988, pp. 1–11.
10. J. A. Neal. *Corrosion Inhibition of Road Deicers*. U.S. Patent 4,668,416 26. 1987.
11. Magnesium. In *Gmelins Handbuch der anorganischen Chemie*, 8th ed. Verlag Chemie G.m.b.H., Berlin, 1937, System Number 27, Part B, p. 114.
12. Magnesium Chloride. In *Encyclopedia of Chemical Technology*, Wiley, New York, 1982, Vol. 14, p. 622.
13. Natrium. In *Gmelins Handbuch der anorganischen Chemie*, 8th ed., Verlag Chemie G.m.b.H., Berlin, 1928, System Number 21, p. 332.
14. W. F. Weeks and S. F. Ackley. *The Growth, Structure and Properties of Sea Ice*. CRREL Monograph 82-1. U.S. Army Engineer Cold Regions Research and Engineering Laboratory, Hanover, N.H. 1982.