Sodium Salts of Carboxylic Acids as Alternative Deicers

DANIEL P. JOHNSTON AND DAVID L. HUFT

Mixtures of the sodium salts of fatty acids with low molecular weight (acetic, formic, glycolic, and lactic) exhibit deicing properties comparable to sodium chloride. They can be manufactured from biomass by reaction with sodium carbonate or made from the acids directly by neutralization with sodium carbonate or sodium hydroxide. Preliminary data suggest that mixtures of sodium acetate with sodium formate may be effective alternative deicers. The only known drawbacks to these deicers are the presence of the sodium ion and their cost. The deicers are readily biodegradable, nontoxic, environmentally acceptable, and mildly or non-corrosive to steel. Tests indicate that the deicers will not cause concrete durability problems. Whether sodium carboxylate deicers truly represent an acceptable alternative to sodium chloride cannot be determined until actual field trials are completed.

In 1980 Dunn and Schenk presented a paper identifying calcium magnesium acetate (CMA) as a potentially effective, noncorrosive substitute for sodium chloride (NaCl) (1). Their paper prompted a spate of research efforts directed at making CMA economical and testing its deicing effectiveness. One of those efforts, which attempted to manufacture CMA from roasted dolomite and sawdust at elevated temperatures and pressures, was undertaken in South Dakota. After several years of work, the effort was abandoned and the research shifted to manufacturing a sodium-based deicer from the reaction of sawdust with sodium carbonate or baking soda.

The deicer produced from this process was primarily a mixture of the sodium salts of acetic, formic, glycolic, and lactic acids; the amount of each carboxylate salt was varied according to the reaction conditions used. Unfortunately, the high temperature and pressures required for its manufacture made this alternative deicer too expensive. Further research was conducted to improve production costs, resulting in a process that created the deicer and a paper pulp by-product, the market value of which was to offset the high production costs. Although tests indicate that the deicer is effective and noncorrosive, efforts to bring it into production have been unsuccessful. A patent was issued for the process in May 1987, but only laboratory quantities of the deicer have been produced.

Investigation of the deicer's properties has often raised more questions than it has answered. Freezing point depression and ice adhesion tests showed that the material could prevent freezing at temperatures as low as -40° C and, if preapplied to a concrete substrate at rates as low as 40 kg/lane-km, that it could also lower the strength of the ice-concrete bond below 100 kPa, the point at which mechanical removal of ice becomes practical.

Further investigation led to an unexpected discovery and a recently filed patent application. Analysis of freezing point depression data for variable composition deicers suggested that certain mixtures of sodium carboxylate salts formed disordered systems with ice and prevented freezing. Since so-dium acetate and sodium formate were the most economical and potentially best deicing salts in the deicer mixtures from the pulping process, a series of dry crystalline solids of variable ratios was prepared and tested for freezing point depression and ice penetration. One composition did not freeze at -38° C and all but one of the sodium acetate-sodium formate (NaA-NaF) mixtures penetrated ice better than NaCl in a comparative test.

ENVIRONMENTAL

Aside from the fact that sodium carboxylate deicers contain sodium and are just as likely to introduce sodium ions into the environment as NaCl, these deicers represent a fairly innocuous environmental threat. They can be considered as generally similar to CMA with regard to toxicity, transport, fate, and effects to the environment. Tests were conducted on the mixed sodium carboxylate deicer to determine tentative values for toxicity and environmental impact (2,3). In comparison with NaCl and CMA (4), the results indicate that sodium carboxylate deicers pose a minimal environmental problem (Table 1).

Although the NaA-NaF deicers have not been tested for toxicity or environmental impact directly, they contain two of the major components in the mixture that was tested and would be used at the same pH/9 to ensure compatibility with concrete. The toxicity of sodium formate is low (LD50 = 11,200 mg/kg), and neither sodium formate nor sodium acetate should pose a serious problem, because both are used as food additives.

CORROSION

The most striking property of the original sodium carboxylate deicer made from sawdust is its inhibition of reinforcing steel corrosion both in solution and in a concrete environment. Tests conducted on No. 3 reinforcing bar tokens in 3 percent solutions of sodium carboxylate, NaCl, CMA, and distilled water showed significant corrosion occurring in all but the sodium carboxylate solution. Another test involved No. 3 reinforcement bars imbedded in ASTM C109 mortar cubes. Groups of three cubes were vacuum-saturated in a 10 percent

Office of Research, South Dakota Department of Transportation, 700 East Broadway Avenue, Pierre, S.D. 57501.

Test		СМА	NaCl	SDD
Oral LD50 (mg/kg)		3150	3750	27000
Skin Irritation		No	Slight	No
Acute Inhalation LC50 (mg/cm ³)		>300	NA	>300
Acute Dermal LD50 (mg/kg)		>5000	NA	Nontoxic
Fish Acute Toxicity LC50 (g/l)		17.5	NA	Nontoxic
Biological Oxygen Demand (rate constant mg//day)	20°C	0.130		0.142
	10°C	0.064		0.092
	2°C	0.020		0.053

TABLE 1 Comparative Toxicity and Environmental Impact

solution of each chemical, allowed to dry for 1 week, and placed in a moisture room at 23°C for 1 week. This cycling was continued until cracks formed in some of the specimens, at which time the cubes were broken to observe the condition of the steel. Half-cell readings of each specimen were taken weekly at the end of each half of the cycle; they correlated extremely well with the corrosion of the reinforcing steel in the specimens. A summary of these half-cell readings for the first four cycles is shown graphically in Figure 1. Neither the control (H₂O) specimens nor the specimens soaked in sodium carboxylate deicer achieved active corrosion half-cell potentials or, on breaking, exhibited any rust. Both NaCl and CMA, on the other hand, had potentials in excess of -350 mV after the wet portion of the cycle, and the reinforcing steel in these specimens was severely corroded.

A major potential problem with any alternative deicer is the possibility of a synergistic enhancement of corrosion in the presence of NaCl, which already contaminates many bridge decks. To determine whether the sodium carboxylate deicer might cause such a response, mortar cubes that contained steel were first saturated with a 10 percent NaCl solution, dried, and then resaturated with the sodium carboxylate deicer or CMA. The results of corrosion testing (Figure 2) indicate that the sodium carboxylate deicer does not interact



FIGURE 1 Steel corrosion in a concrete environment.



FIGURE 2 Corrosion of steel in a concrete environment with NaCl and alternative deicer mixtures.

with NaCl to increase the potential for rebar corrosion. CMA, however, appeared to increase half-cell potentials above the NaCl control.

The proposed NaA-NaF deicer has not been thoroughly tested for potential corrosion problems, but preliminary data indicate that it is mildly corrosive to reinforcing steel at a 3 percent concentration. The corrosion produced is considerably less than that produced by CMA and that produced when sodium acetate and sodium formate were tested separately without pH adjustment. More comprehensive corrosion testing is planned.

CONCRETE DURABILITY

Tests on the effects of the NaA-NaF deicer on concrete durability will be run soon. The literature on the subject is promising: Palmer reported that sodium formate does not spall cured concrete (5), and Grun reported that sodium acetate had no action on concrete (6, p.879). The sodium carboxylate deicer that contains sodium acetate and sodium formate as major constituents did not damage mortar cubes using the method of Stratful (7).

HANDLING

The NaA-NaF deicers are white, crystalline, relatively dense solids that do not tend to dust nearly as badly as CMA. In addition, no free acetic acid is generated from these solids as is from CMA. Solutions of the deicer do have a slight odor of acetic acid at high concentrations, but the overall handling characteristics of these materials should not present insurmountable problems.

DEICING EFFECTIVENESS

Figure 3 shows a comparison of eutectic temperatures for various deicing compounds. The original sodium carboxylate and the NaA-NaF mixture are able to prevent freezing down to -40° C, but the original sodium carboxylate deicer does not have the ice penetration characteristics of the NaA-NaF mixture. Figure 4 illustrates the results of an ice penetration test comparing NaCl with the sodium carboxylate deicer at -3.9° C. The sodium carboxylate deicer is only about 60 percent as effective as NaCl at this temperature, probably be-



FIGURE 3 Freezing point depression of various deicers.



FIGURE 4 Ice penetration of NaCl and sodium carboxylate mixture deicer.

cause of the presence of the higher-molecular-weight salts (lactate and glycolate).

Figure 5 represents a comparative ice melting test that was not done under the rigid environmental control protocol recommended by the Strategic Highway Research Program (SHRP) deicer testing procedures but still reflects the relative ability of these deicer compositions to melt ice. The test was conducted in an upright freezer after overnight equilibration of the ice and chemicals to be tested. Three 0.25-g crystals of each deicer were introduced onto ice formed by freezing 30 mL of distilled water in a petri dish. The temperature of the freezer at the beginning of the test was -25° C; the freezer was opened and the crystals placed onto the ice as quickly as possible. The temperature inside the freezer at the beginning of the test had risen to -19.8°C. After 23 min, the temperature inside the freezer was -24° C, at which time the petri dishes were removed one at a time and the penetration of the ice measured with a micrometer. The NaCl sample was the last to be removed from the freezer. These results do not truly reflect ice penetration characteristics, because the handling procedures undoubtedly contributed to the melting action. Further tests using the SHRP protocol are planned.

Tests of ice bond strength indicate that preapplication of deicer solutions can appreciably weaken the ice-pavement bond (8). Figure 6 shows the typical effect of application rate on the shear strength of ice for one sodium carboxylate deicer. Another mixture actually lowered the ice-pavement shear strength below 100 kPa at an application rate of only 40 kg/ lane-km. Since the NaA-NaF deicer displays similar freezing behavior and appears to form a disordered solid with ice, it should cause a similar bond reduction.

COST

The worst-case scenario for the manufacturing cost of the NaA-NaF alternative deicer using current prices from the *Chemical Marketing Reporter* approaches \$600/ton (9). This is based on \$0.73 to 0.75/kg for acetic acid, \$0.88 to \$0.91/kg for formic acid, and \$0.11/kg for soda ash. Direct manufacture of sodium formate from the reaction of NaOH with carbon



FIGURE 5 Ice penetration of NaA-NaF mixtures compared with NaCl.



FIGURE 6 Reduction in interfacial shear strength between ice and pavement.

monoxide could lower the cost to \$500/ton. Discounts based on acceptable purity, bulk quantities, and other variables could lower the actual cost of manufacturer to somewhere near \$300/ ton. High-purity chemicals are not required to produce acceptable deicing chemical.

CONCLUSIONS

Any alternative deicer that is proposed as a substitute for NaCl will be considerably more expensive than NaCl. Sodium carboxylate deicers, especially NaA-NaF deicers, offer a potential source for alternative deicing chemicals that combine the advantages of mild corrosivity, minimal environmental and toxicity effects, and deicing characteristics similar to NaCl with the disadvantages of high cost and the continued use of sodium salts.

Initial tests indicate that a NaA-NaF deicer can be an acceptable substitute for NaCl, especially in certain critical areas, but further testing of deicing properties, corrosivity, and concrete durability are necessary to obtain a more comprehensive idea of the potential for development.

A field test of the NaA-NaF deicer is necessary to evaluate handling and deicing effectiveness under actual winter conditions.

REFERENCES

- S. A. Dunn and R. U. Schenk. Alternatives to Sodium Chloride for Highway Deicing. In *Transportation Research Record* 776, TRB, National Research Council, Washington, D.C., 1980, pp. 12–15.
- 2. J. A. Roseland. Acute Oral Toxicity of the South Dakota Deicer. South Dakota Department of Transportation, Pierre, 1989.
- 3. S. S. Bang and J. A. Roseland. *Biological Effect of South Dakota Deicer Number 2 on Environment*. South Dakota Department of Transportation, Pierre, 1989.
- G. L. S. Hiatt et al. Calcium Magnesium Acetate: Comparative Toxicity Tests and an Industrial Hygiene Site Investigation. In *Transportation Research Record 1157*, TRB, National Research Council, Washington, D.C., 1988, pp. 20-25.
- 5. D. A. Palmer. Formate as Alternative Deicers. In *Transportation Research Record 1127*, TRB, National Research Council, Washington, D.C., 1987, pp. 34-46.
- 6. R. Grun. Zeitschreift für Angewandte Chemie und Zentralblatt für Technische Chemie (in German), Vol. 51, 1939.
- 7. R. T. Stratful et al. Further Evaluation of Deicing Chemicals. California State Division of Highways, Sacramento, 1974.
- 8. T. Ashworth. A Study of South Dakota Deicer Number 2. South Dakota Department of Transportation, Pierre, 1988.
- 9. Chemical Marketing Reporter. July 27, 1992.