

Formates as Alternative Deicers

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The cost of deicing the nation's road system is roughly 20 times greater than the cost of the salt that is spread. This is due to chloride corrosion, which hits the vehicle fleet hardest. Next hardest hit are the nation's bridges, whose life has been reduced from about 20 to 5 years. Because corrosion inhibitors have proven ineffective, attention has turned to alternative chemical deicers. Though most current government support is dedicated to evaluation of calcium magnesium acetate (CMA), this chemical compound has many technical and economic drawbacks. In fact, CMA might continue to be too expensive to generate much use. At less than half the cost, it may be possible to produce sodium, calcium, or dolomitic lime formates. They can probably be made directly from carbon monoxide, rather than using formic acid. Sodium formate is much less toxic than initially thought. Further, it can probably be spread as a very concentrated solution or even as a slurry. The freezing-point curve of sodium formate is similar to that of sodium chloride down to about -14°C . It has now been demonstrated experimentally that sodium formate does not spall cured concrete.

Maintenance of a workable and safe transportation system is essential to this country's economy. Plowing to remove snow and sanding in icy conditions were the primary tools of winter highway maintenance until the 1950s. Gradually it was discovered that addition of sodium and calcium chloride salts would remove both snow and ice. From 1960 to 1980, salt use in the United States jumped from 2,000,000 to 12,000,000 tons per year (1).

Unfortunately, chloride salts are very corrosive. The corrosion products of iron occupy 2.2 times as much volume (1). The internal pressure of 4,000 psi caused by rebar oxidation is sufficient to crack the concrete. Today, sodium chloride is regarded as the primary cause of bridge failure. Though motorists gain an advantage in the winter, bridge repair is a leading cause of motorist delay and highway maintenance expense at other times of the year. Sodium chloride has reduced average bridge life from 20 to 5 years. The areas where bridges are most corroded are in the Northeast. According to the Environmental Protection Agency, about 100,000 bridges are affected (2). That represents almost one-sixth of the nation's bridge inventory. The replacement cost for those bridges would be about \$900,000,000 in current dollars.

Automotive corrosion is also very severe. In fact, it has been loosely correlated to the amount of salt being used on the roadways (1). The rapid deterioration of our vehicle fleet is the single largest cost of highway desalting. A joint study by the National Bureau of Standards and the Battelle Laboratories concluded that 1975 automobile corrosion costs were about \$12 billion per year (3). Presumably, at least half of that cost is

attributable to salt acceleration. There is no question that today, with car prices much higher, vehicle corrosion is still a major concern.

PREVIOUS RESEARCH ON ALTERNATIVE DEICERS OR CORROSION INHIBITORS

Corrosion inhibitors have been subjected to several large tests. The Illinois Institute of Technology Research Institute (IITRI) found that corrosion inhibitors did retard chloride corrosion. However, the results were marginal, and none of the combinations of salt plus inhibitor gave corrosion rates as low as those with organic salts and no inhibitor. The inhibitors studied included amines, imidazolines, pyrophosphates, polyphosphates, sodium metasilicates, calcium hydroxide, borax, and trisodium phosphate (4). Another study, in 1951, showed that automobile body corrosion was as high in Rochester and Akron, where inhibitors were being used with salt, as in cities where salt alone was used (5).

The ideal deicer would be free or would cost no more than sodium chloride. It would be noncorrosive. It would not spall concrete of any type. It would be nontoxic. It would be nonflammable. It would not harm the environment. It would be nonvolatile. It would have an attractive freezing-point curve. Chemicals such as methanol, which are toxic, volatile, flammable, and harmful to the environment, should be ruled out. From the previous discussion it is clear that chloride chemicals must also be excluded because of corrosiveness.

Freezing-point lowering is a function of the concentration of ions or other species. For that reason, it is advantageous to use molecules that either dissociate into many ions or have low molecular weight, or both. Calcium magnesium acetate (CMA) was recommended in a study carried out by the Bjorksten Research Laboratories. FHWA liked their idea and has placed a great deal of money into CMA research.

Two large CMA research projects were funded with Stanford Research Institute (SRI). Their first effort, biological production of acetic acid from corn grain, was a failure (6). Their idea was to carry out the fermentation in the presence of dolomitic lime to get continuous neutralization of the acetic acid. They eventually concluded that they had been using the wrong organism. Even in their most optimistic economic studies, the cost of their acetic acid was 19 to 27 cents/lb, depending on volume. That represents no improvement over current commercial technology, carbonylation of methanol. (Produced from synthesis gas in the Near East with Monsanto technology and delivered to the United States, acetic acid could cost as little as 15 cents/lb.) Of more significance was the actual production of CMA for research.

SRI manufactured CMA from dolomitic lime and acetic acid, both purchased. The 200-ton sample, which cost about 80 cents/lb, is being used for field tests, primarily in the state of Washington and in other locations. A realistic price of 25 cents/lb plus freight has been quoted by Chevron Chemical Company, which has now begun commercial manufacture.

Washington State consumed half of the SRI sample. They used their regular distribution equipment without modification (7). Three sites were chosen: downtown Spokane on the freeway and two stretches of freeway at the Snoqualmie Pass. They concluded that CMA has a significant advantage when spread just before a snowstorm: it kept the road quite free of snow, even when just a light application was used. It exhibited a number of negative features, however, including the following:

1. CMA is slower to react with snow and ice than are sodium chloride salts.

2. CMA is most useful above 25°F.

3. CMA is very dusty, creating potential safety problems during spreading. Also, personnel moving the CMA had to wear dust masks.

4. CMA has a low density and tends to blow off the delivery truck.

5. CMA tends to cake on the dump-truck bodies and in the chute and spinner assemblies, and the material has to be chipped off.

6. CMA draws frost in areas of previous application. Areas that would normally dry out during daylight hours stay wet and ice up in late afternoon or early morning.

CMA is normally supplied with a bulk density of only 35 lb/ft³. Therefore, it tends to blow off the road, if still a solid, after passage of a few cars. Therefore, W. Rippie of the Iowa Department of Transportation developed a method of coating dark river sand. It is done at the time that the dolomitic lime and acetic acid are reacted to form CMA. The product is heavy and bulky enough (78 lb/ft³) to stay in place on the highway. The dark color also helps promote melting of the ice because of absorption of radiation (8). Nevertheless, the researchers from the state of Washington recommended development of a "hydrated compound of CMA" to solve the stated problems.

The state of Maine produced its own CMA in aqueous solution. This FHWA-supported project planned on using waste acetic acid and dolomitic lime to manufacture the compound. They also observed the dustiness of the dried CMA; however, they only made one application of it. It initially took longer to react than sodium chloride, but persisted for a longer period of time (9).

THE CASE FOR FORMATE DEICERS

It may be premature to focus all development on the acetates as alternative deicers. Formates have been essentially overlooked and merit at least a modest amount of study. Calcium formate was first mentioned in a study by IITRI (4), but that research was possibly missed in the literature survey by the Bjorksten Research Laboratories.

From a strictly theoretical point of view, the formates should be more effective than the acetates. Fewer pounds are needed per equivalent mole of dissolved species. Though formic acid

is just as expensive as acetic acid, formic acid does not need to be used directly. Rather, carbon monoxide can probably be used instead. Its cost would be just a fraction of the cost of acetic acid.

A preliminary freezing-point curve was measured for sodium formate (Figure 1). It is almost identical to the freezing-point curve for sodium chloride, down to about -14°C (+7°F). At that temperature it appears to form a eutectic with water. These preliminary data should be confirmed with more precise measurements. Over the temperature range of interest, this chemical could function almost as well as ordinary road salt. However, that would have to be tested in field trials.

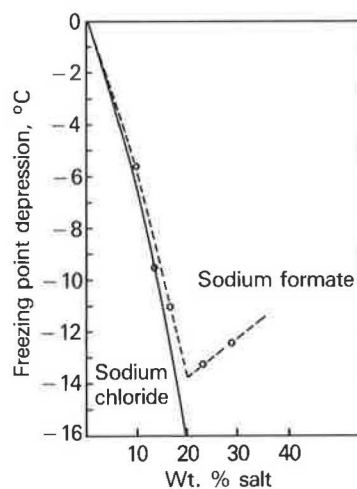


FIGURE 1 Preliminary freezing-point curves for sodium chloride and sodium formate.

One of the very attractive features of sodium formate is its high water solubility. If it is applied at 60°C, its solubility would be approximately 117 lb sodium formate per 100 lb water. This is derived from the somewhat inconsistent data in the literature:

t (°C)	Solubility (lb/100 lb water)
0	44
20	97.2
100	160.

If sodium formate is applied as a solution, there would be no concern over dusting. Also, it is possible that a slurry could be applied, perhaps approaching 250 lb of deicer per 100 lb of water. That would be equivalent to about 133 lb of undissolved deicer per 217 lb of solution.

Another advantage of a sodium formate solution is that it could be used as a deicer at airports. In Chicago, a mixture of urea in ethylene glycol is now used because it can be sprayed onto airplanes as well as runways. Chloride chemicals are not used for deicing at airports because they corrode the aircraft.

United Airlines has indicated by letter that the following technical problems would be of particular interest to them:

1. Composition, particularly of tracts of sulfates, sulfides, and chlorides;

2. Cadmium plate removal;
3. Total immersion corrosion;
4. Polycarbonate craze;
5. Pavement scaling resistance;
6. Slipperiness on concrete and asphalt; and
7. Hydrogen embrittlement of metals.

The Celanese Chemical Company is running tests on these problem areas. The most difficult problem that United Airlines suggested was to have a jet engine manufacturer test the effect on one of their engines of ingesting sodium formate.

Toxicity and environmental effects must be considered. A literature search revealed that acute toxic effects of sodium formate are low; the LD 50 for rats is 11.2 g/kg (nontoxic). Intravenous injection toxicity is also low. The acute toxic effects for calcium formate are moderate; the LD 50 for rats is between 1.9 and 2.6 g/kg. This compound is actually used as a silage preservative and as a food preservative for human consumption. This suggests that regardless of the choice of base, toxicology may not pose a serious problem.

A literature report that calcium formate causes spalling of concrete has been verified at the Celanese Chemical Company. This essentially eliminates calcium formate as an alternative deicer. In a California study, sodium formate was likewise found to cause spalling (10). However, in the Bjorksten study, a similar problem was encountered with CMA. It was traced to application on uncured concrete. Thus, it was thought possible that sodium formate would not spall cured portland cement concrete. Subsequent experiments at Celanese have proven that sodium formate does not spall concrete. It has also been shown that sodium formate does not injure asphalt. It can already be purchased at a price lower than that of CMA from the Celanese Chemical Company.

Celanese has collaborated in two field trials of sodium formate. In Minnesota it was mixed with sand and performed as well as sodium chloride. However, there was some caking due to small particle size. In Ottawa, Ontario, there was another test, but the particles were found to be too small. Celanese will be providing larger-sized particles for subsequent tests.

Overall, sodium formate currently appears to have a bright future as an alternative deicer. It has low toxicity and a very good freezing-point curve. Its good solubility characteristics suggest that it has potential for spreading as a solution or a slurry, as well as dry spreading.

CONCLUSIONS

1. Sodium formate is essentially nontoxic and does not spall concrete.
2. Sodium formate can probably be spread as a saturated solution or slurry. Its high density may make conventional spreading feasible also. However, particle sizes will have to be large.

3. Sodium formate has an attractive freezing-point curve.
4. Sodium formate has no volatility or flammability.
5. Concerns that must be addressed are (a) rapidity with which it reacts with snow and ice, (b) useful temperature range, (c) any caking during dry spreading, and (d) frost absorption.
6. The cost of manufactured formate should be in the range of 7 to 10 cents per pound, based on raw material costs and possible process flowsheets.
7. Some of the technical difficulties with CMA can apparently be overcome with sodium formate.

RECOMMENDATIONS

1. A freezing-point curve should be accurately measured as a function of composition and temperature.
2. A water-solubility curve should be determined for sodium formate as a function of temperature and salt concentration.
3. Other physical properties, such as heat capacity of different solution concentrations, should be studied.
4. The practical questions of sodium formate use should be assessed.

REFERENCES

1. R. Baboian, ed. *Automotive Corrosion by Deicing Salts*. National Association of Corrosion Engineers, Houston, Tex., 1981.
2. D. M. Murray and U. F. W. Ernst. *An Economic Analysis of the Environmental Impact of Highway Deicing*. Report EPA-600/2-76-105. Environmental Protection Agency, 1976. NTIS PB-253268.
3. E. Passaglia and R. A. Haines. The National Cost of Automobile Corrosion. In *Automotive Corrosion by Deicing Salts*, National Association of Corrosion Engineers, Houston, Tex., 1981.
4. D. B. Boies and S. Bortz. *NCHRP Report 19: Economical and Effective Deicing Agents for Use on Highway Structures*. HRB, National Research Council, Washington, D.C., 1965.
5. Corrosive Effects of Deicing Salts (NACE Publication TP-19), *Corrosion*, Vol. 10, 1954, p. 3.
6. C. W. Marynowski et al. *Process Development for Production of Calcium Magnesium Acetate (CMA)*. Report FHWA-RD-82/145. FHWA, U.S. Department of Transportation, 1983. NTIS PB 83-207050.
7. D. D. Ernst, G. Demich, and T. Wieman. Calcium Magnesium Acetate Research in Washington State. In *Transportation Research Record 1019*, TRB, National Research Council, Washington, D.C., 1985, pp. 8-12.
8. M. Sheeler. *Experimental Use of Calcium Magnesium Acetate*. Final Report. Iowa Department of Transportation, Ames, June 1983.
9. M. T. Hsu. Production and Testing of Calcium Magnesium Acetate in Maine. In *Transportation Research Record 962*, TRB, National Research Council, Washington, D.C., 1984, pp. 77-82.
10. R. F. Stratful, D. L. Spellman, and J. A. Halterman. *Further Evaluation of Deicing Chemicals*. California State Division of Highways, Sacramento, 1974. NTIS PB-232890.

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