

## ALTERNATIVE HIGHWAY

### DEICING CHEMICALS

#### I. Objective

To search for chemical alternatives to sodium chloride for highway deicing which will exhibit less harmful side effects.

#### II. Introduction

The well known corrosive effect of sodium chloride (NaCl) upon metals has long begged for replacement of this chemical as a road deicer. It has been demonstrated that this obvious defect is but one of many undesirable results attendant upon the use of NaCl for deicing purposes (1). Accordingly, the present search for viable alternatives was initiated.

Chemical deicing depends upon the general effect of dissolved substances or solutes upon the melting point of the material in which they are dissolved, the solvent. The effect is always to lower the melting point. The amount of lowering is almost solely dependent upon the number of solute molecules or ions present in solution, roughly proportional to this number and almost entirely independent of the nature, size or weight of these solute particles. Thus, low molecular weight materials produce the most freezing point lowering for a given weight dissolved in the solvent. Also, the solubility of the solute determines the degree of lowering it can exert on the melting point of the solvent in which it is dissolved.

##### A. Magnitude of Deicer Usage

In attempting to assess the effects which deicers can have on the environment it is necessary first to get a feel for the order of magnitude of the annual usage.

For example, approximately nine million tons ( $8.16 \times 10^9$  kg) of "salt" or sodium chloride (NaCl) are used for deicing annually in the United States (1). On an equal performance basis, this would require approximately  $9.6 \times 10^6$  tons ( $8.7 \times 10^9$  kg) for ammonium chloride to  $20.4 \times 10^6$  tons ( $18.5 \times 10^9$  kg) for potassium monohydrogen phosphate.

On a smaller scale, current spreading rates vary from 200 to 800 pounds of salt per mile of one lane road estimated at ten feet wide (2, 3, 4). This corresponds to 2.4 acres ( $9.8 \times 10^{-3}$  km<sup>2</sup>) of road surface and therefore, involves 83 to 330 pounds of salt per acre (9.2 to 36.9 gm/m<sup>2</sup>) per application. Repeated applications over a winter result in the spreading of five to 25 tons or more of salt per lane mile ( $2.8 \times 10^3$  to  $14.1 \times 10^3$  kg/lane km) depending upon whether usage is light, moderate or heavy (1, 5). This corresponds to a total expenditure of 4100 to 20,600 pounds or more per acre (0.46 to  $2.3 \times 10^6$  kg/km<sup>2</sup>) of road surface per year.

These figures for salt constitute formidable quantities of material. Most other deicers, however, would be required in substantially larger amounts. An equal performance concentration of other deicers could range up to 47,000 pounds per acre ( $5.2 \times 10^6$  kg/km<sup>2</sup>) for heavy application using a high molecular weight deicer.

##### B. Dissipation of Deicers

Once applied, deicers will dissipate in one or more of several modes. Since water

solubility is a sine qua non, all deicers dissipate by solution, dilution and drainage. Drainage may be into streams, lakes or aquifers. For some, this is the only mechanism, e.g., NaCl and calcium chloride (CaCl<sub>2</sub>). Evaporation into the atmosphere can contribute where the deicer is volatile, e.g., organic solvents such as methanol, ethanol or acetone. Volatilization can also take place as a result of decomposition into volatile products. Ammonium carbonate, for example, will dissociate to volatile gases, ammonia and carbon dioxide. In addition, biochemical processes, though somewhat slower, will convert most organic materials ultimately to carbon dioxide and water. Chemical degradation also can cause a deicer component to become incorporated into the soil, as for example calcium or magnesium salts. Ultimately, they will react with carbon dioxide of the air and precipitate as the carbonates.

### C. Effects of Deicers

In general, the deicers currently in use have deleterious effects on road and bridge surfaces and structures, as well as on vehicles, as has been well documented for sodium chloride (NaCl) and calcium chloride (CaCl<sub>2</sub>). In addition, preliminary indications of damage suggest the need for further evaluation of the effects of these materials on the soils, on the surface waters and the lakes and streams into which these waters run, on the ground water, on public water supplies and on the flora and fauna -- including the human population -- with which the deicers may ultimately come into contact. Attention

also should be directed toward the effects of the deicers on underground structures and equipment.

A factor which has received only minimal attention, but which may be of some importance is that of traffic generated spray of sodium chloride solutions (6). This spray has a serious effect on shrubs, trees, and grass along the roadside, especially on the downwind side and on surfaces not covered by snow. It is not clear whether this is a specific ion effect due to the sodium and/or chloride ion; or whether other ions would be equally deleterious. The volatile deicers would presumably be less harmful, since they would eventually evaporate.

For some of the more volatile deicers, flammability could be a problem. For example, solutions of acetone as dilute as 20% in water have a flammability point below 10°C, thus presenting potential explosion hazard through accumulation in underground structures. On the road, after application, however, the low temperatures and high dilution would seem to minimize any risk of flammability. These factors also reduce the rate of volatilization suggesting that even for the volatile deicers, aqueous solution may still be a major method of dissipation in many instances. Exceptions would be prolonged conditions of high winds and/or prolonged below zero temperatures.

### III Preliminary Screening for Deicer Candidates

If the costs of purchasing and applying alone are considered, there is perhaps no other chemical deicer as cost effective

as NaCl. In the long run the net cost of using NaCl or any other deicer, however, must include the associated damages to the natural and manmade surroundings. It is primarily the cost of these types of damages caused by the use of NaCl which provides the economic justification to search for alternative deicers amongst possibilities which may be more costly to purchase than NaCl.

It was the rationale of this investigation that the purchase cost of the replacement might exceed that of NaCl, but that the excesses in this cost must be made up by a lessened negative impact on the surroundings. Murray and Ernst (1) estimated that the damages caused by the use of NaCl as a deicer were over ten times the cost of the NaCl. Thus, for an alternative deicer which is free of harmful side effects to the surroundings, there is considerable latitude insofar as the purchase price is concerned.

In this study, all combinations of chemical elements were evaluated as potential chemical deicers. Most elemental combinations or compounds were quickly eliminated on the basis of general chemical considerations because they are prohibitively expensive, are extremely toxic, are gases or otherwise unsuitable, or are not available in reasonable quantities. Low water solubility, severe corrosivity to metals and concrete, and potentially severe ecological damage, in combination with high cost and substantial toxicity were the basis for eliminating most other potential elemental combinations. Nine elements appeared

to offer hope to produce effective deicer combinations. These elements are hydrogen (H), carbon (C), nitrogen (N), oxygen (O), sodium (Na), potassium (K), magnesium (Mg), calcium (Ca), and phosphorus (P). All chemical combinations of these nine elements were evaluated further.

#### IV Selection of Two Candidate Deicers

More detailed examination of the compounds representing the possible combinations of these nine elements brought about further eliminations. All of the more complex compounds were eliminated because complexity, which increases molecular weight, adds cost thereby, without correspondingly adding to deicing capability. This consideration was particularly important in restricting the number of carbon containing (organic) compounds which had to be considered. The unique capability of this element of forming endless chemical associations with itself has resulted in a listing of literally millions of organic compounds.

All of the practical combinations of the nine elements were scrutinized by a wide range of criteria as exemplified below for the various sodium, potassium and ammonium salts of the carbonates and phosphates. The bases for the conclusions drawn in each case were obtained from the literature when available. Otherwise, laboratory determinations such as solubility, flammability, etc. were performed as needed.

The sodium carbonates (i.e.,  $\text{NaHCO}_3$  and  $\text{Na}_2\text{CO}_3$ ) and phosphates are not sufficiently soluble. In addition, the sodium ion in them as well as in NaCl tends to harm the

soil by breaking down its structure. By seeping into drinking water supplies, sodium ion can aggravate hypertension. The corresponding potassium salts are more soluble. Potassium has much the same effect on soil structure as sodium. On the other hand, it also supplies important soil nutritive value.

Potassium carbonate has ample solubility to be a good deicer but is extremely caustic. This problem could be overcome with admixture of a sufficient proportion of potassium bicarbonate. Unfortunately, the latter compound is too insoluble to fulfill this function in a deicer.

The potassium phosphates, though more soluble than the sodium counterparts, are still not sufficiently so to serve as deicers. The pyrophosphate is amply soluble. It suffers from the same drawback as the carbonate, however, causticity. It is also relatively expensive on an equal effect cost basis. A further drawback common to all phosphate compounds is their potential for contributing to stream and lake eutrophication.

The ammonium phosphates are barely more soluble than their potassium counterparts. Furthermore, the ammonium ion also contributes to eutrophication, and free ammonia derived from it is toxic to fish in concentrations less than a part per million.

But for this latter drawback of the ammonium ion, the ammonium carbonates would be interesting candidates. They are potentially one of the cheapest deicer systems beside sodium chloride. This deicer system is perhaps unique in that it could be

synthesized on location from liquified component gases, ammonia and carbon dioxide. In the presence of ice or water, these materials rapidly combine giving off enough heat to melt amounts of ice several times the weight of the reactants. The ecological disadvantages of this system are mitigated to some degree by the volatility of the component gases and the tendency of ammonium carbonates to slowly revert to them.

Only a few of the simplest organic compounds required consideration. Alcohols, ketones, glycols, amides, and salts of the acids and a few miscellaneous compounds were explored. Most of these, being very soluble in water, had wide temperature ranges over which they were effective. In most cases they were of modest toxicity, relatively non-corrosive and generally not particularly harmful to the environment.

The main consideration in differentiating among organic deicer candidates came in cost effectiveness. Theoretical estimates of this factor showed methanol by far to be the most economical of the organic deicers in production. Similarly, any deicers which could be produced from waste material with some degree of efficiency might be a candidate.

Fulfilling these latter conditions are the acetates and the salts of other low molecular weight acids. These can be made from waste cellulose by alkaline fusion and other processes. Cost effectiveness and other advantages were seen to be attainable by utilizing calcined dolomitic lime for the conversion of the acids to salts. The resulting product is primarily a mixture of calcium and magnesium acetates (CMA), the calcined lime being

a mixture of hydroxides of these two metals, containing a maximum of 44% of the magnesium hydroxide.

#### V Evaluation of Selected Candidate Deicers

On the basis of information such as that cited above, two candidate deicers were selected for closer screening: methanol and CMA. These were examined from a number of points of view: traction, skidding friction, field performance, compatibility with portland cement (p.c.) concrete, asphalt concrete and road paint, and corrosion of the commonly used metals associated with vehicular and roadway construction. [Various combinations of potassium, ammonium, carbonate, phosphate and pyrophosphate ions were also examined with respect to corrosion.]

Both of the primary deicer candidates can be produced from cellulosic and other types of organic waste by means of high pressure, high temperature technology involving producer gas as an intermediate (7). Methanol is currently produced in large quantities by this type of technology; however, starting from natural gas as the raw material. High yields of a clean product (over 99% pure) are obtained. Methanol of this description was used in all of the tests described below.

In addition to the above producer gas route to acetic acid followed by lime neutralization, there are several potential processes (such as the alkaline fusion process) for producing CMA from waste cellulose (8, 9, 10). However, at the present time no source of calcium and magnesium ace-

tates other than that of the reagent grade chemicals appears to be available. This source was utilized for the small scale laboratory tests alluded to above and for the five month corrosion test mentioned below.

The preferred alkali fusion process is in the laboratory stage of development. Accordingly, only small amounts of CMA were made via this route and they were used in the laboratory traction tests. Instead of leaching the CMA out of the reaction product and crystallizing it, the reaction product was used in an as-is condition for some of the traction tests. This unextracted material was designated "calcium magnesium acetate reaction product," CMARP, CMARP is of interest because of its abrasive character and because it probably would be cheaper to produce than CMA. The CMA content of the material produced in this instance was only 9%. It is reasonably certain that the process could be improved to produce a much higher assay product. The insoluble components are the calcium and magnesium carbonates and oxalates. The oxalates are gradually converted to the carbonates by oxidative processes.

For all other purposes, particularly the road test, CMA was prepared by reacting equimolar mixtures (44% magnesium hydroxide) of mortar grades of the solid hydroxides or calcium and magnesium with the equivalent double molar mixture (64.5% of total weight) of technical grade glacial acetic acid. In the absence of the developed cellulose process, the neutralization proved to be an economical method for producing the amounts of CMA required for field

testing. It merits consideration for this purpose until the waste cellulose process can be inaugurated at the pilot level.

The reaction is rapid and simple and results in a 100% yield. The raw materials cost is dictated primarily by the cost of acetic acid. Acetic acid represents 64.5% of the raw material weight; and the only other ingredient, calcined dolomitic lime, is only a penny or less per pound -- \$5 to \$10 per ton. The raw material cost based on prices contemporary with the Murray and Ernst report is \$0.11 or \$0.12 per pound (\$0.24 or \$0.26 per kg) of CMA depending upon whether the magnesium is taken as it comes in dolomitic lime or purchased separately (1).

#### A. Laboratory Tests

##### 1. Braking Traction and Skidding Friction

A device was constructed for and measurements were made of braking traction and skidding friction of a small rubber tire on ice and on densified snow with and without deicers CMA and NaCl. These measurements were then compared with similar ones made using the British Portable Tester (BPT). The BPT results of course are comparable only to the skidding friction measurements taken on the wheeled device. Tests were carried out at temperatures ranging from  $-1^{\circ}\text{C}$  to  $-30^{\circ}\text{C}$ . Other variables examined were deicer concentration, deicer residence time, wheel speed and vertical loading.

As anticipated, coefficients of traction and friction increased with decreasing temperature, braking tractions significantly exceeded skidding friction; and both NaCl and CMA decreased braking traction and skidding friction.

The reaction product of a laboratory alkali fusion which had not been extracted and separated from byproducts of the reaction, CMARP, was also traction tested. This reaction product, as mentioned previously, contained about 9% CMA, the remainder being insoluble byproducts chiefly calcium and magnesium carbonates together with some oxalates.

CMARP was tested on the BPT and found to exhibit higher readings (coefficients of skidding frictions) than plain ice or ice treated with CMA or NaCl. This result was undoubtedly due in part to the low content of CMA and in part to the insolubility of the byproduct impurities.

The utility, even superiority of the unpurified CMARP relative to CMA, represents a simplification in production, with probable materials cost benefits.

##### 2. Wet-Dry Tests on Reinforced Concrete

Reinforced concrete slabs were exposed to candidate deicers under alternate wet and dry conditions over a period of nine months. Each of the solid deicers was initially applied as solutions at concentrations one-half and one-quarter of saturated, designated NaCl/2, NaCl/4, CMA/2 and CMA/4. Methanol was employed at 50% and 25% by volume in water, MeOH/2 and MeOH/4. Deionized water was used as a control. Each of the seven test environments was replicated three times for a total of 21 slabs. Each slab was poured around two reinforcing bars.

The corrosion of the rebars was followed by periodic resistance measurements on a steel wire embedded between and parallel to the two rebars in each concrete slab. Increased resistance was not observed except

with three of the six NaCl treatments. When the slabs were broken open, all NaCl treated samples had corroding rebars. No other rebars were corroded except for one CMA sample located next to an NaCl slab. The corroded area of this rebar had a chloride ion over ten times that of the normal concrete. It is probable that this chloride was the result of spillage from the adjacent NaCl slab and that the corrosion noted was due to this chloride contamination.

The upper surfaces of the concrete slabs were essentially unaffected by the water and the methanol treatments. All of the sodium chloride treatments produced a generalized roughening of the surfaces of the concrete, exposing a substantial amount of aggregate surface. This attack was at the surface only and apparently unrelated to NaCl concentration.

The high concentration of CMA treatment produced deeper scaling of the concrete surface of samples of two replicates. The low concentration of CMA treatment produced a similar effect in one replicate. There evidently were differences in the quality of the three batches of concrete which comprised the three replicate series of slabs. The CMA damage, however, is believed to be due to the low pH to which the CMA was adjusted for these tests.

Aqueous solutions of CMA are normally slightly alkaline (pH approximately 9). The solutions in these tests, however, were all adjusted to pH=7, for the sake of uniformity. An appreciable proportion of acid is necessary to achieve this alteration of CMA solutions. It would be surprising indeed if this acid did not react with the minute

clusters of calcium hydroxide crystals which ordinarily form with continued curing and which set the very alkaline pH (approximately 13) environment within the labyrinthine polycrystalline network constituting the structure of p.c. concrete.

In time this reaction of the acid with the calcium hydroxide will lower the pH environment of the cement. Such a shift could alter the stability of the crystal structure and the strength of the cement. CMA, whose pH has not been so adjusted, would not possess this capacity to neutralize the calcium hydroxide in the cement.

It is clear that these tests should be repeated with unmodified CMA.

### 3. Freeze-Thaw Deicer and Immersion Tests

Triplicate slabs of p.c. and asphaltic concrete, each painted with a stripe of yellow highway paint, were subjected to similar deicer treatments involving 50X24 hour cycles of freezing and thawing. These tests revealed little differences. Methanol did appear to remove asphalt from some of the surface aggregate of the asphaltic concrete, and it was observed that some of the NaCl solutions mildly attacked the paint on the p.c. concrete samples.

Although in both cases the attack was slight, nevertheless, repetition of the experiments on a more extensive scale would be justified.

Cylinders of p.c. concrete and asphaltic concrete striped with yellow highway paint were partially immersed in solutions of deicers for a period of 170 days at room temperature. The solutions tested were 25% and 50% methanol, one-fourth and one-half saturated NaCl and CMA and deionized water.

The most dramatic and unexpected effect of this study was the softening of the paint strips on the p.c. concrete cylinders immersed in NaCl. The paint became so soft that it could be removed with a gentle wipe of a paper towel. The paint also softened for several inches above the surface of the NaCl solution. All four NaCl treated paint strips exhibited this behavior, whereas no other treatments produced this softening. Interestingly, this damage by NaCl did not occur with the asphalt concrete cylinders. Such attack was observed to a less dramatic degree in the freeze-thaw studies of NaCl solutions described earlier.

#### 4. Metal Corrosion Tests

Deionized water and solutions of CMA, methanol and NaCl of the same concentrations described above (and also saturated CMA and NaCl) were tested for corrosive effect upon A-36 steel, 6061-T3 sheet aluminum, A-3560 cast aluminum and zinc in three series of tests ranging from three weeks to five months duration. As anticipated, the NaCl solutions showed severe corrosion in most cases, the exception being the sheet aluminum, where its corrosion compared to that of water.

CMA showed corrosion rates equal to or less than that of plain water. In the five month test on steel, CMA corrosion rates were two orders of magnitude less than those of plain water. CMA also exhibited significant inhibition of corrosion with cast aluminum.

As anticipated, methanol produced corrosion rates comparable to those of water with zinc and cast aluminum. Its corrosion of steel was less than that of water. But

surprisingly, with sheet aluminum, it exhibited a rate of corrosion greater than those of water and of the other deicer solutions.

Miscellaneous carbonate and pyrophosphate solutions were tested on zinc and the two aluminums over a range of basic pH conditions. They were not tested on steel because it was well known that no corrosion would occur in the basic solutions.

The decidedly basic solutions of the straight tetrapotassium pyrophosphate and potassium carbonate strongly corroded both aluminums. With both metals, the attack diminished in the less basic solutions containing respectively increasing amounts of hydrogen phosphate and bicarbonate. With ammonium carbonate and various mildly basic mixtures with ammonia the two aluminums exhibited little or no attack.

The behavior of zinc contrasted markedly with the two aluminums. It showed slight or negligible attack in the potassium solutions of either pyrophosphate or carbonate regardless of pH. In the ammonium carbonate system, however, it was severely attacked in all but one instance, probably due to zinc ammonia complex formation.

#### B. Field Testing of Candidate Deicers

##### 1. General

Several deicing tests were conducted on two road sites, a parking ramp and one sidewalk during winter months in 1978 and 1979. In each case, candidate deicers CMA and methanol were compared with NaCl as a control.

From these tests it became clear that CMA behaves similarly to NaCl both in rate

of melting and degree of effectiveness. Methanol melts the snow or ice much more rapidly than either CMA or NaCl but is less persistent. It is effective, however, at temperatures well below the operating temperatures of either of the two solid deicers. It appears that CMA could be dispensed from equipment similar to that used for NaCl. Methanol, by contrast, requires fluid handling equipment and it seems to be important to apply it directly on the snow or ice. It does not spread by rebound as readily as the solid deicers do.

## VI Summary and Conclusions

The two selected candidate deicers, as indicated above, were scrutinized from a number of points of view: highway deicing capabilities, handling characteristics, toxicity, metal corrosion, chemical compatibility with nonmetallic highway and bridge materials, effects on flora, fauna and other ecological components, and cost. Both methanol and CMA (calcium magnesium acetate) have compared favorably relative to NaCl in most of these respects and comparably in most of the remaining ones. The performance of the two candidates is summarized below using NaCl as the standard of comparison. Only a few key references have been cited; the final report (FHWA-RD-79-108) should be consulted for further documentation.

### A. Methanol

Methanol exhibits a eutectic (the lowest temperature at which melting can occur) with water,  $-120^{\circ}\text{C}$ , far below that of sodium chloride or any other inorganic deicer candidate. In deicing field tests methanol works much more rapidly and at far lower

temperatures than either CMA or NaCl. Under some conditions, its deicing effect improves with lower temperature. At temperatures above  $-15^{\circ}\text{C}$  and on a short term basis, it performs comparably with CMA and NaCl on an equal osmolar (equal number of molecules or ions) basis. Beyond a few hours, however, more than equal osmolar amounts must be added in order to match the persistence of CMA and NaCl. The methods of handling and dispensing liquids such as methanol, though different, are simpler than those for solids and subject to much finer control.

In only one test series out of six did methanol cause a greater degree of corrosion of a metal (6061-T3 sheet aluminum), than plain water. In one instance out of the same six (A-36 steel) it caused less corrosion than water. By contrast, NaCl caused serious corrosion five out of the six same test series, the one exception being 6061-T3 sheet aluminum, where the corrosion compared to that of water.

Methanol exhibited no adverse effect on portland cement concrete in the test series, one of nine months duration. It gave one instance of minor attack on asphalt concrete, namely the partial uncovering of a number of aggregate particles at sample surfaces in the freeze-thaw test series. Reinvestigation of this result is perhaps merited.

Methanol has been used as an antifreeze for gasoline engines, but was replaced by the glycols because of its relatively high evaporation rate. At snow and ice temperatures volatility is much reduced. The remaining volatility, however, serves to minimize the concentration of methanol in the runoff

and correspondingly, its contribution to BOD. It also facilitates house cleaning, since spills are self removing. Methanol vapor is about 10% more dense than air while gasoline by comparison is several hundred percent more dense. Accordingly, methanol vapor is much less prone to collect in low spots and is much more easily dispersed than gasoline vapor.

The flash point of methanol, 60°F (15.6°C) is nearly 30°F (15.6°C) above the freezing point of water. By comparison, the flash point of gasoline is fifty degrees below 0°F (-46°C). The flash point of an aqueous methanol solution is, of course, even higher than that of the pure material. Fires can be extinguished with water, by contrast to gasoline, because methanol and water are miscible in all proportions. The problem of methanol's flammability appears to be limited to the period of storage and application. Once applied, even puddled on a snow covered road, we have been unable to ignite the material. Obviously, smoking and fires should be excluded from storage and handling areas.

As with all substances, it has toxic limits. But these limits are relatively high, methanol having been cleared as a food additive (11). No ill effects have been found upon prolonged exposure to low concentrations or to short intermittent exposures at high concentrations of its vapors (12). Its label as a toxic substance is due to its occasional misuse as a substitute for ethanol and is unwarranted in the context of its usage as a road deicer. Although it is absorbed slowly through the

skin, a person literally would have to bath in it to produce toxicity by this route. Prolonged inhalation of vapors in an enclosed storage space could create risks; but reasonable aeration should remove this risk. Methanol has very few undesirable environmental properties. It is neutral. It contains no nitrogen or phosphorus, thus contributes nothing to eutrophication problems. Methanol carried into streams and ground water does create an increase in BOD. Its volatility appears substantially to reduce this problem, as already noted. Furthermore, its accumulation from use as a deicer would occur during periods of minimal microbial activity in water with maximum oxygen holding capacity. Therefore, harmful BOD effects of methanol should be minimal or nonexistent.

Air quality may be significantly affected by vapors from methanol applied to roads. The material will gradually break down, however, and its breakdown products are simply water and carbon dioxide. It is true that methoxyl radical is postulated as a part of "the smog chain" of chemical reactions which results in the  $\text{NO}_x$  catalyzed production of ozone in the troposphere. But the significance of this seems tenuous at best.

It would appear that with reasonable precautions, methanol's use as a deicer should pose no significant operational, health, environmental or ecological problems.

Although purchase costs are higher, the total costs, including purchase, application and environmental, highway and vehicular damage associated with using methanol as a highway deicer appear to be less than half those

associated with the use of NaCl (Appendix A).

#### B. Calcium-Magnesium Acetate (CMA)

Late 19th and early 20th century research showed that cellulosic solid waste can be converted to alkaline earth salts of lower carboxylic acids, predominantly acetic, by relatively simple technology and in yields sufficiently large to be interesting. Most of these salts show sufficient water solubility to function as deicing agents. The ice melting ability of such a mixture benefits synergistically from the deicing capabilities of the individual components. The acronym CMA is used to include the minor soluble salts, as well as the two main constituents.

There are cost and other advantages to be gained, however, by omitting the purification step necessary to free these soluble salts from insoluble byproducts which occur during production. The unpurified CMA reaction product, CMARP, contains calcium and magnesium carbonates (and some oxalates) as the insoluble byproducts and can be produced in granular form. The grains can be dark in color, a feature which would enhance insolation and so accelerate melting. The insoluble carbonates and oxalates appear to improve wheel traction as well as skidding friction.

The water eutectics of the two primary components, calcium and magnesium acetates, are  $-15^{\circ}\text{C}$  and  $-30^{\circ}\text{C}$  respectively, thus bracketing that of NaCl ( $-21^{\circ}\text{C}$ ). In road and sidewalk deicing tests CMA performs comparably to NaCl on an equal osmolar basis. On this basis, both salts take effect in about the same time and persist in their effects for similar periods. CMA can be spread

with the same equipment used for NaCl.

Braking traction and skidding friction are decreased by both NaCl and CMA when these deicers are applied at dosages insufficient to melt through the ice. By contrast, a sample of impure CMA made from cellulose without recrystallization of the reaction product (CMARP) improved both braking traction and skidding friction under the same conditions.

CMA, in repeated tests, has shown no significant corrosion of steel, zinc or aluminum. On the contrary, it has exhibited significant corrosion inhibition effects with respect to A-36 steel and A-3560 cast aluminum. By contrast, the current prototype deicer, NaCl, has been observed to significantly promote corrosion of steel and zinc. While reinforcing bars embedded in concrete were consistently corroded in the presence of NaCl during nine month wet-dry tests on reinforcing concrete, those in the presence of CMA were untouched except for a small region accidentally contaminated with chloride ion.

In one of the series of portland cement concrete compatibility tests, several of the samples exposed to CMA solutions showed localized scaling on the surface of the cement. The effect may be related to the fact that the naturally basic pH of CMA had been reduced to neutrality (pH=7) at the start of these tests to match the pH of other test solutions. The attack on the calcium hydroxide in the cement by the reservoir of acetic acid thereby created may have been responsible for the superficial weakening of the concrete in these instances. Con-

sideration of the implications of these acid-base equilibria strongly suggest that scaling would not have occurred had the CMA solution not been acidified at the outset. The effect of NaCl was restricted to a general roughening of the surface of the concrete samples and exposure of a substantial amount of aggregate surface. NaCl solutions appear to foster slow extraction of calcium hydroxide from p.c. concrete.

Neither calcium nor magnesium ion presents any more toxicity hazard than sodium ions. They are less of a hazard with respect to cardiac patients. Acetate ion is a food substance, vinegar, and no more hazardous to health than chloride ion. CMA is mildly basic, however, and minimal skin and respiratory protection against dust would be desirable in prolonged exposures during handling.

Environmentally, the most harmful thing that the calcium and magnesium ions contribute is water hardness. This hardness, on the other hand, would mitigate the low degree of toxicity which high levels of acetate, upon long exposure, can display toward sensitive aquatic life such as trout. However, such high levels of acetate, while conceivable, are not likely to be encountered through usage of CMA as a road deicer.

These salts do not contribute significantly to eutrophication. The acetate is indeed organic, but it is broken down slowly during the cold winter months, which reduces any potential BOD (biochemical oxygen demand) stress. The calcium and magnesium are gradually precipitated as the car-

bonates and thereby removed from solution where their presence might otherwise influence water density and interfere with the turnover of the lakes.

Soils in the eastern half of the United States, where most deicing is done, are deficient in calcium and magnesium. Addition of these nutrient elements to the soil in these areas as through a road deicer could be beneficial. These divalent (doubly charged) cations (positively charged atoms or molecules) tend to improve the structure of the soil where, by comparison, sodium and to a lesser degree other monovalent cations (e.g., potassium and ammonium) tend to cause the breakdown of soil structure. Such breakdown results in a decreased permeability for both water and air, often a serious agricultural problem.

CMA is essentially nonflammable, generally nontoxic and retards corrosion of most metals in comparison to NaCl or even water. The one observation of harmful behavior is probably attributable to improper pretreatment of the CMA. The acidification pretreatment of the CMA rather than the CMA itself, may have been responsible for the greater degree of p.c. concrete scaling noted in one test series relative to NaCl. Rerunning of these tests has been recommended.

Presuming that unacidified CMA will not produce scaling of p.c. concrete, then the total estimated cost of using CMA as a highway deicer, including the cost of all side effects, appears to be less than half that of using NaCl (Appendix A).

## VII Recommendations

(1) It is our opinion that the only question detracting from a predominance of superior properties of CMA over NaCl as a highway deicer is that of scaling attack on p.c. concrete. It is highly probable that the attack would not have occurred had the CMA solution not been acidified so as to bring the pH to neutrality from its natural mildly basic value around 9.

Accordingly, it is recommended that the CMA, NaCl and water wet-dry tests on reinforced p.c. concrete be repeated and extended. The extension would include studies of the interaction of pH on the effect of CMA on concrete, with particular attention to scaling. The degree of solution of calcium by aqueous CMA as well as by aqueous NaCl and water should be followed, for instance, by employing radioactive calcium ( $^{45}\text{Ca}$ ) in the cement. The effects of treatments upon concrete strengths should be measured on the samples studied in this research as well as those in the above projected test series.

These tests should include consideration of the effects of CMA on p.c. concrete which has previously been treated with NaCl as well as on virgin concrete. Effects on corrosion, as well as on scaling, should be followed in the case of the NaCl pre-treated concrete.

(2) The alkali fusion of cellulosic waste materials to produce CMA should be studied from several points of view, first on a laboratory and then a pilot plant scale. The first objective would be optimization of yields using modern concepts and practices of chemical kinetics, e.g.,

fluidized bed heat transfer control of exotherms. A 30% yield would be a first goal, 60% would not appear at this time to be unreasonable.

A second objective would be to study the advantage of isolating the CMA by aqueous extraction and recrystallization versus using the reaction product, with impurities, in an as-is condition. The choice will be somewhat dependent upon the level of yields obtainable in connection with the first objective. This evaluation would naturally include traction testing since presently reported tests indicate some benefits in this respect from the presence of the impurities.

A third objective would be studies on the latitude in choice of cellulosic raw materials which may be used without negatively affecting yields and properties. Materials of interest, of course, would include waste paper, sawdust, wood chips, bark, foliage trimmings, etc.

A final, perhaps implicit, objective is the achievement of the simplest and least expensive technology consistent with the optimization of the above objectives and the determination of scaleup factors which will permit construction of efficiently operable plants.

(3) It would appear to us that in a number of respects methanol may offer important advantages over NaCl as a road deicer. At the same time, its inherent differences raise important questions which bear further investigation.

Methanol's superiority over NaCl below  $15^{\circ}\text{F}$  ( $-9.4^{\circ}\text{C}$ ), for example, is clear enough. However, the optimum method of dispensing it

is in need of better definition. The Connecticut DOT jet dispensing system, used with brine deicer, is an obvious starting point. More passive distribution (i.e., dripping) accompanied by some kind of mechanical stressing of the ice covering is another possibility to be explored. Independently suspended disc cutters or flails are examples of such mechanical stressing.

Studies of these and other techniques directed toward optimum utilization of methanol as a road deicer would appear to be in order.

The solvent nature of methanol plus the one indication of attack on asphalt concrete, although minor, suggests the desirability of further examination of methanol's effect on other organic materials associated with highways and highway vehicles. Important examples of such materials are vehicle tires, car waxes and bridge coatings.

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APPENDIX A

Relative Total Costs of Candidate

Deicers

A prudent buyer is concerned with the hidden, as well as the explicit costs. Given prudence on the part of the taxpayer in the purchase of highway deicing, the effect of deicing chemicals upon vehicular, roadway and other environmental assets will be no less of interest than the costs of purchasing (or manufacturing) and applying the deicer.

The overall cost of a deicer is the sum of three elements: (1) cost of the deicer,  $D$ ; (2) cost of applying it,  $A$ ; and (3) the total cost to the environment of using the deicer,  $E$ . Where the subscript  $N$  is used to represent sodium chloride, a report by D. M. Murray et al(1) has established the approximate relationship between the cost of the chemical and the cost of application.

$$A_N = 0.5D_N \quad (1)$$

The same agency estimated that the cost of the total environmental damage plus the cost of buying and applying NaCl was approximately 15 times the cost of the buying and applying.

$$D_N + A_N + E_N = 15 (D_N + A_N) = 22.5 D_N.$$

In the case of the candidate deicers methanol and calcium magnesium acetate (CMA) evidence adduced in the course of the present work suggests that  $E$  is negligible, any slight disadvantage being offset by the slight advantages.

The parent report provides assessments of purchase costs of candidate deicers relative to that of NaCl for equal effect.

Using subscripts  $C$  for CMA and  $M$  for methanol:

$$D_C = 5.6 D_N,$$

and

$$D_M = 5.5 D_N.$$

The costs of applying the candidate deicers are related to that of NaCl by the weight ratios, for equal effect, times the respective inverse specific gravity ratios. Bulk specific gravities,  $\rho$ , for NaCl, and CMA and methanol are:

$$\rho_N = 1.14$$

$$\rho_C = 0.80$$

$$\rho_M = 0.81$$

The handling characteristics of CMA and NaCl appear to be quite similar. Methanol, as with mobile liquids in general, is easier to handle than a granular solid, albeit the equipment to do so is different.

Ignoring the capital equipment costs which would be associated with switching to methanol and considering operating costs only, the spreading costs are related as follows:

$$A_C = A_N (25/16) \cdot (1.14/0.80) = 2.23 A_N = 1.12 D_N$$

and

$$A_M = A_N (19/16) \cdot (1.14/0.81) = 1.67 A_N = 0.84 D_N.$$

The numbers 25, 19 and 16 are the respective parts by weight of CMA, methanol and NaCl which will melt 100 parts of ice at  $-10^\circ\text{C}$  (see the final report, No. FHWA-RD-79-108).

In summary, the ratio,  $R$ , of the total cost to the taxpayers of the candidate deicer compared to NaCl is:

for CMA,

$$R_C = (D_C + A_C + N_{11}) / (D_N + A_N + E_N) =$$

$$(5.6D_N + 1.12D_N) / (22.5D_N) = \underline{0.30}^*$$

and similarly for methanol,

$$R_M = \underline{0.28}^*$$

\*The savings resulting from the application of these deicers would accrue to the individual taxpayer, primarily due to less environmental and corrosion damage costs resulting from their use. Highway departments might recover limited amounts of these savings possibly by decreased bridge maintenance but would probably have to face increased deicer material costs (approximately five times that of NaCl) when using these materials.

1. Report No. FHWA-RD-79-109		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle Alternate Highway Deicing Chemicals. Executive Summary			5. Report Date March 1980		
			6. Performing Organization Code		
7. Author(s) Dr. Stanley A. Dunn and Dr. Roy U. Schenk			8. Performing Organization Report No.		
9. Performing Organization Name and Address Bjorksten Research Laboratories, Inc. P.O. Box 9444 Madison, Wisconsin 53715			10. Work Unit No. FCP31L9-022		
			11. Contract or Grant No. DOT-FH-11-9100		
12. Sponsoring Agency Name and Address Federal Highway Administration Offices of Research and Development Department of Transportation Washington, D.C. 20590			13. Type of Report and Period Covered Final Report July 1976 to October 1979		
			14. Sponsoring Agency Code M/0634		
15. Supplementary Notes This contractual study is a work unit in Program 1L. FHWA Contract Manager: Dr. Brian Chollar (HRS-23).					
16. Abstract A search has been made for road deicing chemicals to replace sodium chloride (NaCl). The impetus for this search stems from the numerous drawbacks associated with the prevalent use of NaCl as a road deicer. All types of chemical compounds were reviewed. Selections were made on the basis of criteria such as water solubility and freezing point lowering, corrosion, toxicity, relative cost or cost potential, effect on soils and plants and water supplies, flammability, concrete compatibility, traction, friction, highway performance, etc. Information was sought first in the literature, then supplemented or verified in the laboratory as needed.  Two candidate deicers were found to be as effective as sodium chloride. One, methanol, reacts almost immediately upon contact with snow and ice but is less persistent than NaCl. The other candidate, calcium magnesium acetate (CMA), acts at about the same rate as NaCl in the temperature range of common activity and shows about the same persistence. It gives rise to about the same decreases in coefficients of braking traction and skidding friction as NaCl. In strong contrast to NaCl, CMA is a corrosion inhibitor, is beneficial to most soils and has no potential for harming drinking supplies.  The unpurified CMA derived from solid wastes, primarily cellulose, gives improved traction and reduces production costs. The methodology for CMA production, cost evaluated above, is unsophisticated 19th Century technology. Application of modern technology may further lower production costs.					
17. Key Words Deicing, Chemical, Alternate, Sodium Chloride, Calcium Acetate, Magnesium Acetate, Methanol, Waste Cellulose, Dolomitic Limestone, Corrosion Inhibitor, Braking Traction,			18. Distribution Statement No restrictions. This document is available through National Technical Information Service, Springfield, Virginia 22161.		
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