- Vegetation: Various applications of CMA to vegetation by spraying and flooding did not affect the yield, cover, vigor, or rooting of various herbaceous and woody plants. All species tested withstood root zone applications of up to 2500 mg/L. This concentration is much higher than expected from routine deicing treatments. Concentrations of 5000 and 10 000 mg/L reduced yield or killed the plants tested.
- Aquatic biota: Under varying nutrient regimes in laboratory tests, CMA demonstrated the potential to either inhibit or enhance algal growth, depending on conditions and the algal forms involved. Aquatic invertebrates survived and reproduced in the laboratory at concentrations up to 500 mg/L. They were harmed by osmotic stress and low oxygen at higher concentrations. Fish were resistant to CMA in aerated chambers; hatching and survival were high at concentrations up to 1000 mg/L. Experiments in the test ponds, where concentrations never approached these levels, did not yield detectable effects.

On the basis of these findings, and in anticipation of subsequent full-scale verification, the study provided several interim guidelines for CMA's use. It was concluded that CMA was likely to be safe in most situations, with some possible exceptions. In particular, to avoid extreme concentrations of CMA and oxygen loss in natural waters, the study recommended that CMA not be used near poorly flushed ponds, in catchment areas where highway runoff would not be sufficiently diluted before reaching receiving waters, or when large quantities of CMA could drain beneath the ice cover of receiving waters. In addition, to avoid the possibility of heavy-metal mobilization, it was recommended that use be restricted on highways that might have high metal concentrations in roadside soils or that are near protected surface waters and aquifers used for drinking or inhabited by sensitive water life.

The study indicated that full-scale experiments with actual CMA treatments were needed before permanent use guidelines could be developed.

## Other Studies

Several follow-up investigations of CMA's environmental and health-related effects have been conducted during the past few years, including the following:

- Chevron Chemical Company (Hiatt et al. 1988) has studied the short-term toxicity of CMA to humans. Among the tests conducted were oral and inhalation toxicity experiments and eye and skin irritation tests. In addition, highway maintenance workers at several field sites were observed and interviewed after handling CMA. All tests indicated that CMA has low toxicity to humans; however, highway workers at one field site complained of eye and skin irritation. A subsequent investigation indicated that dust exposure levels at the site greatly exceeded the threshold limit for occupational exposure to nuisance dusts, but respirable dust levels were reported to be much lower. The authors concluded that CMA's potential to adversely affect worker health is no greater than that of road salt, but they recommended that standard protective measures, such as exhaust ventilation and dust masks, be observed when working with CMA.
- In work sponsored by the Austrian Federal Ministry for Construction and Technology (Washuttl n.d.), experiments were carried out in laboratories and field plots to determine the effect of CMA on plants. The tests indicated no adverse effects on wheat, rape, and cress. Likewise, high application rates caused no adverse symptoms in exposed spruce, pine, maple, and salt-tolerant shrubs.
- A study conducted in central Alaska tested the effects of CMA on small roadside ponds (Rea and LaPerriere 1986). Three ponds were treated with CMA and three were untreated. The ponds were observed for variations in cation (e.g., calcium, magnesium, sodium, and potassium) concentrations, algal growth, and oxygen levels. Calcium levels were substantially elevated in the CMA-treated ponds, and dissolved oxygen was significantly reduced at times, as predicted by Horner (1988).
- In a follow-up study to Horner (1988), Brenner (1990) compared the effects on surface water of a pure reagent-grade CMA and a CMA product containing organic and inorganic impurities. Results indicated a potential for greater BOD effects from CMA produced from agricultural products than from the reagent-grade CMA, mainly because of the decomposition of organics occurring in agricultural products.
- The effect of CMA on copper and zinc mobility in soils was studied by Elliot and Linn (1987). In tests on acidified (pH 4) soil solutions, CMA initially increased metal mobility; however, this effect was subsequently counteracted by the pH-neutralizing effect of the acetate. On the basis of these findings, the authors concluded that CMA could initially mobilize some soil metals, but that prolonged use would probably inhibit substantial, long-term movement.

- The effect of CMA on soil metals was also investigated by Amrhein and Strong (1990). Roadside soils were collected from around the United States and incubated and leached with CMA and NaCl concentrations likely to be generated by highway deicing. The authors identified three processes that normally cause soil to retain, or immobilize, metals: (a) ion exchange, (b) precipitation from solution with organic compounds, and (c) the formation of complexes with organic matter. Test results indicated that the first process (ion exchange) caused some displacement of trace metals but that the latter two processes offset that effect by impeding metal mobility. As a result, the authors concluded that CMA is likely to have no more effect on metal mobility than NaCl.
- In a study in northern California, water samples were taken from 10 lakes and incubated with various concentrations of CMA to determine effects on phytoplankton growth (Goldman et al. 1990). Eight of the 10 lakes, including Lake Tahoe, showed no significant response in algal growth when CMA concentrations of 0.1, 1, and 10 mg/L were tested. One lake showed a weak stimulation in algal growth at concentrations of 10 mg/L, and one lake showed an inconsistent response, with some growth enhancement at the intermediate concentration of 1 mg/L. The authors concluded that CMA appeared to have negligible effects on phytoplankton growth within the scope of the investigation.
- In a study of CMA's BOD effects sponsored by Chevron (Connolly et al. 1990), experiments indicated that the acetate in CMA degrades rapidly in natural waters. A model of a mixed pond indicated that, for most situations, the use of CMA would have minimal effects on oxygen. The model conservatively assumed no water flow through the pond, no wind enhancement of reaeration, and a CMA-contributing roadway area on the order of one-third the pond area. However, the model did not consider all possible circumstances, such as a body of water in which reaeration is limited by ice cover. The authors noted that under some conditions of ice cover, significant oxygen loss could occur until the ice melts.

## Summary of Health and Environmental Evaluations

The only known effect of CMA on humans is its tendency to create a nuisance dust that may require the use of dust masks and well-ventilated storage and handling areas. Studies indicate that CMA is likely to have negligible effects on drinking water. Because it is biodegradable and exhibits poor mobility in soils, it is less likely than salt to reach groundwater. CMA has demonstrated no detrimental effects on soil compaction or strength, and it may increase the fertility and permeability of some roadside soils. In preliminary environmental evaluations, the potential for CMA to extract heavy metals from soils was identified; however, results from follow-up studies do not indicate this effect.

Neither irrigation nor spraying with CMA has caused detrimental effects in most common roadside plants tested. CMA is apparently safe for use near most aquatic environments, having produced no deleterious effects on organisms representing the aquatic food chain when tested at concentrations likely to be generated by highway deicing. A concern that remains is the potential for CMA to reduce dissolved oxygen levels as it decomposes. Hence, heavy CMA treatments near small, poorly flushed, or poorly diluted ponds and streams may require special monitoring and further study.

These findings may not apply to CMA derived from feedstocks other than reagent-grade chemicals, natural gas, and agricultural products. Alternative feedstocks, such as municipal solid waste and pulp and paper mill biomass, could introduce contaminants that alter its known environmental effects or create new ones.

## COMPATIBILITY WITH AUTOMOTIVE AND HIGHWAY MATERIALS

After preliminary environmental evaluations of CMA proved positive, several studies were undertaken to evaluate its impact on automotive and highway materials. Study results are summarized in the following sections.

### Automotive Components and Materials

The most comprehensive study of CMA's compatibility with automobiles was conducted by Slick (1987) for FHWA. The study compared the effects of CMA and sodium chloride on common automotive parts, components, and materials. Evaluations consisted of a variety of standard experiments, including immersion dips, spray-fog exposures, and electrochemistry measurements. Among the materials and components tested were paints, primers, and undercoatings; exterior adhesives and plastics; tires and rubber; brake linings; and steels, aluminum alloys, and combined metals, such as chrome, aluminized steel, and nickel-zinc coated steel.

Major findings were as follows:

- Paints, coatings, and adhesives: Automotive paints and coatings exposed to CMA exhibited some breakdown, but the same specimens exposed to salt exhibited more severe effects. Neither salt nor CMA affected adhesives.
- Plastics and rubber: Specimens of plastic, elastomers, and lens materials were affected similarly by CMA and salt, as were hardness properties and tensile strengths of rubber compounds and tires.
- Brake systems: Automotive brake linings exposed to CMA displayed better friction characteristics than specimens exposed to salt. In addition, hydraulic brake line tubes exposed to salt experienced more severe corrosion than specimens exposed to CMA.
- Metals: Salt caused more frequent and severe corrosion of automotive steels, aluminum alloys, stainless steels, and combined metals. In particular, pitting and crevice corrosion, which is the principal danger to automotive metals in actual highway conditions, was more prevalent in salt specimens than in CMA specimens.

Results from this laboratory study indicate that CMA is less harmful than salt to most automotive components and materials and much less corrosive to automotive metals. Whether the interactive effects of automobile operating systems and actual highway environments could modify some of these findings has not been studied. The potential for CMA spray to adhere to windshields and body parts, reported by some field users, would probably require further study before more widespread use.

## Bridge and Highway Materials

The preliminary laboratory tests of CMA conducted by Dunn and Schenk (1980a) indicated that it would be less corrosive than salt to steel and most other metals commonly used on bridges and highways. Since the initial tests, several studies have been conducted to verify these findings and further evaluate CMA's compatibility with bridge and highway materials.

### *Bridge Materials*

Bridges contain various applications of steel and metals that are susceptible to corrosion, including expansion joints, gutters, railings, beams, and rebars. A study by the state of Michigan compared the effects of CMA and salt on many of these applications (McCrum et al. 1985). The study consisted of experiments with representative samples of bridge metals (except rebars in concrete), which were exposed to various concentrations of CMA and salt. The results verified earlier findings by Dunn and Schenk (1980a) indicating that CMA was less corrosive than salt. On the basis of weight loss data and general observation, the average corrosion rate of CMA was one-third to one-tenth the corrosion rate of salt for most metals tested. Most CMA specimens exhibited only shallow pitting, compared with deep pitting in salt specimens.

A study by FHWA attempted to determine CMA's effect on rebars in concrete. After comparing reinforced concrete slabs ponded with CMA and salt solutions for 4 years, Chollar and Virmani (1988) found that CMA had no effect on the slabs, whereas salt had significant effects. After 4 years, the slabs ponded with CMA solutions displayed no signs of deterioration, whereas the slabs ponded with salt had many cracks and rust stains. Moreover, whereas the corrosion (electrical) potential of the slabs ponded with salt increased rapidly within the first 3 months of exposure, the slabs ponded with CMA did not show any significant shifts in potential during the 4-year test period.

Additional tests of CMA's compatibility with bridge materials were conducted by Locke and Kennelley (1985) for FHWA. The study consisted of weight-loss and electrochemical measurement tests of bridge metals immersed in solutions of CMA and NaCl. Rebars embedded in concrete (slabs and mortar cylinders) and simulated pore solutions, which were contaminated and ponded with CMA and NaCl, were also tested.

Major findings were as follows:

- Corrosion rates of exposed steel immersed in CMA solutions were one-half to one-fifth those of steel tested in salt solutions, on the basis of weight loss data. The corrosion rates of steel tested in tap water were equal to or slightly higher than those of steel tested in CMA solutions.
- Corrosion of aluminum exposed to CMA was minimal, resembling a passive system. Corrosion rates were $\frac{1}{10}$ those of aluminum exposed to salt, resulting in only slight pitting.
- CMA was much less corrosive to rebars than salt when applied to previously unsalted simulated bridge decks.
- The addition of CMA to simulated pore solutions led to changes in composition, evidenced by a lower pH and a more electronegative

(active) corrosion potential. The authors noted that this effect, if real, might result in an increased rebar corrosion rate when CMA is used on previously salted bridge decks because of the possibility of an increased potential difference between the top rebar mats (exposed to CMA and salt) and lower rebar mats (exposed only to salt).

On the basis of these findings the authors concluded that CMA was likely to be one-half to one-fifth as corrosive as salt to structural steels, one-tenth as corrosive to bridge aluminum, and significantly less damaging than salt to new (uncontaminated) reinforced concrete. They surmised, however, that CMA might accelerate corrosion of reinforcing steel in concrete that has already been contaminated by salt because of the wide variations in electrochemical potential in different areas of the deck. Accordingly, the authors called for additional ponding tests to better determine CMA's effect on the corrosion of rebars in previously salted decks and research on the transport characteristics of CMA to determine how quickly it diffuses into concrete slabs.

FHWA is currently conducting ponding research to determine whether the addition of CMA to previously salted decks accelerates corrosion. Tests are being conducted on rebars embedded in mortar cylinders containing admixtures with varying concentrations of CMA and salt. After 28 days of curing under 100 percent humidity, cylinders of each type were ponded in solutions of salt and CMA. The electrochemical potentials and corrosion currents of the rebars are measured periodically. Results after 500 days were promising; the CMA corrosion potentials measured significantly more passive than reported by Locke and Kennelley (Peart and Jacoby 1991a; Peart and Jacoby 1991b). On the basis of these findings, the FHWA researchers concluded that CMA is not likely to accelerate corrosion of previously salted bridge decks.

In summary, the evidence indicates that CMA is less corrosive than salt to virtually all exposed steels and metals commonly used on bridges for applications such as joints, gutters, railings, and beams. Recent research by FHWA indicates that CMA is less corrosive than salt to rebars in new concrete and will not accelerate corrosion of rebars in chloride-contaminated concrete, as previously surmised. However, there is insufficient evidence to determine whether CMA has a passivating effect (i.e., reduces the rate of corrosion) on concrete that is already contaminated with salt, which is the condition of many older bridges in the snowbelt states of the Northeast and Midwest (see Chapter 3).

### *Other Highway Materials*

The most comprehensive investigation of CMA's compatibility with highway materials was conducted by Slick (1987) for FHWA. The study examined CMA's effect on portland cement concrete, asphalt, paints, adhesives, joint sealants, drainage pipes, and sign sheetings. Tests performed included concrete compression, abrasion, and scaling-resistance tests; static loading and impact tests; and friction, adhesion, and hardness evaluations.

Major findings were as follows:

- Pavement materials: The compression strengths of portland cement concrete and asphalt products were not affected by either salt or CMA. Scaling did not occur in any asphalt products; however, some scaling occurred in portland cement concrete. Scaling was more severe in salt specimens than in CMA specimens. Roughly the same pattern of scaling occurred on joint sealant specimens.
- Road-marking materials: Road-marking materials, such as paints, plastics, and tape, were affected by both salt and CMA. Specimens exhibited chalking, erosion, and flaking. In all cases, however, specimens exposed to salt were damaged more severely than specimens exposed to CMA.
- Construction materials: The hardness properties and impact resistance of bridge-bearing materials were not affected by either salt or CMA. Crushing strengths of concrete, corrugated metal, and plastic pipes were also not affected by either deicer.

In follow-up work sponsored by the Ontario Ministry of Transportation, Pianca (1987) tested the scaling properties of salt and CMA on typical concrete mixes used in Ontario. The study findings indicated that good-quality new concrete was resistant to scaling by both salt and CMA, but that the scaling was more severe in poor-quality new concrete exposed to salt.

## Summary of Compatibility with Automotive and Highway Materials

CMA is much more compatible with automotive parts than salt. Virtually all automotive materials and components tested have exhibited fewer negative reactions when exposed to CMA than when exposed to salt. The tendency of CMA spray to adhere to windshields and body parts, which has been reported by some field users, would probably require further study before more widespread CMA use.

Laboratory tests also indicate that CMA is less detrimental than salt to common highway materials, including those used for paving, road marking, and construction. CMA is also less corrosive than salt to exposed steel and other metals commonly used on bridges for applications such as joints, gutters, railings, and beams. Recent findings indicate that CMA is less corrosive than salt to new reinforced concrete and does not accelerate corrosion of older, chloride-contaminated concrete. However, there is insufficient evidence that CMA reduces the rate of corrosion of steel in concrete that is already contaminated with chlorides, which is the condition of many older bridges in the Northeast and Midwest.

## PRODUCTION TECHNOLOGIES AND PRICE

CMA is produced by reacting dolomitic lime with acetic acid. The resulting solution is dried and processed to obtain the final product. Except for expensive food-grade applications (such as vinegar),[6] acetic acid is usually derived from natural gas, which is CMA's chief cost component.

Attempts have been made to reduce CMA's production costs by exploring alternatives to natural gas. Soon after CMA's discovery, Marynowski et al. (1983), under contract with FHWA, surveyed acetate production technologies. The authors and FHWA concluded that a bacteriological fermentation process would yield the least expensive acetic acid. Preliminary process designs and economic analyses indicated that the fermentation process would lower CMA production costs by between $300 and $400 per ton if corn were used as a feedstock for fermentation.[7] Subsequent work by researchers at the University of Georgia (Ljungdahl et al. 1986) led to the production of CMA by this process. An economic evaluation of the process, however, indicated that production costs (not including shipping) would be on the order of $500 per ton, which is not significantly different from costs associated with the natural gas process.

Recently, Dynatech Scientific, Inc., under contract with the New York State Energy Research and Development Authority (NYSERDA) and several cosponsors, has explored fermentation processes using regional industrial and agricultural wastes (Leuschner 1988). The objective of the research is to develop processes for using locally generated waste materials. Feedstock sources considered include agricultural residues, such as grape and apple pomace, and industrial wastes, such as dairy whey and pulp and paper mill sludges. Preliminary engineering and economic analyses based on the use of dairy whey as a feedstock projected an ultimate CMA price of $280 per ton (Leuschner 1988).[8]

NYSERDA is also considering woody biomass (such as paper and pulp mill waste) as a possible feedstock, because it is available in much larger quantities than most other organic wastes (Wise and Augenstein 1988; DeSouza and Wise 1991). Significantly more work is required before initial cost projections for this process can be substantiated with actual production costs (personal communication with NYSERDA project manager). Other processes for using waste material, including municipal solid waste, have recently been considered by Trantolo et al. (1991). However, the potential environmental effects of these processes, resulting from the introduction of impurities into CMA, have not been adequately evaluated.

In a study sponsored by the Ontario Ministry of Transportation, Sheridan Technical Associates (1990) reviewed various technologies for CMA production. On the basis of economic evaluations of capital and operating costs for the most promising technologies, the authors estimated that CMA could be produced at a cost of approximately $300 per ton by using municipal solid waste as a source of energy for acetic acid production. The cost estimates, however, assume production of 1 million tons of CMA per year.

Chevron Chemical Company, the only major producer of CMA, uses acetic acid derived from natural gas. Chevron produces CMA for highway agencies that use it on a selective basis. In anticipation of greater demand for CMA in the future, Chevron sells it for $600 to $700 per ton (delivered). These prices are intended to cover full-scale production costs if CMA were sold in much larger quantities (personal communication with Chevron deicing products representatives).

Highway deicing is the primary market for CMA, but attempts are being made to find other markets. Chevron recently began marketing CMA as a deicer on airport runways and parking garages and as a dust-control chemical for dirt and gravel driveways (personal communication with Chevron deicing products representative). Potential use of CMA as an additive in coal-fired furnaces (such as those used by electric utilities) to facilitate combustion and remove sulfur from emissions has been explored (Wise et al. 1991). There is not yet sufficient evidence to determine whether these applications will be economically successful or will have a significant impact on the price of CMA used for highway deicing.

## NOTES

1. Environmental concerns about methanol include its potential volatility during handling and storage and its lethality to humans and animals if ingested.
2. The relationship is based on the requirement (for ideal solutions) of equal concentrations of ions from NaCl and from CMA for the same lowering of the freezing point.
3. In addition, CMA is being or has been used in locations in Pennsylvania, Tennessee, Arkansas, Louisiana, Minnesota, Arizona, Winnipeg, Atlanta, and Oklahoma.
4. CMA does not dissolve as readily as NaCl, thereby slowing initial action. In addition, because the ions in CMA are larger than those in NaCl, the rate of diffusion into the liquid film surrounding ice is slower, which further delays CMA's reaction time compared with NaCl.
5. Calcium and various acetates are sometimes used to extract metals from soils in chemical reactions. Metal automotive parts, radiator fluid, tire compounds, fuel, and emission from traffic contribute to heavy-metal contamination in roadside soils.
6. Vinegar is created using an aerobic fermentation process.
7. Corn was chosen as a feedstock partly because it is grown in virtually all regions of the country.
8. Unlike corn grain and paper mill waste, which require treatment before fermentation, dairy residues are already in a form that allows for direct fermentation. NYSERDA initially selected dairy whey as the preferred feedstock because of this advantage (Wise and Augenstein 1988, 455).

## REFERENCES

### ABBREVIATIONS

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| FHWA | Federal Highway Administration |
| NCHRP | National Cooperative Highway Research Program |
| TRB | Transportation Research Board |

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