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Calcium Magnesium Acetate

What is known about calcium magnesium acetate (CMA) is reviewed in this chapter. The discussion is organized into five sections covering its (a) discovery and development, (b) field experience, (c) environmental and health evaluations, (d) compatibility with automotive and highway materials, and (e) production technologies and market price.

DISCOVERY AND DEVELOPMENT

During the 1970s the Federal Highway Administration (FHWA) initiated a research program aimed at reducing the overall cost of highway deicing. An important part of this program was an investigation of deicing chemicals as possible replacements for salt (sodium chloride, or NaCl) (Dunn and Schenk 1980a). Most chemicals considered were eliminated quickly in preliminary evaluations because they were prohibitively expensive, not available in sufficient quantities, had unsuitable physical or chemical properties (e.g., were gaseous or not water soluble), or were corrosive, flammable, toxic, or harmful to the environment. On the basis of literature surveys and limited laboratory studies, the field was narrowed to two candidate chemicals, methanol and CMA (Dunn and Schenk 1980b, 13).

Methanol, a liquid sometimes used as an antifreeze, is particularly effective at very low temperatures. CMA, a solid, has a deicing range closer to that of salt. Whereas both chemicals were deemed suitable from the standpoint of a number of deicing criteria, CMA was selected for continued development because of its greater environmental acceptability and handling and spreading characteristics that more closely resembled those of salt.[1] Preliminary laboratory tests and literature reviews indicated that it is harmless to plants and animals, noncorrosive to metals, and nondestructive to concrete and other highway materials. Because its main ingredient, dolomitic lime, is abundant throughout much of the country, it was anticipated that economical methods of production could be developed quickly.

Soon after CMA's discovery, FHWA, with financial support from 24 state highway agencies, began to investigate its deicing properties and use characteristics in the field. Initial field tests were conducted by Michigan and Washington State during the winters of 1983 and 1984 (Defoe 1984; Ernst 1984). Each state was provided 100 tons of an early test product to use on freeway sections in comparison with salt. The main objective of these tests was to determine CMA's deicing effect. Other areas of investigation were its storage, handling, and spreading characteristics. Test results were generally promising, although the following drawbacks were reported:

- Because of its low density and small particle size, the test material was dusty during handling and storage and tended to blow off the roadway after spreading. When exposed to moisture, it frequently caked and clogged spreading equipment.
- The test material was often less effective than salt in colder conditions and slower acting and less successful in penetrating heavy snowpack and ice.
- Typically, twice as much CMA had to be used as salt (by weight).

On the basis of these findings, both states recommended that CMA's physical form be altered to either a liquid or larger particles to improve its spreading and handling qualities and its ability to penetrate packed snow and ice (Defoe 1984; Ernst 1984).

On completion of the field trials, efforts to improve CMA's performance were already under way. In 1983, FHWA sponsored additional research aimed at determining the optimum calcium/magnesium (Ca/Mg) ratio (Schenk 1985). The test product used in Michigan and Washington State had a Ca/Mg ratio of 1 to 1. However, findings from this subsequent research indicated that the higher solubility and lower freezing point of magnesium acetate favored a Ca/Mg ratio with a higher proportion of magnesium, on the order of 1 to 2.3 (Schenk 1985).

The primary producers of CMA at the time—Chevron Chemical Company, Verdugt, Inc. (Netherlands), and Gancy Chemical Company—changed their CMA products to reflect this formulation. In addition, the largest producer, Chevron, developed a harder, pelletized version that was expected to be less dusty, flow more freely from spreading equipment, and penetrate ice faster than the lighter, powdery material used in Michigan and Washington State (Figure 6-1).

FIELD EXPERIENCE

Since 1985, at least six jurisdictions—California, Massachusetts, Wisconsin, the city of Ottawa, and the Canadian provinces of Alberta and Ontario—have reported on their field evaluations of CMA. Summarized in the following sections are results from these evaluations and responses from other CMA users who were interviewed for this study. Findings concerning CMA's deicing performance are reviewed first, followed by its storage, handling, and spreading characteristics.

Deicing Performance

The theoretical amount of CMA relative to salt needed for comparable ice melting is 1.7 to 1 by weight.[2] In practice, however, ice-

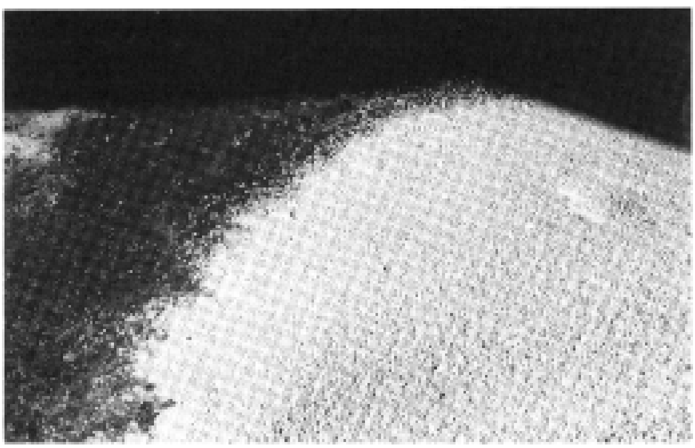

FIGURE 6-1 Pelletized CMA in storage.

melting capacity is not the only characteristic important to deicing. As the following results from field tests indicate, chemical deicing also involves ice prevention, penetration, disbonding, and interactions with traffic and weather.

Ontario

Ontario compared CMA with salt by spreading each deicer on different sections of the same freeway segment (Manning and Crowder 1989). During the two winters tested (1986–1987 and 1987–1988), 34 storms occurred. Most were short and mild; temperatures seldom dropped below −5°C (23°F), and snowfalls were typically light. CMA and salt were applied at specified rates, and the number of applications was dictated by conditions.

During the first winter, CMA/salt application rates were initially specified at 1.7 to 1 by weight; however, this rate was deemed excessive and eventually lowered to 1.5 to 1. In general, CMA was found to be effective in penetrating light snowpack and preventing the pavement-ice bond, which facilitated mechanical snow removal by traffic action and plowing. The authors noted that when applied at the outset of storms, it performed well as an anti-icer, preventing the accumulation of snowpack and ice. The CMA treatments were also found to be more effective during longer storms, and the tendency of CMA residue to adhere to the pavement was thought to have reduced treatments during subsequent storms.

Overall, CMA was found to be as fast and effective as salt in achieving bare pavement under the conditions tested. Its endurance during longer storms, residual effect from storm to storm, and performance as an anti-icer, however, were found to be advantages that helped reduce the total number of CMA applications required compared with salt. During the entire test period, 20 to 40 percent more CMA was used than salt.

Wisconsin

Field tests in Wisconsin were part of a second round of FHWA-state efforts to evaluate the deicing properties and operational characteristics of CMA (Wisconsin Department of Transportation 1987; Smith 1989). As in Ontario, the tests were conducted on freeway sections. During the two winters tested (1986–1987 and 1987–1988), 43 storms occurred, most of which were short and mild.

CMA was applied in quantities ranging from 1.2 to 1.6 times greater than those of salt. At these rates its deicing performance was comparable with that of salt. It required no additional time to achieve bare pavement, although it was slower starting than salt (by about 20 min). It was effective in preventing the pavement-ice bond but less successful than salt in melting snow and ice accumulations, requiring traffic action or plowing for mechanical removal. It was less effective than salt when applied to fluffy (dry) snow and when temperatures dropped below approximately −5°C (23°F). In contrast to results in Ontario, no endurance or residual effects were noticed during longer storms or from storm to storm. By the end of the test period, approximately 60 percent more CMA had been applied than salt.

Massachusetts

Massachusetts first tested CMA in the field as part of its reduced salt experiments during the winter of 1986–1987 (Massachusetts Department of Public Works 1987). The test site was a 4.8-mi section of two-lane suburban highway. An adjoining 4.9-mi section of salt-treated highway was monitored for comparison. CMA was used on 19 storms; with few exceptions, storm conditions were typical of southeastern Massachusetts, with high humidities, wet snowfall, and temperatures ranging from −5°C to above 0°C (23°F to above 32°F).

Throughout much of the winter, CMA was released from spreader trucks at the same rate as salt (300 lb/lane-mi). Rates were increased by approximately 20 percent during colder and drier (low-humidity) conditions. As reported in other field tests, CMA did not perform as well as salt when temperatures dropped below −5°C (23°F) and during heavy snowfall and freezing rain. Traffic action or plowing was important for snow removal when melting was inadequate. Because of recording errors and problems with study design, reliable comparisons of salt and CMA application quantities were not made.

Ottawa

During the winter of 1987–1988, the city of Ottawa sponsored field tests of CMA to determine its effectiveness on city streets (Sypher-Mueller International 1988). CMA and salt were tested on separate test routes selected from low- and high-traffic urban streets. A total of 53 storm and weather conditions were tested. Most storm temperatures exceeded −5°C (23°F).

Depending on storm conditions, CMA was applied in quantities ranging from 1 to 3 times those of salt, but typical amounts were between 1.3 and 1.8 times greater. By experimental design, the frequency of application did not vary by deicer. Unlike the experience in Ontario, no residual or endurance effect was reported. As in previous field tests, the CMA treatments were slower acting than the salt treatments and less effective in colder temperatures (below −5°C) and low traffic. Overall, roughly 60 percent more CMA (by weight) was applied than salt during the total test period.

California

California regularly used CMA on a number of mountain highways during successive winters from 1986 to 1989, primarily to reduce tree damage along scenic highways (California Department of Transportation 1989). The test sites experienced heavy snowfalls and storm temperatures ranging from mild to very cold. CMA was found to be most effective in preventing the formation of snowpack. Accordingly, attempts were made to apply it at the beginning of storms, when it could mix with initial snowfall and change the consistency to plowable meal or slush. The CMA treatments were generally slower and less effective than the salt treatments in removing heavy snowpack; the pellets penetrated slowly and often did not yield sufficient brine to flow under accumulations and break the pavement-ice bond.

Comparisons of salt use data from previous years suggested that CMA was used in quantities slightly greater than those of salt. On the basis of storm-to-storm observations, however, maintenance engineers estimated that CMA/salt use ratios were approaching 1 to 1 as familiarity with the product increased.

Alberta

Alberta tested CMA during the winters of 1987–1988 and 1988–1989 as part of its research program to reduce corrosion of bridges (Chichak and Filipiak 1989). The Peace River Bridge in northwest Alberta was selected as a test site because of its frequent corrosion problems and harsh climatic conditions [storm temperatures average −13°C (9°F)].

During initial tests, CMA was found to be less effective when temperatures dropped below approximately −5°C (23°F) and under conditions of heavy snowpack, causing maintenance crews to switch back to salt. At temperatures above −5°C (23°F), its deicing performance was rated as satisfactory—although somewhat slower than salt—when applied in amounts 1.3 times greater.

Other Users

During the past five winters, a few highway agencies have been using CMA on a more regular, although highly selective, basis. According to estimates provided by Chevron, about 10,000 tons of CMA has been purchased since 1986 (Chevron deicing technology representative, personal communication). Current or recent users include

- California, on several mountain highways in the Sierra Nevada;
- Denver, on new concrete viaducts;
- Massachusetts, on a six-lane Interstate highway and a two-lane suburban highway (Figure 6-2);
- Michigan, on a new long-span segmental bridge (Zilwaukee Bridge);
- Nebraska, on new concrete viaducts and highway sections;
- Nevada, on mountain highways near Lake Tahoe;
- Ontario, on a two-lane rural highway; and
- West Virginia, on a four-lane, single-span bridge constructed with weathering steel (New River Gorge Bridge).[3]

FIGURE 6-2 Massachusetts highway treated with CMA.

Each of these users was contacted for this study and asked about CMA's performance. Most comments concerning CMA's deicing effect were similar to those from reports cited previously. In general, CMA was described as an acceptable deicer, although not quite as effective or consistent as salt. Often it was described as slower acting than salt, taking 15 to 30 min longer to start melting. Most users noted that it had to be applied early during a storm cycle; otherwise its effectiveness was significantly reduced. When applied at the outset of a storm, it was judged effective in preventing snowpack and pavement bonding. Typically, it was used in the same temperature range as salt, although it was less effective at temperatures below about −5°C (23°F). Some users reported that it did not work well in freezing rain and fluffy snow.

Several highway agencies estimated that CMA/salt ratios were starting to approach 1 to 1 as experience with the product increased. Nebraska and West Virginia found that about 30 to 50 percent more CMA than salt (by weight) was required for the first application during a storm but that application amounts could be reduced during follow-up treatments. Three highway agencies suspected that CMA provided some residual deicing effect (during secondary storms) by adhering to the pavement for several days.

Storage, Handling, and Spreading Characteristics

In its early test form, CMA proved difficult to adapt to handling and spreading practices. After initial field trials in 1983–1984, Michigan and Washington State reported that it was dusty during handling, often blew off the roadway, and adhered to spreading equipment when exposed to moisture (Defoe 1984; Ernst 1984).

Since the preliminary tests, CMA's physical form has been changed to alleviate some of these problems. Chevron developed a pelletized version designed to be more resistant to attrition, less prone to dusting and blowing, and better able to penetrate packed snow than the powdery CMA product used in earlier field trials. In field applications since 1985, CMA's storage, handling, and spreading characteristics generally have been described more favorably. Findings from evaluations and interviews with CMA users are summarized as follows:

- Ontario reported storage, handling, and spreading characteristics comparable with those of salt (Manning and Crowder 1989). CMA stockpiles were stored in an enclosed shed. Some dusting occurred during loading, but protective dust masks were not required.

However, because dusting tended to increase during prolonged storage (periods exceeding 6 weeks), well-ventilated storage facilities were recommended. Regular salt-spreading equipment was used for all treatments. Some blowing occurred during spreading, but not enough to require the covering of trucks. As in previous field trials, some inconveniences were created by wet CMA clogging and sticking to spreading equipment. Releasing CMA over a slowly rotating spinner wheel (rather than through the chute used for salt) and periodically knocking the clogged material from equipment helped minimize these difficulties.

• Wisconsin also reported few difficulties in storing, handling, and spreading CMA (Wisconsin Department of Transportation 1987; Smith 1989). The test material was stored in ½-ton sacks in an enclosed shed. Initial attempts to empty the sacks into spreader trucks proved cumbersome and time-consuming, but more efficient loading techniques were eventually discovered. Some dusting and blowing occurred, but protective dust masks were not required. Trucks were covered with tarpaulins to reduce wind scatter; otherwise, equipment was not modified. When wet, CMA occasionally clogged equipment, and CMA spray sometimes adhered to the windshields of trucks and passing cars. Overall, CMA's handling and spreading characteristics were described as close to those of salt, though somewhat less convenient for routine use.

• Massachusetts purchased CMA in bulk and stored it in stockpiles in a wooden shed (Massachusetts Department of Public Works 1987). Regular salt-spreading equipment was used for all applications, though trucks were covered to reduce blowing. In general, dusting and blowing were found to be less severe under moist conditions. Contact with moisture, however, increased caking and sticking. Overall, these problems were rated as only minor drawbacks that did not significantly affect handling and spreading.

• California normally purchased CMA in bulk and stored it in enclosed sheds (California Department of Transportation 1989). Rather than build additional storage facilities, small purchases were made frequently. Regular salt-spreading equipment was used, although spreader trucks were sometimes covered during wet and windy conditions. As in other field trials, the CMA tended to stick to and clog equipment when it became wet from tire splash and precipitation; however, its storage and handling qualities were generally described as manageable.

• Many of the CMA users interviewed for this study reported some difficulties in handling and spreading CMA, but most were characterized as minor. When wet, CMA tended to clog spreading equipment and adhere to truck beds. Several reported that CMA spray occasionally stuck to the windshields of passing cars. All experienced dusting during loading and unloading, which sometimes required workers to use dust masks. Most stressed the importance of storing CMA indoors and covering trucks to prevent blowing and reduce exposure to moisture. One user, Ontario, resolved some of these problems by storing CMA in a watertight silo to reduce exposure to moisture and minimize handling through gravity loading.

Summary of Field Experience

Although findings are not always consistent, the experiences of CMA users provide some general insights into CMA's field performance relative to salt. Most users reported that CMA worked adequately but not quite as effectively or in quite the same manner as salt. Unlike salt, it did not produce significant surface melting and flowing brines that melt ice from top to bottom. It worked best when applied at the outset of a storm, before significant snow and ice accumulation. When applied early, it was able to mix with the falling snow and prevent the formation of snowpack and the bonding of ice to the pavement. It performed best when accompanied by plowing or traffic activity, which was important for removing loose snow and ice from the pavement. In situations characterized by light traffic and limited plowing or when ice and snowpack were allowed to accumulate, its performance was often markedly reduced. Whereas salt also worked best when accompanied by traffic and plowing, its ability to produce surface melting made traffic activity and early application less important factors.

Users also reported that CMA performed somewhat less successfully than salt at lower temperatures and in certain types of storm conditions. Although slightly slower acting, its performance was generally comparable with salt's at storm temperatures above −5°C (23°F).[4] At these temperatures, it started to penetrate light snowpack within 15 to 30 min of salt (salt acted almost immediately). When used during colder conditions, however, its relative effectiveness diminished. For instance, at storm temperatures below −5°C (23°F), its performance was frequently judged inadequate. It was also described as less effective than salt during freezing rain and storms characterized by fluffy snow.

Most users indicated that between 20 and 70 percent more CMA than salt was required during the winter. Spreader units were typically calibrated to release about 50 percent more CMA than salt, although CMA was sometimes applied less frequently during longer storms. Several highway agencies found that early application (i.e., at the outset of the storm, before significant snow and ice accumulation) was critical and helped improve its effectiveness and reduce the amount used. As might be expected, highway agencies with the most experience using CMA developed more successful use strategies that helped reduce application quantities over time.

The general conclusion reached by most users was that CMA's handling and spreading characteristics are comparable with those of salt. No major problems were identified. The most frequently cited drawback was its tendency to cake and stick to spreading equipment, which required operators to periodically chip or knock loose accumulations between applications and during cleanup. Generally, however, this problem was described as only a minor inconvenience. The field reports indicate that dusting and blowing were less troublesome than reported in pre-1985 field trials, though in many cases protective dust masks and truck covers were still required during handling and spreading.

CMA had to be kept dry during storage, usually in enclosed and well-ventilated shelters. Because most tests were conducted using small quantities, users could not project storage requirements for prolonged and larger-scale use. CMA is less dense than salt, requiring about 60 percent more space per ton. As a practical matter, therefore, the effect of larger-scale use on existing storage and truck capacities is likely to be an important consideration for users. Hence, on the basis of product density differences alone (not including differences in tonnage requirements), one would expect that significantly more storage and truck capacity would be required if CMA is used as a more general replacement for salt.

HEALTH AND ENVIRONMENTAL EFFECTS

During initial investigations that identified CMA as a promising replacement for salt, no potentially significant environmental or health-related impacts were uncovered (Dunn and Schenk 1980a). Literature reviews indicated that the calcium and magnesium in CMA might increase water hardness, but only if unusually large amounts entered a water system.

Since the initial work, FHWA, states, and private industry have sponsored research aimed at more thoroughly examining impacts on the environment and human health. Findings from the two most comprehensive studies, conducted by the California Department of

Transportation (Caltrans) and the National Cooperative Highway Research Program (NCHRP), are summarized in the following sections.

Caltrans Study

The purpose of this FHWA-sponsored study (Winters et al. 1985) was to examine CMA's environmental impacts before initial field tests were conducted. The study consisted of an extensive literature review and limited laboratory tests to identify potential impacts on aquatic life, terrestrial vegetation, and air and water quality. Tests consisted of aquatic bioassays on fish and plankton, irrigation and foliar spray applications to potted plants, and soil-leaching experiments. A reagent-grade mixture of calcium acetate and magnesium acetate was used in the tests.

Major findings were as follows:

- CMA was less toxic to fish (rainbow trout and fathead minnows) than NaCl. Continuously maintained CMA concentrations of 5000 mg/L were associated with slightly delayed hatching in rainbow trout.
- CMA was more deleterious to plankton (algae and water flea) than NaCl at high exposure levels. Inhibitory effects in algae occurred at CMA concentrations of 85 mg/L, and effects in water flea occurred at concentrations between 125 and 250 mg/L. Algae did not exhibit any inhibition from NaCl (at test concentrations), and the detrimental concentration for water flea was 2500 mg/L.
- CMA solution, when leached through soils, tended to exchange calcium and magnesium with other metals already present in the soils. Results indicated that CMA could extract iron, aluminum, sodium, and potassium from roadside soils.[5]
- CMA was less harmful to plants than NaCl. Of the 18 tree species tested, only one, the Russian olive, was damaged more by CMA than NaCl.
- No potential health, water, or air quality impacts were uncovered in the literature.

On the basis of these findings, the study authors concluded that at concentrations likely to be generated by highway deicing, CMA was likely to be less environmentally damaging than salt and did not appear to pose health hazards that precluded further controlled field testing. The study recommended, however, that before widespread use of CMA was considered, additional laboratory and field tests be conducted to investigate impacts on metals in roadside soils and to track environmental effects over an extended period of time.

NCHRP Study

Following completion of the Caltrans study, researchers at the University of Washington embarked on an NCHRP-sponsored study (Horner 1988) to further assess CMA's environmental impacts and to develop interim guidelines for its safe use. As in the Caltrans study, bioassays were designed to examine effects on aquatic life, common roadside plants were irrigated and sprayed with CMA, and soils were tested to evaluate physical and chemical impacts. In addition, the study included a model predicting CMA's transport characteristics in runoff, groundwater, and soil water. The CMA product used was manufactured from acetic acid derived from corn silage.

Major findings were as follows:

- Transport characteristics: The transport model predicted that average highway spray and runoff concentrations of CMA would range from 10 to 100 mg/L, and extreme concentrations would not exceed 5000 mg/L. Average annual CMA loadings of 10 tons per mile were predicted.
- Soil: In soil at air temperatures above 10°C, a high level of CMA (acetate) decomposition was achieved within 2 weeks, whereas at 2°C, 4 weeks was required for full decomposition. CMA did not significantly affect the physical properties of soil (e.g., permeability, plasticity, and strength); however, laboratory and field tests indicated a potential for CMA to mobilize and release trace metals from soils. The metal quantities released in the soils tested did not appear to pose any environmental hazard, but it could not be determined whether more hazardous quantities could be released from highly contaminated soils.
- Surface water: Results indicated that full CMA (acetate) decomposition would occur in 100 days in water at 2°C and much faster in warmer water. Oxygen depletion in water due to biochemical oxygen demand (BOD) from CMA decomposition was found to be a potentially important effect, because CMA concentrations as low as 10 mg/L were associated with reduced oxygen in test ponds. The potential for phosphorus enrichment of surface waters exposed to high concentrations of CMA derived from agricultural products was also reported. Phosphorus enrichment can lead to eutrophication, especially in small, poorly flushed ponds and lakes.