



## The effect of CMA deicers on concrete properties

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### Abstract

The paper presents the results of an investigation of the effects of concentrated calcium–magnesium acetate (CMA) solutions on concrete. Concrete specimens were manufactured following guidelines for structures exposed to freeze–thaw cycles and deicers (water–cement ratio,  $w/c = 0.45$  and air-entraining admixture) employing two cements obtained by blending a Portland clinker with 20% of ground limestone, or 40% blast furnace slag. Following 28 days of curing, the specimens were immersed for 8 months at 20°C in two concentrated (25%) CMA solutions prepared using (a) a commercial CMA-based deicing chemical or (b) pure calcium and magnesium acetates blended to obtain the same Ca/Mg molar ratio (0.43) as the deicer. Continuous exposure to both CMA solutions led to a significant decrease in load capacity, mass loss and marked visual deterioration. The aggression was particularly strong in the case of the deicer solution, and was mitigated by the use of the slag cement. © 2000 Elsevier Science Ltd. All rights reserved.

**Keywords:** Durability; Compressive strength; Granulated blast-furnace slag; Concrete; Calcium–magnesium acetate deicers

### 1. Introduction

The use of deicing and anti-icing products is widespread throughout countries enduring cold and snowy weather to ensure safe winter-driving conditions. For many years, chloride-based products, in particular sodium and calcium chlorides, have dominated the deicer market which, in the US alone, amounts to more than one-third of the US\$1.5 billion expenditure associated with winter maintenance [1]. However, as the negative effects of chlorides on motor vehicles, infrastructures, and the environment have been understood, concerns have risen regarding the use of these salts for deicing roads.

The effort to avoid the undesirable and costly side effects associated with chlorides and to find an economic solution to road and traffic management has led to extensive investigations of possible replacement deicing chemicals. Today, calcium–magnesium acetate (CMA)-based deicers, manufactured by reacting dolomitic lime with acetic acid, are considered the most valuable technical alternative to traditional deicing products. While the use of these products

as a general replacement for traditional deicers is unlikely, due to their high cost (more than 20 times greater than that of sodium chloride), cost–benefit analyses performed by the United States Federal Highway Administration [1] suggest that their selective use might be warranted in environmentally sensitive areas and on new corrosion-prone structures and highway sections.

Despite the numerous investigations on the performance of acetate-based deicers, it appears that limited information, and sometimes conflicting data, are available regarding the effect of these salts on concrete. The work presented in this paper, initiated at the beginning of 1996, is aimed at contributing to this topic and follows previous research performed by the authors [2] on this subject, which had indicated the aggressive nature of these solutions toward concrete, particularly for high values of the water–cement ratio ( $w/c$ ), and the mitigating effect produced by substitution of part of the Portland clinker with fly ash. The experimental program presented here was designed to simulate long-term exposure conditions for newly constructed structures that, as mentioned above, appear to be the most likely candidates for deicing/anti-icing treatment with CMA. It sought in particular to investigate the aggressive nature of a CMA-based commercial deicer, and to evaluate the performance of concrete manufactured with a binder rich in slag.

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With these objectives in mind, the paper examines the effects, in terms of decrease in compressive strength, visual deterioration, and mass loss, of continued immersion of concrete specimens in concentrated (25%) calcium–magnesium acetate solutions over a period of 8 months. The specimens were manufactured employing two different cements (obtained by blending Portland cement with crushed limestone and blast-furnace slag, respectively), and following specifications for structures exposed to freezing and thawing in presence of deicing chemicals. Two deicing solutions are examined: one obtained using a commercial deicing product and another manufactured in the laboratory from pure calcium and magnesium acetates.

## 2. Background

Following the identification in 1980 by the U.S. Federal Highway Administration of calcium-magnesium acetate as a possible replacement for traditional deicing chemicals, investigations of its deicing properties and use characteristics, as well as field trials comparing its performance to that of sodium chloride, were undertaken throughout the US in the following years. At the same time both laboratory and field studies were conducted to determine its environmental acceptability and its compatibility with automotive and highway materials. These experiences verified that, despite the high up-front cost, CMA-based deicers present some advantages over traditional chloride products, which ultimately reduce the total cost associated with deicing. These advantages include, in particular, absence of significant adverse effects on human health and the environment [3], an extended duration of the deicing action [4] and reduced corrosion of automotive and infrastructure metals [5].

CMA's compatibility with concrete structures, however, is still not clear. Some data available in the literature indicate that CMA is not aggressive to concrete and is therefore preferable also in this respect to traditional deicers. Such were the conclusions drawn, for example, from the work performed at the Transport Research Laboratory in the UK [6] in which no significant scaling of concrete specimens ( $w/c = 0.42\text{--}0.64$ ) was observed following 50 freeze–thaw cycles in the presence of 3% and 25% CMA solutions. In the same tests, solutions of NaCl,  $\text{CaCl}_2$ , urea and glycol, were found, instead, to cause varying degrees of deterioration of the concrete.

In contrast to the above, research previously presented by the authors [2] suggests that exposure to acetate-based deicers may cause significant deterioration of concrete structures. In Ref. [2], the durability of concrete specimens continuously exposed to acetate solutions over a period of 12 months was investigated as a function of the material characteristics (cement type,  $w/c$ , use of an air-entraining agent) and of the testing conditions (temperature, concentration and molar ratio of the acetate solutions prepared in the laboratory from calcium and magnesium acetates). The results indicated that concrete was attacked by the CMA solutions through a delamination process of the cement matrix most likely associated with leaching of the calcium hydroxide. This resulted in mass and strength loss, as well as in significant visual deterioration. These negative effects were reduced at lower temperatures ( $5^\circ$  versus  $20^\circ\text{C}$ ) when the  $w/c$  was decreased (from 0.60 to 0.45), and by employing Portland cement blended with fly ash. The aggression increased with the concentration of the solution and was more severe for a particular Ca/Mg molar ratio equal to 0.43, while it was less significant in the solutions of the pure calcium and magnesium acetates.

Prior to the authors' work, evidence of the aggressive nature of CMA solutions had been presented by Peterson [7], who reported on both the role of the salt's molar ratio and concentration, as well as on the diminished aggression at higher temperatures. In addition, Fujii [8] indicated that the presence of CMA in acid solutions ( $\text{pH} = 3$ ) was associated with significant leaching of calcium hydroxide from cement pastes ( $w/c = 0.30$  with addition of fibers).

## 3. Materials

### 3.1. Cements

The chemical compositions of the raw materials (Portland clinker, limestone and blast-furnace slag) used to manufacture the two cements employed for the experimental program are summarized in Table 1. The two cements (type II/A-L and III/A, according to the European standard norm EN 197/1), both of strength class 42.5, were obtained by mixing the Portland clinker with 20% ground limestone and 40% blast-furnace slag, respectively.

Selection of the limestone-Portland cement was based on the fact that, along with being the most widely used cement in Europe today, it was shown in previous research [2] to promote rapid and marked attack by CMA solutions.

Table 1  
Composition of raw materials employed for cements

Oxide (%)	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{CaO}$	$\text{MgO}$	$\text{SO}_3$	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$	$\text{TiO}_2$	L.o.i
Portland cement	20.31	4.82	2.67	60.91	3.19	3.24	0.18	0.98	0.30	2.65
Limestone	—	—	—	55.58	—	—	—	—	—	43.57
Blast-furnace slag	36.21	17.27	2.51	36.25	4.61	0.81	—	—	—	0.51

Table 2  
Composition of concrete mixtures

Mixture (no.)	Cement type	Cement (kg/m <sup>3</sup> )	Aggregate (kg/m <sup>3</sup> )	Water (kg/m <sup>3</sup> )	Super-plasticizer (kg/m <sup>3</sup> )	Air-entraining agent (kg/m <sup>3</sup> )
1	II/A–L 42.5R	389	1731	175	–	0.16
2	III/A 42.5R	392	1745	176	1.51	0.15

Table 3  
Properties of two concretes

Mixture (no.)	Slump (mm)	Unit weight (kg/m <sup>3</sup> )	Air (% by vol)	Compressive strength (MPa)		
				1-day	7-days	28-days
1	170	2300	6.0	14.5	33.7	42.7
2	210	2319	4.7	3.8	28.5	40.0

The slag cement (III/A) was employed as this binder is recommended for structures exposed to chloride-based deicing salts.

### 3.2. Aggregates

The limestone natural aggregate used for the concrete mixtures was obtained by combining four aggregates in the following proportions: 25% (4–20 mm), 25% (4–16), 15% (1–10), 35% sand (< 4 mm).

### 3.3. Chemical admixtures

An air-entraining admixture was used at a dosage of 0.42% by mass of cement to manufacture all the concrete specimens used for the testing program. In the mixture manufactured with the slag cement, a 40% aqueous solution of a naphthalene-based superplasticizer was also employed, at a dosage of 0.38% by mass of cement, to obtain the same fluid consistency displayed by the other mixture.

### 3.4. Concrete mixtures

Table 2 summarizes the composition of the two mixtures that were manufactured employing the same water–cement (0.45) and aggregate–cement ratios (4.45) and using an air-entraining admixture. Thanks to the low water-cement ratio and use of an air-entraining agent, the concrete mixtures meet the specifications for structures exposed to freeze–thaw cycles and deicing treatment.

Following the mixing procedure, concrete cubic specimens (100 × 100 × 100 mm) were cast from the two mixtures. Measurements of the slump, the unit weight and of the quantity of air were performed on the fresh concrete. The results of these measurements are summarized in Table 3. Curing occurred at room temperature at 100% R.H. for 7 days and at 65% R.H. for an additional 21 days. Measurements of the compressive strength were performed during the curing phase at 1, 7 and 28 days. The values shown in the last three columns of Table 3 are the average of the two measurements obtained at each time.

### 3.5. Acetate solutions

Three different solutions were prepared: a reference solution of tap water and two solutions of CMA both at a concentration of 25%. The first of these solutions was prepared using a commercial product obtained by combining dolomitic lime and acetic acid and sold as a deicing agent worldwide. The second solution was manufactured using commercially available calcium and magnesium acetates combined in the laboratory at a Ca/Mg molar ratio of 0.43, equal to the one with which the two salts are combined in the commercial product.<sup>1</sup> This was aimed at verifying if the presence of additional proprietary components in the commercial deicer could inhibit the aggression of the cement paste by the acetates observed in Ref. [2]. Both solutions were prepared at a concentration of 25% (already used in the previous experimental investigation), which is the concentration at which CMA-based deicing chemicals are commercially available in liquid form.

## 4. Methods

After 28 days of curing, the concrete specimens were placed in the water and in the two acetate-based solutions. Immersion in the solutions was continuous and temperature conditions were maintained at 20°C over the entire testing period. While the condition of continuous immersion in the solution is quite severe, it is intended to correspond to a much longer period of exposure of concrete structures to the aggression of deicers in the field. The selection of 20°C as the testing temperature was based on previous experience that had indicated that the aggression by CMA was more significant at higher temperatures. Despite the fact that the use of deicers occurs in cold temperatures, the presence of these salts is expected, particularly in the case of pavement

<sup>1</sup> This value of the molar ratio, provided by the manufacturer of the deicer, was verified by the authors by performing an ion chromatography.



Fig. 1. Visual rating scale.

structures, to extend beyond the cold winter period during which the treatment is administered.

After the first 2 months of immersion, and every 30 days thereafter, the following properties of the concrete were evaluated: compressive strength, variation in mass and visual deterioration. While, due to the destructive nature of the compression test, one specimen was used at each testing time, the variation of mass and the visual rating were performed on one control specimen selected at the beginning of the program.

Measurements of the compressive strength were performed using a hydraulic load frame equipped with a 60-ton load cell. The tests were performed rotating the position of the specimen by 90° with respect to the direction of pouring to avoid errors associated with the nonperfect planarity of the top and bottom sides of the specimens.

The variation in mass was evaluated at each testing time by weighing the control specimens, previously patted with a damp cloth to remove excess water, and using the mass of the specimen measured after 1 day of immersion in the solutions as the initial reference mass.

Visual rating of the deterioration of the specimens was based on a scale varying between A (intact specimen) and E (marked deterioration of the specimen on all sides with complete exposure of the aggregates and significant loss of material) developed by the authors. Fig. 1 shows examples of specimens which were assigned the ratings from A to E.

## 5. Results and discussion

### 5.1. Compressive strength

Fig. 2 shows the curves of compressive strength versus time of immersion for the concrete specimens manufactured employing the type II/A-L cement. The three curves presented in the figure are relative to specimens immersed in the reference water bath, and in the two acetate solutions. The data are presented in terms of the absolute value of the nominal compressive strength (left-hand axis) and as a percentage of the 28-day value (right-hand axis). The use of the nominal compressive strength, i.e., the maximum compressive force divided by the original area of the specimen, is justified by the need to account for the fact that when a specimen undergoes a reduction in mass and thus in cross-sectional area, the maximum sustainable load decreases proportionally to the deterioration level, even if the remaining concrete is not significantly deteriorated.

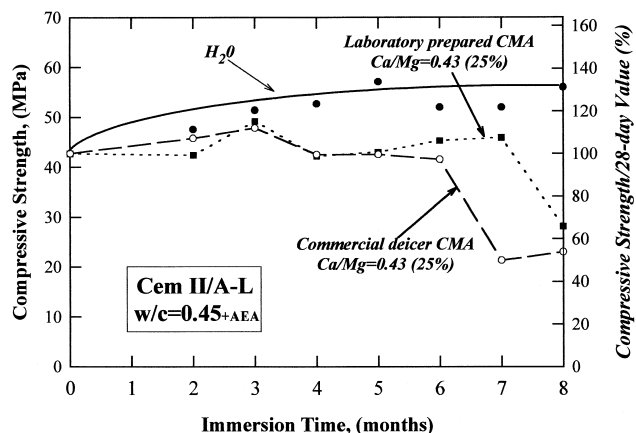


Fig. 2. Compressive strength versus immersion time (limestone-portland cement).

A similar set of curves relative to the specimens manufactured with the type III/A cement is presented in Fig. 3.

For both concretes, the specimens immersed in water show an increase in strength, on the order of 20–35%, associated with the phenomenon of post-hardening, during the first 4–5 months of immersion. This effect is significantly reduced in case of immersion in the two acetate solutions and a slight increase in the strength (approximately 10%) is observed only during the first 2–3 months. Following this period, the compressive strength maintains an approximately constant value for some time, until prolonged immersion in the acetate solutions eventually causes it to decrease. This phenomenon is especially marked for the concrete manufactured with the II/A-L cement (Fig. 2), in particular when immersed in the solution obtained from the commercial deicer. In this case the strength decreases only slightly between three and six months, and then falls rapidly, reaching a value as small as 50% of the 28-day value at the end of the testing period. A qualitatively similar, albeit less marked, trend of decreasing strength, is observed for the specimens immersed in the other acetate solution. For these specimens, however, the significant drop in strength is

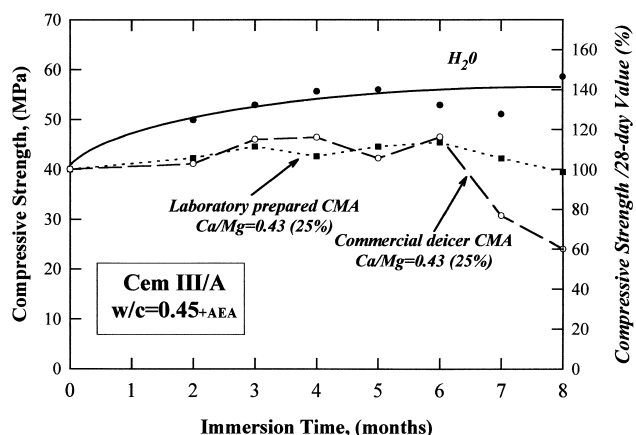


Fig. 3. Compressive strength versus immersion time (slag cement).

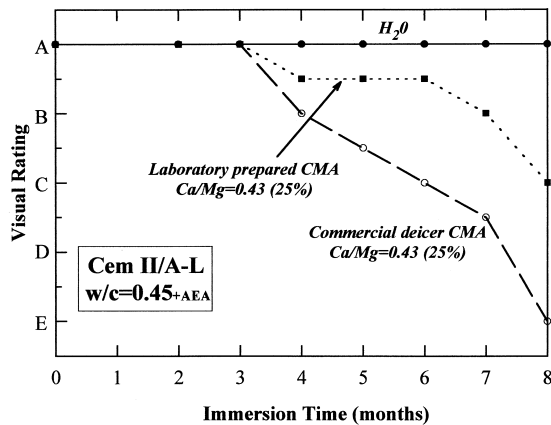


Fig. 4. Visual rating versus immersion time (limestone-portland cement).

delayed by approximately a month and the final value of the strength is slightly larger (65% of the 28-day value).

The results for the slag cement concrete (Fig. 3) exhibit similar trends. As described above, the solution obtained from the deicing product is observed to be more aggressive than that manufactured in the laboratory from the pure chemicals. Comparison of the results for the two types of concrete indicates, however, an improved durability of the concrete manufactured with the type III/A cement to the aggression of the two acetate solutions. In particular, in the case of the specimens immersed in the solution of the laboratory-prepared CMA, the strength after 8 months of immersion is virtually the same as the 28-day value. This result indirectly supports previous research [2,8] that suggested that the aggressive nature of CMA solutions was associated with leaching of calcium hydroxide. In fact, in concretes manufactured with a slag cement, the  $Ca(OH)_2$  produced by hydration of the cement is at least partially consumed in the reaction with the slag.

### 5.2. Visual rating of concrete specimens

The results of the visual rating operation are presented in Figs. 4 and 5. While the specimens immersed in water

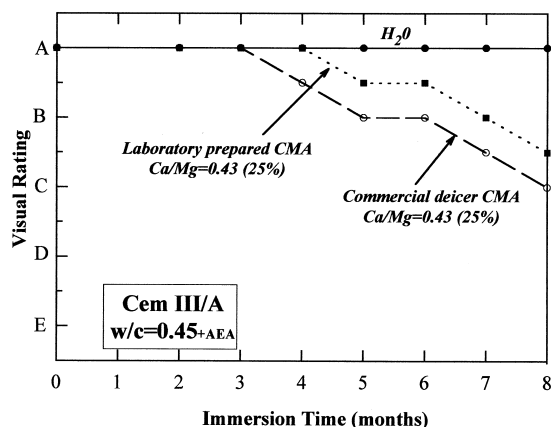


Fig. 5. Visual rating versus immersion time (slag cement).

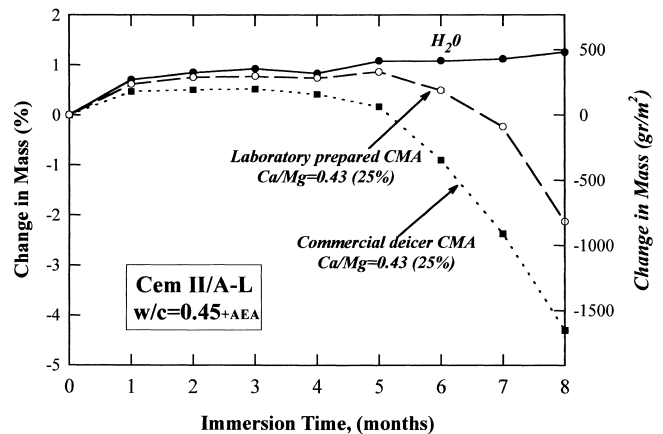


Fig. 6. Change in mass versus immersion time (limestone-portland cement).

maintain a perfect rating of A (intact conditions) throughout the 8 months of experimentation, visual observation of the specimens immersed in the acetate solutions indicates the progressive deterioration of the cement matrix of the concrete. The first signs of deterioration are observed as early as 3 months after immersion and are particularly marked in the case of the specimens exposed to the solution of the commercial deicer. This is shown clearly in Fig. 4, in which the curves relative to the two acetate solutions diverge progressively as the period of immersion increases. As observed for the compressive strength results, the concrete manufactured with the slag-based cement exhibits higher resistance to the aggressive action of the acetates. Comparison with the compressive strength data indicates that until the observed specimen deterioration reaches a level corresponding to class C of the rating system (see Fig. 1), no significant reduction in strength is observed.

### 5.3. Mass loss of concrete specimens

The changes in mass produced by immersion in the three solutions are presented in Figs. 6 and 7 for specimens

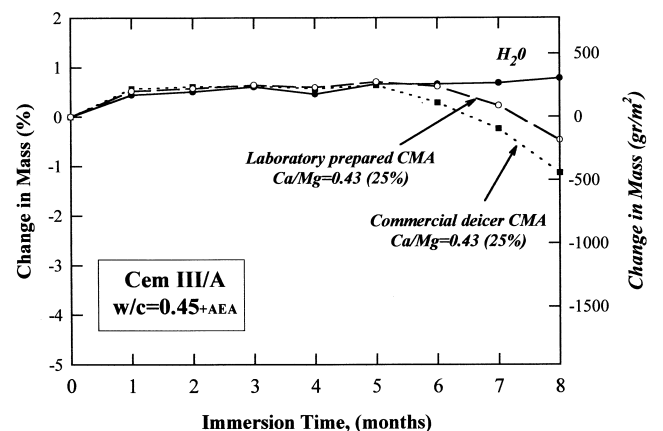


Fig. 7. Change in mass versus immersion time (slag cement).

manufactured using the limestone-Portland and slag-Portland cements, respectively. Again the data are presented in double form: in terms of the mass loss normalized by the surface area exposed to the solutions (i.e., in grams per square centimeter) on the right-hand axis, and as a percentage of the value measured after 1 day of immersion on the left-hand axis.

The results are in substantial agreement with the compressive strength and visual rating data. The specimens immersed in water display an increase in mass over the first few months before attaining a virtually constant value. In the case of the concrete specimens manufactured with the type II/A-L cement (Fig. 6), a marginally smaller increase in mass is measured during the first 3 months of immersion in the acetate solutions. After 4 months the specimens immersed in the solution of the commercial deicer present increasingly significant mass loss, up to a maximum value of approximately  $-4.5\%$  (ca.  $-1500 \text{ g/m}^2$ ) after 8 months. This process is slightly delayed, by about a month, for the specimens immersed in the other acetate solution. The final mass loss at 8 months is also observed to be less significant ( $-2\%$ , ca.  $-800 \text{ g/m}^2$ ).

Qualitatively similar observations apply to the specimens manufactured with the type III/A cement (Fig. 7), despite the less significant variations in mass measured (e.g., approximately  $-1\%$  versus  $-4.5\%$ , after 8 months of immersion in the deicer solution). In addition, in this case hardly any difference between the specimens stored in the reference solution and in the two acetate solutions is observed for the first 5 months. However, following this period the specimens immersed in the CMA solutions, and particularly those stored in the deicer solution, manifest loss of material and subsequent decrease in mass.

## 6. Conclusions

The research presented in this paper has confirmed previous work performed by the authors [2] indicating that the cement matrix of concrete is severely attacked by CMA solutions. The conclusions drawn from the data presented can be summarized as follows:

- Even for concretes manufactured following guidelines for structures exposed to freezing and thawing in presence of deicing chemicals ( $w/c = 0.45$  and air-entraining agent), continuous exposure to concentrated CMA solutions (25%) leads to significant degradation of the concrete.
- The attack manifests itself through deterioration of the cement matrix and exposure of the aggregates, and

results in mass loss and in a marked decrease in the load capacity (as great as 50%).

- The aggression is mitigated when a slag cement (40% slag) is used in place of a limestone-Portland cement, supporting the hypothesis [2,8] that the aggression is associated with leaching of calcium hydroxide present in the cement paste.
- The deterioration of the concrete appears to be marginally greater in the case of immersion in solutions manufactured using a commercial CMA-based deicing product, rather than employing pure calcium and magnesium acetates (under conditions of equal concentration and molar ratio).

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