

Edited by O.E. Gjorv, K. Sakai and N. Banthia

CONCRETE UNDER SEVERE CONDITIONS 2

Environment and Loading



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An imprint of Routledge

Volume one

CONCRETE DETERIORATION CAUSED BY EXPOSURE TO CALCIUM-MAGNESIUM ACETATE AQUEOUS SOLUTIONS

M. SANTAGATA and M. COLLEPARDI

Department of Material and Earth Sciences, University of Ancona, Italy

Abstract

The present paper reports data on the effect of calcium-magnesium acetate (CMA) aqueous solutions on concrete. This was evaluated in terms of reduction in compressive strength, loss in mass and visible deterioration of concrete specimens.

Concretes with two portland cement based binders (blended with 20% of fly ash or ground limestone), manufactured with two water-cement ratios (0.60 and 0.45), with and without an air-entraining agent, were continuously exposed at 5°C and 20°C to CMA aqueous solutions up to nine months. 28-day cured concrete specimens were immersed in calcium magnesium acetate solutions with different Ca/Mg molar ratio (0, 0.43, 1.26, ∞) and different concentrations (12, 25, 38%). They were also immersed in pure water for comparison purposes.

The CMA attacked the concrete surface through a delamination process of the cement matrix. The attack was milder when a lower water-cement ratio was adopted and it was mitigated by the use of fly ash-portland blended cement in the concrete mixtures. No significant benefit in reducing the CMA aggression was recorded through the use of an air-entraining agent. The CMA attack increased with higher concentrations of the acetate solutions and was particularly severe with a specific Ca/Mg molar ratio (0.43). It occurred more quickly at higher temperature (20°C versus 5°C).

X-ray diffraction analysis on cement paste specimens indicated that continuous exposure to the acetate solutions caused leaching of the calcium hydroxide present in the cement paste.

Keywords: calcium-magnesium acetate, concrete deterioration, deicing salts

1 Introduction

Sodium and calcium chlorides have long been the most widely used deicing salts because of their quick melting characteristics, easy storage and application

requirements, and low overall capital costs. However, over the years many studies have pointed out the adverse effects of the use of these salts which lead to ever increasing maintenance costs associated, in particular, with vehicular and infrastructure damage. Focusing on this second aspect, it has been long known that the chloride present in these salts promotes corrosion of steel structures as well as of concrete reinforcements [1]. More recently it has been shown that, particularly at low temperatures, calcium chloride can specifically act as an aggressive agent towards the cement matrix through the formation of an hydrated calcium oxychloride which causes disruptive hydraulic pressure [2]. On the other hand, sodium chloride can represent an aggressive agent for concrete if alkali-reactive aggregates are present [3].

For all these reasons much research has been directed towards the development of alternate deicers. In particular over the last 25 years products based on calcium-magnesium acetate (CMA) have been developed and commercialized. Although these deicers are significantly more expensive than the traditional chloride based products, there is some evidence in the literature that their performance may be superior in terms of duration of the deicing action [4], reduction of corrosion risks [5], and inhibition of corrosion when used in combination with traditional salts [5]. In addition, they do not appear to have any significant negative impact to the environment [6]. These advantages seem to warrant the use of this type of product in deicing particularly important bridges and approaches, especially in environmentally sensitive areas. In fact, in the US, the federal administration is encouraging the use of acetate-based alternate deicers for this type of application with a contribution of 80% of the cost of the material.

Data on the interaction of acetate-based deicers with concrete are still scarce and the effect of these chemicals on the cement matrix of concrete is not clear. In assessing the behaviour of alternate deicers, Lancaster [7] reported that acetate-based deicers did not cause significant scaling damage to air-entrained pavement quality concrete. However, experimental work by Peterson [8] indicates that CMA salts may cause deterioration of concrete. Peterson reported that concrete specimens immersed in solutions of calcium-magnesium acetate underwent significant mass loss and degradation of the mechanical properties. The effect was more significant at 20°C than at 5°C and particularly marked in the specimens with higher water content which showed losses in strength as large as 40% after 22 months of immersion in CMA aqueous solutions. However, the influence of parameters such as salt Ca/Mg molar ratio, concentration of the solution, type of cement remains still not well understood.

2 Scope of research

As part of an ongoing broader research program aimed at investigating the interaction of deicing agents with concrete, an experimental investigation on the effects of acetate-based deicers on concrete was undertaken in 1996 at the University of Ancona. This paper reports data for the first nine months of testing and discusses how the following parameters affect the deterioration of concrete caused by continuous immersion in solutions of calcium and/or magnesium acetates:

- type of cement,
- water-cement ratio of the concrete exposed to the acetates,
- use of an air-entraining agent,

- concentration of the acetate solution
- Ca/Mg molar ratio of the acetate solution,
- temperature (5°C vs. 20°C).

The effects of the acetate solutions on the concrete were evaluated in terms of reduction in compressive strength, mass loss and visible deterioration of the concrete specimens.

3 Materials

Two different cements were employed to manufacture concrete and cement paste specimens (40x40x160 mm): a type II/A-L 42.5R blended portland cement (80% of portland clinker and 20% of ground limestone) and a type II/A-V 42.5R fly ash blended portland cement (80% portland clinker and 20% of fly ash) according to the European standard norm EN 197/1. A limestone natural aggregate was used with 75% of sand (0-4 mm) and 25% of gravel (4-8 mm).

Concrete mixtures with two w/c (0.45 and 0.60) for each cement type were produced. Air-entrained mixtures were also manufactured at a w/c of 0.45. In order to emphasize the action of the CMA solutions on the cement matrix of the concrete, relatively cement-rich mixtures were employed. Therefore an aggregate-cement ratio as low as three was adopted by using a relatively small maximum size of the coarse aggregate. Table 1 shows the composition of all the concrete mixtures placed at a flowing consistency. The specimens were wet cured (100% R.H.) for 7 days and air cured (65% R.H.) at 20°C for additional 21 days before the immersion in CMA aqueous solutions. Cement pastes with w/c of 0.45 and 0.60 were also produced and cured as the concrete specimens before the immersion in the CMA aqueous solutions. These specimens were used for the X-ray diffraction analysis to detect chemical changes, if any, in the cement matrix caused by the exposure to the CMA salts.

Table 1. Concrete mixtures.

Component	Composition (kg/m ³)					
	495	-	520	-	485	-
limestone-portland cement II/A-L 42.5R	495	-	520	-	485	-
fly ash-portland cement II/A-V 42.5R	-	490	-	510	-	490
sand (0-4 mm)	1114	1103	1170	1148	1091	1103
gravel (4-8 mm)	371	367	390	382	364	367
water	297	294	234	229	218	220
air-entraining agent	-	-	-	-	1.6	1.1
w/c	0.60	0.60	0.45	0.45	0.45	0.45
28-day compressive strength (MPa)	30.6	33.5	52.7	55.2	40.0	39.0
air (% by volume)	2.5	1.9	2.9	2.8	8.6	7.9

Commercially available calcium and magnesium acetates were utilized to produce the solutions. Along with a reference environment of pure water, seven aqueous solutions, differing in the acetate concentration (12, 25, and 38%) and in the Ca/Mg molar ratio (0, 0.43, 1.26, and ∞), were prepared. The selection of the 0.43 Ca/Mg molar ratio was based on the desire to simulate as closely as possible an existing commercial calcium-magnesium acetate deicing product. On the other hand, the higher molar ratio (1.26) was selected in an attempt to verify the results presented by Peterson [8].

4 Methods

The concrete and paste specimens were immersed in the solutions at 5°C or 20°C in order to study how temperature affects the behaviour of the material in a CMA environment. The 28-day compressive strength was taken as the datum with respect to which the percent increase or decrease in strength after immersion in the acetate solutions was calculated.

The first compressive strength measurements on specimens kept in the acetate solutions were performed after two months of immersion. After that, measurements were performed every 30 days. The data presented in this paper refers to the first nine months of testing.

At each testing time one specimen from each of the solutions was broken in bending with a three point bending configuration. Compression tests were performed on the two halves of the specimens obtained from the bending test and the two results available for each curing time were averaged. The results are presented in terms of nominal compressive strength, i.e. maximum compressive force divided by the original area of the specimen. This is done to account for the fact that, when a specimen undergoes a reduction in mass and thus in cross-section area, the maximum sustainable load decreases proportionally to the deterioration level, even if the remaining concrete is not significantly deteriorated. On the other hand, the measurement of the actual compressive strength - maximum compressive force divided by the remaining area of the specimen - would underestimate the real deterioration level since it would refer to a less or not deteriorated portion of the specimen.

At each testing time a control specimen from each of the solutions was weighed to determine the mass loss or gain. The mass of the same specimens after one day of immersion in the solutions was used as the initial reference mass in these calculations.

At regular intervals the control specimens were visually examined to determine the degree of deterioration of the concrete. A grade varying between A (intact condition) and E (strongly deteriorated specimen) was assigned to each of the control specimens. Figure 1 shows examples of specimens which were assigned the ratings from A to E.

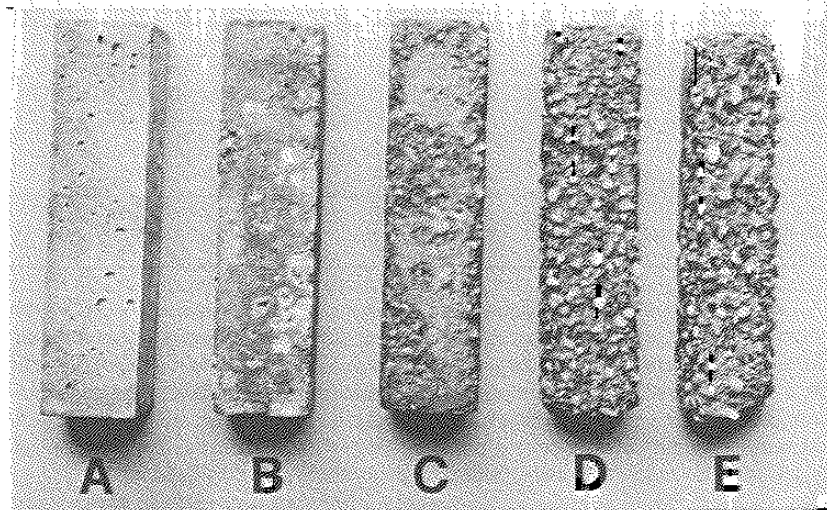


Fig. 1. Visual ratings (from A to E) of deteriorated concrete

5 Results

Fig. 2 shows the compressive strength results for specimens manufactured with the type II/A-L cement at a w/c of 0.60, immersed in acetate solutions at 20°C. The two solutions, both at a concentration of 38%, differ in the calcium-magnesium-molar ratio (Ca/Mg): 0.43 and 1.26 respectively. The compressive strength results for the corresponding specimens cured under water are also presented for comparison purposes. As expected, with respect to the 28-day curing time, the specimens cured under water show a continuous slight increase in compressive strength with time due to a post-hardening effect. On the other hand, the specimens stored in the two acetate solutions, and particularly those immersed in the solution with Ca/Mg of 0.43, exhibit a significant loss in compressive strength from the very early stages. After nine months of immersion the compressive strength decreased by 68% and 50% with respect to the initial value in acetate solutions with Ca/Mg equal to 0.43 and 1.26 respectively. The compressive strength of the concretes immersed in the acetate solutions show some scatter. Most likely this is due to some local and erratic deterioration of the surface which causes the faces of the specimens to be not perfectly parallel to each other. This effect is particularly marked for the highly deteriorated specimens.

Similar results are presented in Fig. 3 for specimens with the blended fly ash-portland cement (type II/A-V 42.5R) at equal w/c (0.60). In this case the post-hardening effect in pure water after 28 days is more remarkable than in the corresponding limestone-portland cement concrete due to the pozzolanic reaction of the fly ash which occurs at longer ages. The concrete with the fly ash-portland cement in general appears to be more resistant to the aggressive action of the two acetate solutions. In particular, the specimens immersed in the solution with the higher Ca/Mg molar ratio shows a negligible loss in strength after nine months of immersion. The visual ratings of the specimens (Fig.4-5) and the mass loss measurements (Fig.6-7) both confirm the compressive strength results: a) the specimens manufactured with the fly ash-portland cement are less damaged than those with the limestone-portland cement, particularly when exposed to the higher Ca/Mg molar ratio (1.26) solution; b) the solution with lower Ca/Mg molar ratio (0.43) causes a more significant degradation of the specimens. The loss in mass of the specimens immersed in this solution was remarkably high, 31% and 22% for the concretes manufactured respectively with the limestone-portland and the fly ash-portland cement, and a thick cementitious slurry was deposited at the bottom of the tank containing this solution.

The data relative to mixtures with w/c of 0.45 - not shown in the present paper for the sake of brevity - confirm the better resistance to the acetate attack by the concrete manufactured with the fly ash-portland cement and the more aggressive nature of the acetate with the lower Ca/Mg molar ratio (0.43). In general, the decrease in w/c from 0.60 to 0.45 reduces the entity of the damage to the concrete as measured by the loss in compressive strength, the visual rating and the mass loss.

A third set of results relative to air entrained concrete specimens - again, not shown for the sake of brevity - indicate that the presence of air bubbles does not seem to lead to any improvement in the durability performance of the concrete specimens.

As discussed above, in the experimental program performed, acetate solutions of different concentration were investigated. In particular, for the solution with the Ca/Mg molar ratio of 0.43, three concentrations were investigated: 12, 25 and 38%. For the sake of brevity only the compressive strength results for the 0.45 w/c concrete

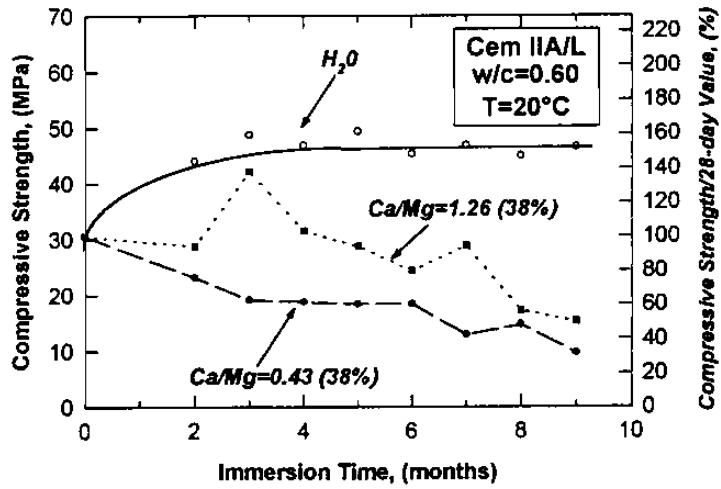


Fig. 2. Compressive strength versus immersion time (limestone-portland cement; $w/c=0.60$)

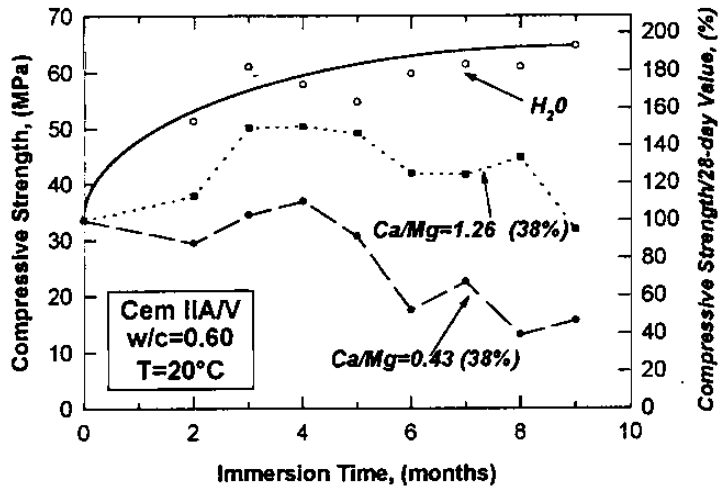


Fig. 3. Compressive strength versus immersion time (fly ash-portland cement; $w/c=0.60$)

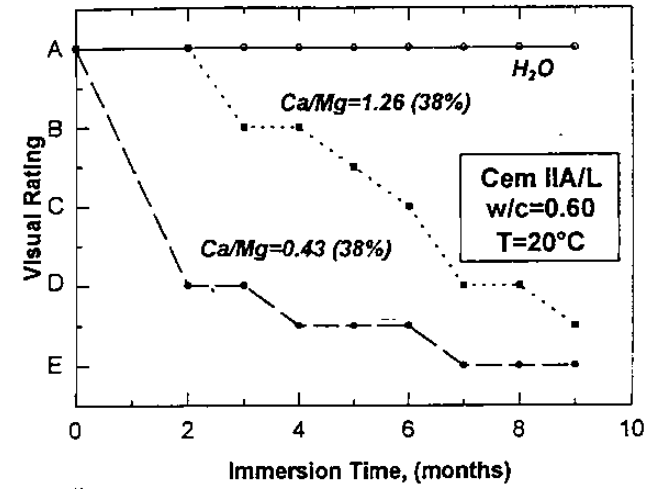


Fig. 4. Visual rating versus immersion time (limestone-portland cement; $w/c=0.60$)

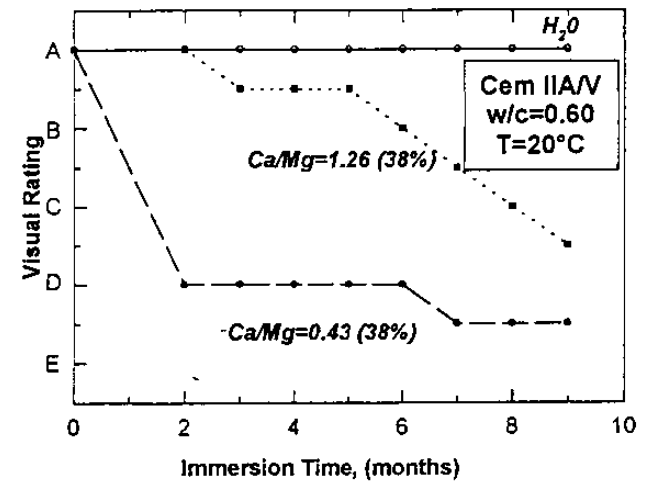


Fig. 5. Visual rating versus immersion time (fly ash-portland cement; $w/c=0.60$)

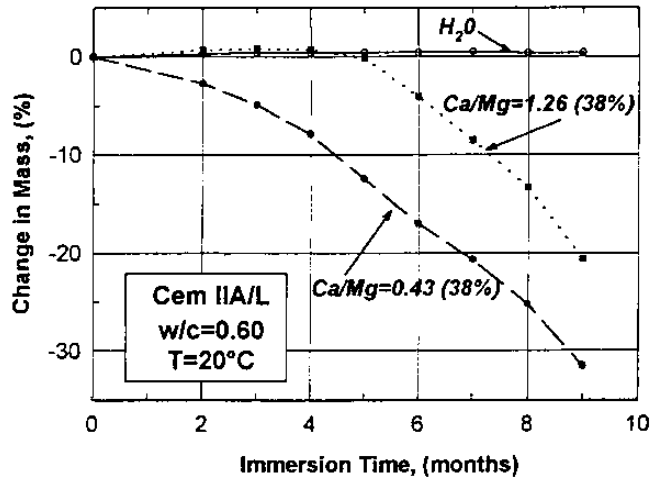


Fig. 6. Mass change versus immersion time (limestone-Portland cement; $w/c=0.60$)

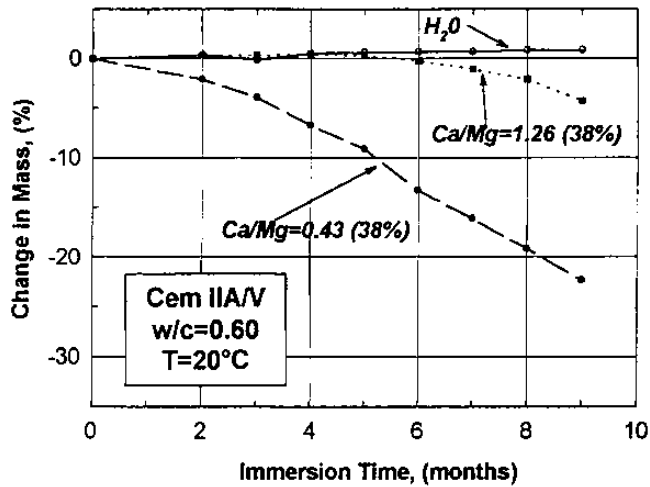


Fig. 7. Mass change versus immersion time (fly ash-Portland cement; $w/c=0.60$)

specimens manufactured with the limestone-Portland cement (II/A-L 42.5R) are considered in the present paper. Fig. 8 shows the compressive strength values versus the period of immersion for specimens cured in water and in the three acetate solutions with Ca/Mg equal to 0.43. The results indicate that, for lower concentrations of the solution (12 and 25%), the deterioration of the concrete is not as significant as that observed for the specimens kept in the 38% solution.

Fig. 9 shows how the molar ratio of the calcium-magnesium acetate used for the solutions affects the deterioration of the concrete specimens. The figure presents the curves of compressive strength versus time for specimens, manufactured with the limestone-Portland cement (II/A-L 42.5R) and w/c of 0.45, immersed in three acetate solutions of equal concentration (25%): one is a solution with Ca/Mg molar ratio of 1.26, the other two are solutions of pure calcium ($Ca/Mg=\infty$) and magnesium ($Ca/Mg=0$) acetates. Again the behaviour of the specimens immersed under water is also shown for comparison purposes. The calcium acetate solution ($Ca/Mg=\infty$) appears to be the least aggressive towards concrete whereas the magnesium acetate solution ($Ca/Mg=0$) is as aggressive as the CMA solution with Ca/Mg molar ratio of 1.26. Similar conclusions can be drawn for the concrete manufactured with the fly ash-Portland cement. These results are not presented in this paper for the sake of brevity.

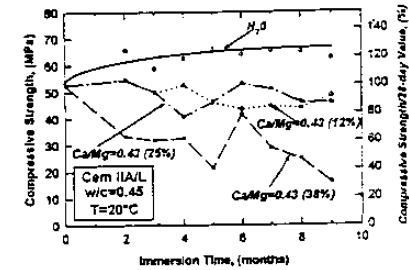


Fig. 8. Influence of salt concentration on compressive strength of specimens immersed in CMA solutions

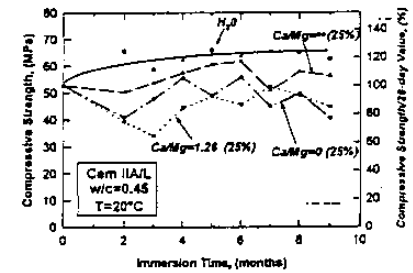


Fig. 9. Influence of Ca/Mg molar ratio on compressive strength of specimens immersed in CMA solutions

Fig. 10 presents the curves of compressive strength versus time for specimens manufactured with the limestone-portland cement (II/A-L 42.5R) cement and w/c of 0.60 immersed in the two most aggressive solution examined (Ca/Mg=0.43 and 1.26 at 38%) at the temperature of 5°C. It appears that at the lower temperature the deterioration of the concrete - in terms of strength loss with respect to the 28-day compressive strength - caused by the acetate solution is negligible, if any. However, the surface of the concrete showed some deterioration and after nine months a visual rating of C was assigned to these specimens. Similar results - not presented in the paper for the sake of brevity - were obtained for concretes manufactured with lower w/c and fly ash-portland cements.

XRD analysis were carried out on the cement paste specimens and on the slurry deposited at the bottom of the tanks containing the acetate solutions. Fig. 11 shows the XRD patterns relative to cement pastes manufactured with the limestone-portland cement and w/c of 0.60 immersed in water and in two 38% CMA solutions with Ca/Mg molar ratio of 0.43 and 1.26 respectively, for five months. The most significant difference in chemical composition between the material immersed in pure water and that deteriorated by the CMA attack is the decrease or even the disappearance of the calcium hydroxide peaks in the cement pastes immersed in the acetate solutions. This seems to indicate that the acetate solutions are able to cause leaching of the calcium hydroxide present in the cement paste. The XRD results confirm the more aggressive nature of the solution with Ca/Mg molar ratio of 0.43. In this case, in fact, the Ca(OH)₂ peaks are completely missing while they are still visible, although attenuated, when the cement pastes are kept in the solution with higher Ca/Mg molar ratio (1.26).

The result of the XRD analysis performed on the slurry collected from the bottom of the tank containing the 38% solution with Ca/Mg molar ratio of 0.43 is shown in Fig. 12. The pattern indicates the presence of a hydrated calcium acetate ((CH₃COO)₂Ca·H₂O, indicated with the letter x) most likely produced by the reaction of the calcium hydroxide leached from the cement paste with the acetate solution.

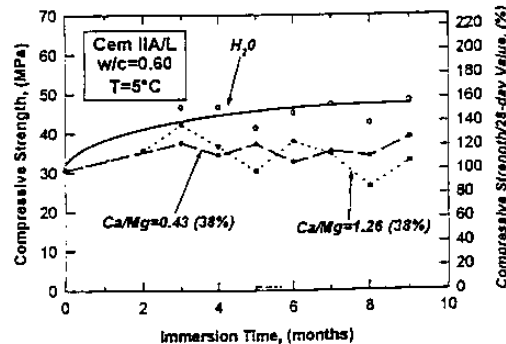


Fig. 10. Compressive strength versus immersion time at 5°C (limestone-portland cement; w/c= 0.60).

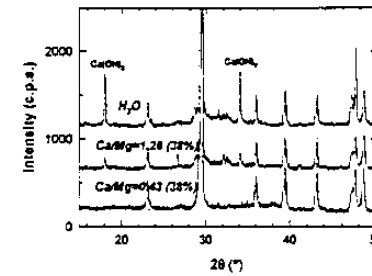


Fig. 11. XRD patterns of cement paste specimens (limestone-portland cement; w/c=0.60) after five months of immersion in water or 38% CMA solutions (T=20°C)

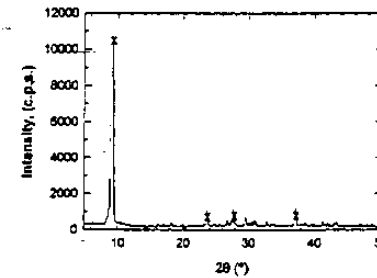


Fig. 12. Typical XRD pattern of the slurry formed at 20°C in a CMA solution (38% Ca/Mg=0.43). X indicates the main peaks of Ca(CH₃COO)₂·H₂O.

6 Conclusions

Calcium magnesium acetate solutions attack very severely the cement matrix of concrete. Although the exact mechanism of deterioration is not yet completely understood, it has been found that continuous exposure to a CMA solution causes leaching of the calcium hydroxide present in the cement pastes. As far as the concrete performance is concerned, the following conclusions can be drawn:

- CMA attack on concrete specimens manifests itself through delamination of the cement matrix and can be assessed in terms of strength reduction, mass loss and visual deterioration;
- CMA aggression is more severe when the concentration of the CMA solutions is increased (in the range 12-38%);

- concrete deterioration is more severe for a particular Ca/Mg molar ratio equal to 0.43 and it is less significant when pure calcium or magnesium acetate solutions are employed;
- concrete aggression by CMA is reduced by decreasing the water-cement ratio in the range 0.45-0.60;
- CMA attack is mitigated by the presence of fly ash in the blended portland cement;
- no benefit - in terms of better resistance to the CMA attack- is recorded in air-entrained concretes;
- CMA attack is more severe when concrete specimens are continuously exposed to the aggressive solutions at 20°C rather than at 5°C.

7 Acknowledgements

The authors wish to thank the company ENCO of Spresiano, Italy for manufacturing the over 500 concrete specimens employed in the experimental program. Thanks are also expressed to Miss Marta Bettucci who performed many of the tests presented as part of her Master's thesis research.

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