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CHEMICAL EFFECTS ON CEMENT MORTAR OF CALCIUM MAGNESIUM ACETATE AS A DEICING SALT

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ABSTRACT

Two different products of calcium magnesium acetate (CMA) were tested. Their molar ratios, Ca/Mg, were 1.26 and 0.91 respectively. Both products were used as concentrated solutions. In addition, the 0.91 product was also used in a solution, which was diluted so that its freezing point depression was as great as that of a 3 percent (by mass) sodium chloride solution. - Prisms of 0.60 mortar expanded more in a concentrated solution of 1.26 CMA than in one of 0.91 CMA. - The loss of mass in mortar prisms on immersion in concentrated solutions was more rapid in 0.91 CMA than in 1.26 CMA, and much more rapid at +20 than at +5°C. Immersion in the dilute CMA caused an increase of the mass during the first six months. - With respect to the flexural and compressive strength, the dilute solution of 0.91 CMA caused the greatest decreases. However, in several cases the compressive strength after immersion in concentrated solution could not be determined.

Introduction

In (1), calcium magnesium acetate (CMA) was recommended as a de-icer; it is noncorrosive on steel and aluminum, and is also likely to be noncorrosive on concrete. At a discussion with staff from the Swedish Road and Traffic Research Institute, in Linköping, and from the Swedish National Road Administration, at Borlänge, an investigation by our division at Lund Institute of Technology was decided upon in order to determine whether a magnesium compound like CMA really is noncorrosive on concrete.

Methods

1. Models of concrete

Two types of mortar served as models, the water:cement ratios of which were 0.45 and 0.60.

The 0.45 type was a test mortar according to ISO R 679, in which the water content was reduced from 250 to 240 g, and the cement content was increased from 500 to 533 g. The masses of all three fractions of standard sand - the coarse, the medium, and the fine fractions, were 500 g.

In the 0.60 type mortar, the water content in each batch was also 240 g. The cement content (density 3.1 g/ml) was reduced from 533 to 400 g. This caused a loss of the solid volume of fine materials, which was compensated for by increasing the content of fine standard sand (density 2,6 g/ml) from 500 to 612 g. The contents of medium and coarse standard sand were kept unchanged at 500 g of each.

2. Test specimens

For determination of mass changes and, at the end of the investigation, also of strength, sets of three prisms (4 x 4 x 16 cm) were made. For determination of length changes, sets of three prisms (2 x 2 x 28 cm) were made, each with dowel rods at the ends.

After molding, the prisms were protected with plastic film for two days, and then stripped. The prisms were stored in water for 3 - 6 days. After this period, the 4 x 4 x 16 cm prisms were weighed, and the 2 x 2 x 28 cm prisms were gauged for length. The prisms were transferred to a box, the air in which was kept at a relative humidity of 75 percent, until the prisms had reached an age of 28 days.

3. Boxes for immersion in different liquids

In each box were stored six prisms sized 4 x 4 x 16 cm and six prisms of 2 x 2 x 28 cm. Three prisms of each size were made of 0.45 type mortar, and three prisms of 0.60 type mortar. The box contained about 29 dm^3 of liquid. For each liquid, one box was stored in a room with the temperature at +5°C, and another in a room with the temperature at +20°C.

4. Immersion liquids

1 Tap water from the Lund network, as a reference.
Sodium chloride solutions:
2 Saturated.
3 3 percent by mass.
Calcium magnesium acetate solutions (CMA):
4 Concentrated with molar ratio Ca/Mg equal to 1.26.
5 Concentrated with molar ratio 0.91 recommended by Kent Gustafsson in (2), p. 36.
6 6.5 g per 100 g water, molar ratio 0.91. This dilute solution has a freezing point depression, equal to that of 3 % sodium chloride solution, by mass.
7 Calcium acetate, saturated solution.

5. Length change

The 2 x 2 x 28 cm prisms were checked with a dial indicator at 8 days of age after storage in water, and once a month during storage in one of the test liquids.

6. Mass change

The 4 x 4 x 16 cm prisms were weighed at 8 days of age after storage in water, and once a month during storage in one of the test liquids.

7. Strength test

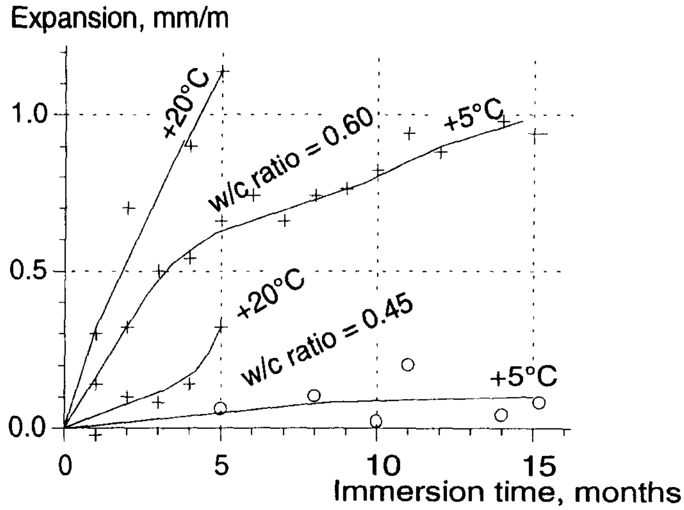

FIG. 1
Length change on immersion in concentrated solution of CMA, type 1.26

As soon as the immersion period was completed, all sets of 4 x 4 x 16 cm prisms, which were stored in a +5°C solution, were tested for flexural strength, and afterwards the two pieces of each prism were tested for compressive strength. However, after storing in a strong solution of calcium magnesium acetate, the flexural test could be performed only after correcting the section modulus of the prisms for loss of mortar from the surfaces. The loss also obstructed a number of compressive strength tests.

Results

1. Length change

FIG. 1 shows that a concentrated solution of CMA with the molar ratio Ca/Mg equal to 1.26 causes a mortar with the water:cement ratio 0.60 to expand essentially more than a 0.45 mortar. An attempt to explain this difference is given in connection with FIG. 4. - The figure also shows that the rate of expansion is greater at +20°C than at +5°C. As an instance, 0.60 mortar at +20°C expanded 1.2 mm/m within 6 months.

FIG. 2 shows that the concentrated CMA solution with the lower molar ratio Ca/Mg=0.91 caused hardly any expansion of the mortar prisms, except in one case, viz. the 0.60 mortar, stored at +20°C, which expanded about 0.35 mm/m, not immediately from the start, but during the period 4 - 6 months.

FIG. 3 shows that the dilute solution of CMA of type 0.91 causes prisms of mortar to expand continuously during a test period of six months. The 0.45 mortar prisms expanded about twice as much as the prisms of 0.60 mortar, and the expansion rate was greater at +20°C than at +5°C. An attempt to explain these results is made in connection with FIG. 4. In no case is the expansion great enough to be deleterious to the prisms.

FIG. 4 shows that a saturated solution of calcium acetate causes a very strong expansion, especially of mortar with the water:cement ratio 0.45. Still, no cracks could be observed. Mortar of type 0.60 expands far less, and the expansion proceeds much more rapidly at +20°C

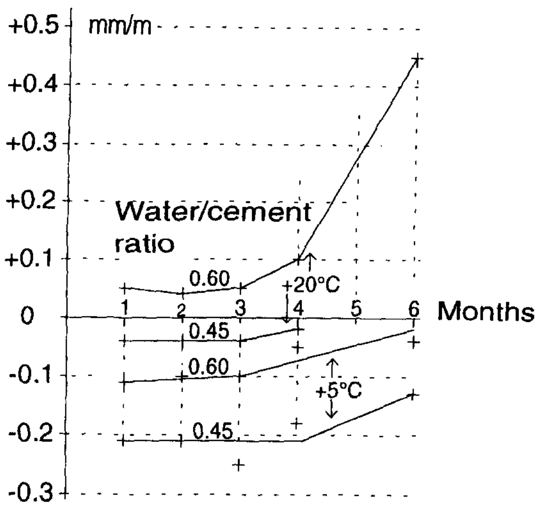

FIG. 2
Length change on immersion in concentrated solution of CMA, type 0.91

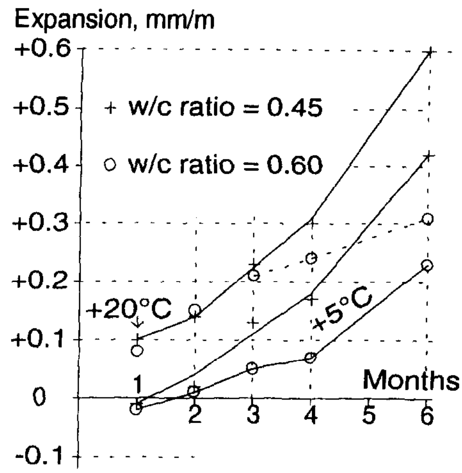

FIG. 3
Length change on immersion in dilute solution of CMA, type 0.91

than at +5°C. - Probably the calcium acetate penetrates the pore system of the hardened cement paste in the mortar. There, a double salt is likely to be formed with the portlandite (calcium hydroxide) of the hardened cement paste.

It is reasonable to assume that this double salt contains calcium ions, acetate ions, hydroxide ions, and some form of water, but I have not managed to find any literature on such a compound. This double salt may explain why the mortar expands, and the additional pore volume in the 0.60 type mortar can explain why this type of mortar seems to accept the volume of the recently formed mineral with less expansion than the one which occurs in the more compact mortar of type 0.45.

The double salt seems to be viscous in consistency, which may explain why so great an expansion as more than 15 mm/m can be accepted without formation of cracks. After 22 months, much of the double salt had carbonated, and its consistency had changed from viscous to brittle. At this time, cracks were observed in the mortar.

The different degrees of expansion, just observed in FIG. (1 - 3), may be explained as a consequence of the calcium acetate content of the calcium magnesium acetate (CMA) solutions. If this is correct, the greater expansion in FIG. 1 is due to the greater molar ratio Ca/Mg=1.26, as compared to 0.91 in FIG. 2 and FIG 3. Whether the concentrated CMA solution belongs to type 1.26, as in FIG. 1, or to type 0.91, as in FIG. 2, the mortar of type 0.60 has the greatest expansion. This is in contrast to the behaviour of the mortars in saturated calcium acetate solution according to FIG. 4. In this figure, at each temperature, the type 0.45 mortar has the greatest expansion. Probably the explanation of this difference is that the type 0.60 mortar has a greater pore volume, which allows a more rapid penetration of the CMA solutions into the mortar. When the solution slowly reacts with the cement paste, magnesium is lost as magnesium hydroxide, and calcium acetate remains, more from the 1.26 type of CMA than from the 0.91 type. Thus, the expansion rate is in corresponding degree greater in the 0.60 mortar, and especially at immersion in CMA solution of the 1.26 type.

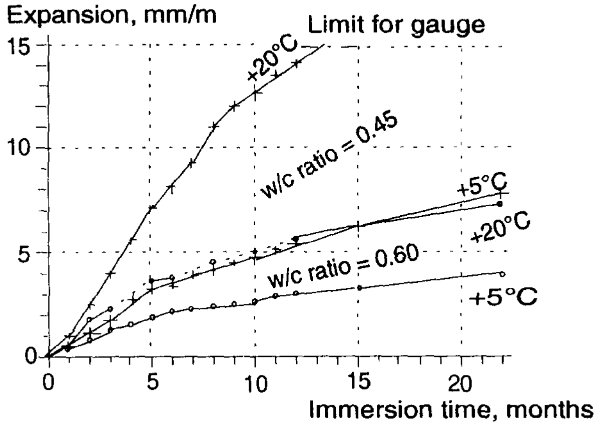

FIG. 4
Length change on immersion in a saturated solution of calcium acetate

In FIG. 3, the CMA solution is dilute (6,5 g/100 g water). All mortar in these baths forms a thin white layer on the surface, and microscopic examination in transmitted light indicate that this layer consists of brucite (magnesium hydroxide). This mineral is precipitated when the pH value of the solution is increased in contact with the portlandite (calcium hydroxide) of the mortar, and the molar ratio Ca/Mg of the solution is gradually increased. The formation of a double salt of calcium acetate and calcium hydroxide is promoted. This generates an expansion. Though the range is moderate, the rate is essentially greater in the dilute solution than in the concentrated solution.

2. Mass change

FIG. 5 shows that the concentrated solution of the 1.26 type CMA attacks the mortar fairly rapidly at +20° C, but only slowly at +5°C. Strangely enough, the prisms of mortar with the water:cement ratio 0.45 lost their mass most rapidly, but at +20° C the loss in the 0.60 type mortar overtook the loss in the 0.45 type mortar after 7 months.

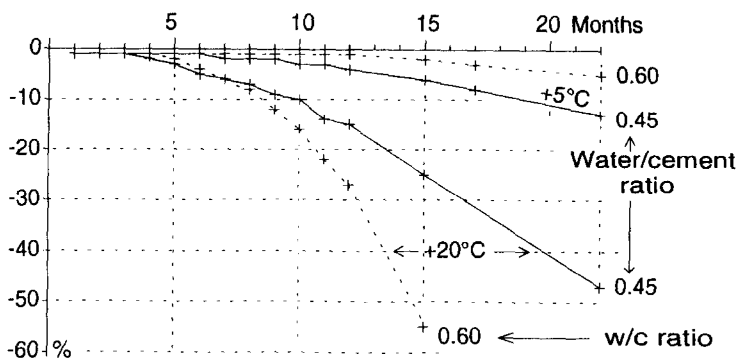

FIG. 5
Loss of mass, in percent, of mortar prisms immersed in concentrated solutions of CMA. Molar ratio Ca/Mg=1.26

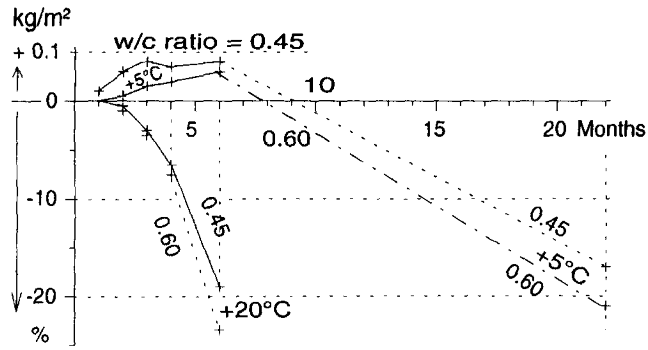

FIG. 6

Increase of mass, in kg/m^2, or loss of mass of mortar prisms, in percent. The prisms were immersed in concentrated solutions of CMA. Molar ratio Ca/Mg=0.91

FIG. 6 shows that the concentrated solution of the type 0.91 CMA attacked the type 0.45 mortar at +5°C so that the loss after 22 months was almost as great as in the type 1.26 solution. However, no loss happened during the first six months, either in the type 0.45 or in the type 0.60 mortar. - As expected, but unlike the type 1.26 solution, the type 0.91 CMA attacked the type 0.60 mortar somewhat more rapidly than the type 0.45 mortar.

As to the observations after 22 months, attention should be paid to the fact that the loss of mass has been promoted by brushing away loose material in order to facilitate the determination of the section modulus of the prisms. All other losses of mass, which can be read in FIG. 5 and 6, are spontaneous, and not promoted in any way. - At +20° C, the loss after 6 months in the type 0.91 solution was about 20 percent, to be compared with 5 percent for the 1.26 type solution. This indicates that the higher content of magnesium acetate in the type 0.91 CMA solution has accelerated the dissolution of the hardened cement paste, but only in the +20° C test and not at +5°C.

FIG. 7 shows a fairly slight increase of mass in all mortar prisms which were immersed in the dilute solutions of CMA, type 0.91. This increase was almost linear during the first 6 months. During the period 6 - 22 months at +5°C, the change of mass was practically negligible. - The gain in mass can not be explained only as a result of some reactions between magnesium

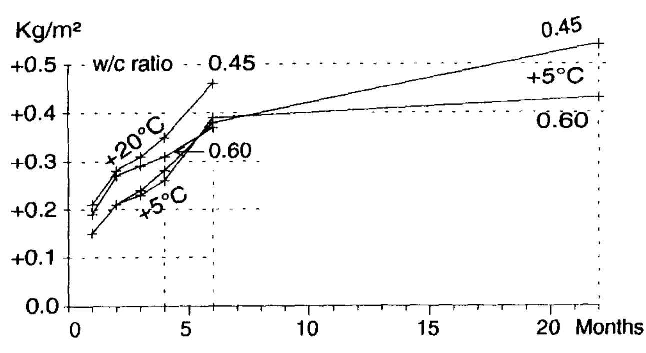

FIG. 7

Gain of mass, in kg/m^2, of mortar prisms immersed in dilute solutions of CMA. Molar ratio Ca/Mg=0.91

ions and the hardened cement paste. An increase in mass due to formation of magnesium hydroxide should in the long run be more than counterbalanced by a corresponding loss in mass because of dissolution of calcium hydroxide. Together, those two reactions will increase the content of calcium acetate in the solution. FIG 4 shows that a calcium acetate solution reacts in some way with hardened cement paste, most probably with the portlandite phase. This reactions may contribute to the increase of mass in the prisms by formation of some new mineral. - However, the fact that the mortar prisms did not lose any mass does not necessarily mean that no impairment of the strength of the mortar has taken place.

3. Strength change

The results of the flexural strength test are presented in FIG. 8. Only values from specimens which were stored at +5°C are inserted in the figure.

In the first work when the calcium magnesium acetate (CMA) had the molar ratio Ca/Mg=1.26, the flexural strength of the prisms changed in the following manner on storage for 22 months in the different salt solutions, compared to prisms of the same type stored in water: Saturated calcium acetate solution, type 0.45 mortar prisms +11 percent, type 0.60 mortar prisms -16 percent. - Saturated sodium chloride solution, type 0.45 mortar prisms +10 percent, type 0.60 mortar prisms -5 percent. - Concentrated CMA solution, type 0.45 mortar prisms, -2 percent, 0.60 mortar prisms +23 percent.

In the subsequent work, a type of calcium magnesium acetate (CMA) with the the lower molar ratio Ca/Mg=0.91 was used. The flexural strength of the prisms changed in the

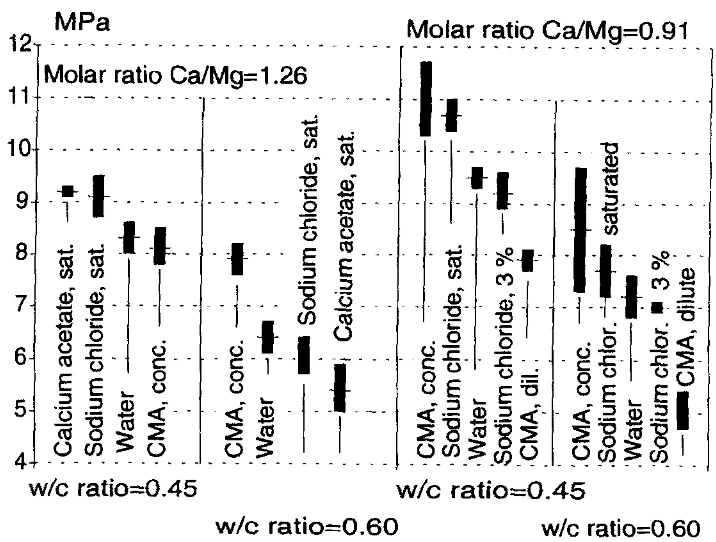

FIG. 8

Flexural strength tests of specimens stored at +5°C.
The vertical blocks indicate the deviation ranges.
The left part of the figure shows the results from the work with CMA with molar ratio Ca/Mg=1.26
The right part shows the corresponding results with CMA, molar ratio 0.91.
In each of these two parts, results from mortar with water:cement ratio 0.45 are placed to the left, and results from mortar with water:cement ratio 0.60 to the right.

following manner on storage for 22 months in the different salt solutions, compared to prisms of the same type stored in water: Solution of CMA, concentrated, type 0.45 mortar prisms +16 percent, type 0.60 mortar prisms +18 percent. Since this concentrated solution dissolved the surface layer of the prisms, the ultimate *load* of the prisms was less than that of full size prisms stored in water, while the ultimate *stress* was greater. - Dilute CMA solution (6.5 g per 100 g water), type 0.45 mortar prisms -17 percent, type 0.60 mortar prisms -29 percent. - Solution of sodium chloride, saturated, type 0.45 mortar prisms +13 percent, type 0.60 mortar prisms + 7 percent. Dilute sodium chloride solution (3 percent, by mass), type 0.45 and type 0.60 mortar prisms -3 percent.

Not all prisms could be tested for compressive strength. The results of the tests which could be performed are put together in FIG. 9. All specimens were stored at +5°C.

Irrespective of the CMA type and the water:cement ratio of the mortar, the prisms which were stored in water had the greatest compressive strength. - In the first work when the calcium magnesium acetate (CMA) had the molar ratio Ca/Mg=1.26, the compressive strength of the prisms changed in the following manner on storage for 22 months in the different salt solutions, compared to prisms of the same type stored in water: Sodium chloride, saturated solution, mortar prisms of either type 0.45 or type 0.60 -12 percent. - Concentrated calcium magnesium acetate solution (CMA) attacked the surfaces of the prisms so much that compressive strength could be determinated only for mortar of type 0.60; the relative strength value -19 percent was obtained. - Calcium acetate, saturated solution, type 0.45 mortar prisms

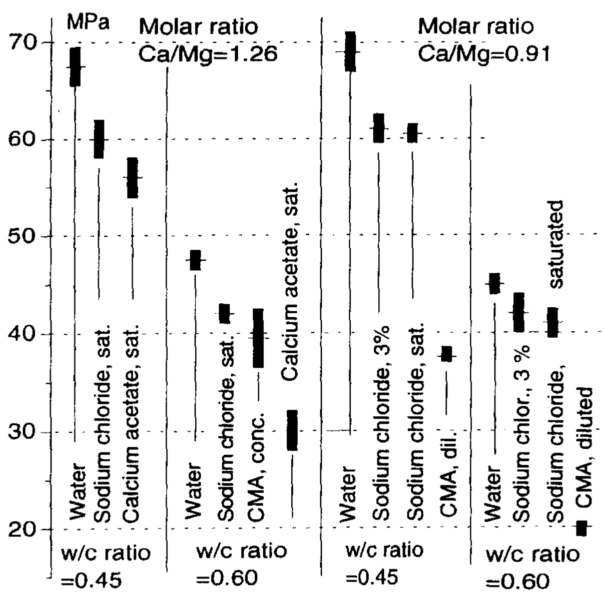

FIG. 9
Compressive strength of specimens stored at +5°C.
The vertical blocks indicate the deviation ranges.
The left part of the figure shows the results with CMA, molar ratio Ca/Mg=1.26.
The right part shows the corresponding results with CMA, molar ratio 0.91.
In each of the two parts, results from mortar with water cement ratio 0.45 are placed to the left, and results from mortar with ratio 0.60 to the right.

-17.1 percent, type 0.60 mortar prisms -36.5 percent.

In the subsequent work, a type of calcium magnesium acetate (CMA) with the lower molar ratio Ca/Mg=0.91 was used. The compressive strength of the prisms changed in the following manner on storage for 22 months in the different salt solutions, compared to prisms of the same type stored in water: Sodium chloride, saturated solution, type 0.45 mortar prisms -12.3 percent, type 0.60 mortar prisms -8.9 percent. - Sodium chloride, dilute solution (3 percent by mass), type 0.45 mortar prisms -11.6 percent, type 0.60 mortar prisms -6.7 percent. - Calcium magnesium acetate, CMA, dilute solution (6.5 g per 100 g water), type 0.45 mortar prisms -45.5 percent, type 0.60 mortar prisms -56 percent. These results show that the deleterious action of a salt mixture such as calcium magnesium acetate on cement mortar is not necessarily in proportion to the concentration of the salt solution.

Conclusions

1. Like other solutions of magnesium salts (3), a concentrated solution of calcium magnesium acetate (CMA) dissolves the hardened cement paste in cement mortar, and in all likelihood also in portland cement concrete. The dissolution is rapid at +20°C, but very slow at +5°C. This temperature dependence makes it, from a technical point of view, possible to use the CMA as a de-icing agent in spite of the fact that the substance may dissolve hardened cement paste. The results show that this dissolving effect does not necessarily prevent the flexural strength of the residual core of the prisms from being increased.

2. When the concentration of the CMA solution was decreased from about 38 to 6.5 g per 100 g water, the dissolving effect of the solution certainly was reduced. Yet the strengths of the prisms were strongly reduced, flexural as well as compressive.

This degree of dilution was selected in order to shape a salt solution with the same freezing point depression as that of a 3 percent sodium chloride solution, by mass. According to Verbeck and Klieger (4), such a sodium chloride solution is the most deleterious when freezing in contact with concrete. After storing at +5°C, the flexural strength increased somewhat in saturated solution, and the compressive strength decreased, whether the solution was saturated or 3 percent by mass.

It is reasonable that the strong effect of diluting the CMA solution is a consequence of chemical reactions rather than of general physical principles. The content of magnesium ions in the dilute solution is rapidly replaced with calcium ions on contact with the hardened cement mortar, and the solution changes to calcium acetate. Olof Peterson, in (5), p. 33, found the following change of calcium and magnesium content on storage for 9 months at +20°C.

Sample of solution taken from box	Ca^{2+} mol/dm^3	Mg^{2+} mol/dm^3	Molar ratio Ca/Mg
Fresh solution	0.223	0.245	0.910
Solution after 8 months of contact	0.274	0.177	1.55

The sample was taken from a box with 29 dm^3 of solution with totally 1885 g of calcium magnesium acetate, directly after preparation and after contact with six 4 x 4 x 16 cm prisms and six 2 x 2 x 28 cm prisms. The prisms contained totally 2465 g of type 0.45 mortar and 2429 g of type 0.6 mortar. Very reasonably, the part of the solution which penetrated into the internal areas of the prisms had changed to a still higher molar ratio of Ca/Mg.

The serious effect on the *compressive* strength is very probably a consequence of the surface layer of brucite, magnesium hydroxide, which had formed on the surface of the mortar prisms. The consistency of this surface layer seems to be such that the layer acts as a lubricant during the compressive test, thus changing the system of forces between the prism sides and the load platens.

The loss in *flexural* strength is much less than the loss in compressive strength. If the loss is due to formation of calcium acetate solution in the mortar, it could be anticipated to be similar to the loss on storage in saturated calcium acetate solution.

Water cement ratio	0.45	0.60
Saturated calcium acetate solution	+11 percent	-16 percent
Dilute CMA solution, 6.5 g/100 g water	-17 percent	-29 percent

The similarity follows so far that the loss is greater for type 0.60 mortar prisms than for type 0.45 mortar prisms. Any type of mortar prism suffers a greater loss in flexural strength after storage in dilute CMA solution than after storage in saturated calcium acetate solution.

3. The molar ratio Ca/Mg of the concentrated CMA solution influenced the performance of the mortar prisms in the following way.

Molar ratio Ca/Mg	1.26	0.91
Expansion at +5°C after 15 months (type 0.60 mortar)	1 mm/m	No exp.
Mass change, type 0.45	-13 percent	-17 percent
Mass change, type 0.60	-5 percent	-21 percent
Flexural strength, type 0.45	-2 percent	+16 percent
Flexural strength, type 0.60	+23 percent	+18 percent

4. Solutions of sodium chloride had hardly any influence on the length or mass of the prisms. The flexural strength had a tendency to increase for type 0.45 mortar prisms; the compressive strength had a tendency to decrease for both types of mortar prisms.

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