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Preface

This work has been sponsored by The Swedish National Road Administration.

The main part of the results have previously been presented to the Swedish audience at a meeting, arranged in Linköping in January 1988 by The Swedish Road and Traffic Research Institute.

Professor Arne Hillerborg proposed the contacts with The Swedish National Road Administration which came to give the idea of the work. He gave me much support during the work, and also proposed the periodic reports to The Swedish National Road Administration, which turned out to be very helpful for governing the direction of the work.

Mr Bo Johansson has mixed the two types of cement mortar, and he cast the normal prisms. He gave much advice about the photographic documentation, and he performed the photographic processing.

Mr Wojciech Roszak arranged for following the length change, and also cast the slender prism. He weighed the normal prisms and measured the slender prisms.

Mr Ingemar Larsson acquired the different boxes for storing the test specimens in the different liquids.

Mrs Britt Andersson has designed the figures and diagrams, necessary for elucidating the text.

Professor Göran Fagerlund, finally, has very carefully read my draft of the paper, this way helping me to keep clear of lacuna in the logical flux.

I express my thanks to all them who have supported me in producing this work.

Lund, May 1991

Olof Peterson

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Appendix: Results in tables

Summary

The Swedish National Road Administration has spent much work for replacing chloride salts with calcium magnesium acetate (CMA) for use as de-icers.

As magnesium salts are known to attack concrete in various ways, a work was started in May 1985 at the Division of Building Materials of the Lund Institute of Technology at the request of The Swedish National Road Administration. The effect on cement mortars of a strong solution of a mixed type of calcium magnesium acetate was compared with the effects of water and saturated solutions of sodium chloride, calcium acetate, and since December 1985, also calcium chloride. The specimens were fully immersed in baths of the different liquids. The baths were kept at two different temperatures, +5 and +20°C, and the test specimens were not subjected to freezing.

As model for concrete, two types of cement mortar prisms were used, with the water cement ratios 0,45 and 0,60.

Results of the study are:

Slender prisms (2 x 2 x 28 cm) of 0,45 mortar in calcium acetate solution at 20°C expanded more than 15 millimeter per meter within 15 months. The expansion was much less at 5°C and in 0,60 mortar.
In spite of the high value, there did hardly form any cracks, but the prisms became strongly distorted.

Standard prisms (4 x 4 x 16 cm) of 0,45 mortar in calcium magnesium acetate solution at 20°C lost 270 gram out of 580 gram within 22 months, and the mechanism behind this mass loss was pure dissolution of the hardened cement paste. After 8 months, the mass loss in 0,60 mortar prisms had caught up that in 0,45 prisms, and after 22 months the 0,60 prisms were broken down into fragments. The explanation is that the dissolution was accompanied by a rather strong expansion, but only in the 0,60 mortar at 20°C.

At 5°C and after 22 months, the 0,45 mortar prisms had lost 76 gram out of 575 gram, and the 0,60 mortar prisms 29 gram out of 565 gram. No expansion was observed at this temperature.

The pH value was 9,25 - 9,4 in the calcium magnesium acetate solution, compared with about 11,5 in water, sodium chloride, and calcium acetate solutions.

In saturated calcium chloride the pH value was almost neutral. Still the surfaces of the test specimens did not show any signs of attack. However, after a dilution of the salt solution to 3,0 mol per liter, the prisms were destroyed by expansion within a few days, and the pH value rose to 10,7. This value is not very much lower than those of water, sodium chloride solution, or calcium acetate solution.

The fracture surfaces of mortar prisms after storing for 966 days in saturated calcium chloride solution were totally dry, except for the mortar just at the surface of the prism, where salt solution had penetrated by capillary suction.

1. Introduction

In 1984, Professor Arne Hillerborg of the Division of Building Materials at the Lund Institute of Technology, proposed a literature study of the attack on concrete of strong chloride solutions. A copy of the study (1984) was sent to Dr Hans Ingvarsson of The Swedish National Road Administration. He confirmed in a letter that the use of chloride salts for deicing bridge decks very often caused damage to concrete in the bridge itself and to neighbouring structures. He told that the Administration considered changing to Calcium Magnesium Acetate (CMA) for deicing purpose. American experience (1980) indicated that this mixture might be a good replacement for chloride salts.

In cooperation with the Swedish Road and Traffic Research Institute, in Linköping, the Swedish National Road Administration, at Borlänge, started laboratory and field tests with the purpose to find out whether CMA works as a good deicer salt, which does not damage concrete structures close to bridge decks.

In the study mentioned above (1984) it is told that the presence of chloride ions is no condition for the ability of a magnesium salt to attack concrete. However, there exists a type of damage by expansion which can occur only in presence of magnesium ions and chloride ions together.

Typical for any magnesium salt solution is that its pH value is not allowed to exceed the range 9 - 10, because this would precipitate solid magnesium hydroxide. Hardened portland cement paste normally contains calcium hydroxide, and its other mineral components are in equilibrium with calcium hydroxide. Thus, the pore liquid of the cement paste will have a pH value of 12,5 or still higher.

In presence of a magnesium salt solution, this high pH value will precipitate magnesium hydroxide, and an equivalent amount of calcium hydroxide will dissolve as a calcium salt, thus bringing the cement paste to gradually lose mass and strength.

The low solubility of magnesium hydroxide makes a magnesium salt solution to act as a weak acid on concrete.

I told Dr Ingvarsson about my doubts as to the harmlessness of using such a magnesium salt mixture in contact with concrete.

The Swedish National Road Administration decided to sponsor an investigation at the Division of Building Materials of the Lund Institute of Technology, with the purpose to investigate whether calcium magnesium acetate could attack concrete in the same way as inorganic magnesium salts.

At a meeting in Lund in 1985, it was decided to limit the investigation to the chemical reactions. The mortar specimens should be stored in test solutions at +5°C, so that no freezing could take place. As the attack at this temperature probably will proceed slowly, another set of specimens should be tested at +20°C.

Water storing should serve as a standard. Besides, a saturated sodium chloride solution should be used as a well known comparison solution.

As the action of the acetate in the CMA deicing mixture is not very well known, an examination with a pure calcium acetate solution was intended to serve as a magnesium free analogue to the CMA.

The importance of the concrete quality should be evaluated. Normally, structural concrete should be well compacted and it should be composed with a water cement ratio of 0,45 or lower. Mortar of this water cement ratio should be used as a model for dense concrete and, for comparison, a mortar with the water cement ratio of 0,60 should be used.

2. Salt solutions

2.1 Arrangement of the bath

All solutions were stored in plastic boxes, and the volume of each bath was 29 liters. During the storing, the box was covered with a plastic lid in order to avoid absorption of carbon dioxide from the air, and a rubber seal served to reduce the exchange of air in the space below the lid. The efficiency of this seal was moderate.

No change of the solutions was made during the test time, which was as long as 22 to 32 months.

2.2 Water

As an innocuous reference liquid was used 29 kilograms of normal drinking-water from the Lund network.

2.3 Sodium chloride

As a reference liquid with possibly deleterious properties was used a saturated solution of 9,0 kilograms of pure sodium chloride in 25,7 kilograms of tap water.

A saturated solution of sodium chloride at 0°C contains 357 gram of dry salt in 1000 gram of water. This means a molality of 6,10 mol per 1000 gram of water. As sodium chloride dissociates into two ions, this saturated solution has an ion molality of 12,2 mol per 1000 gram of water. At a temperature somewhat below 0°C, the solid phase changes from sodium chloride to sodium chloride monohydrate, and this change may alter the solubility at the eutectic point in the system sodium chloride - water.

2.4 Calcium magnesium acetate (CMA)

The main deicing agent for this work, the calcium magnesium acetate, was delivered from the road maintenance authority in the District of Hässleholm in Scania, Sweden. This product was not the pure double salt, but a technical product, which was produced in the Netherlands from natural dolomite stone by dissolving the stone in acetic acid. Afterwards the excess water is evaporated.

The composition with respect to calcium and magnesium depends on the choice of dolomitic stone. A chemical analysis of our salt mixture gave a concentration of 0,69 mol magnesium and 0,87 mol calcium per liter of liquid. This corresponds to 3,12 mol of acetate per liter and an ionic molarity (not molality) of 4,68 mol per liter of solution, to be compared with 12,2 mol per 1000 gram of water for the sodium chloride bath.

10,6 kilograms of the CMA salt mixture was dissolved in 23,9 kilograms of tap water. The raw mixture was viscous and contained a reddish brown slurry, probably mainly consisting of some basic iron(3)acetate. We allowed this slurry to settle to the bottom, and than we transferred the almost clear liquid to a clean plastic box by means of a siphon.

The analysis indicates that this solution does not dissolve solid ice so effectively as a saturated sodium chloride solution.

Some time after the dissolution, the clear solution grew turbid again, and gradually more of the reddish brown slurry precipitated. Very probably, some of the iron in the dolomite stone was in the divalent state. Then, oxygen from the air gradually oxidized the divalent iron into the trivalent state. In this way the slightly soluble basic acetate could form, causing the gradual formation of a slurry.

2.5 Calcium acetate

The purpose of the fourth solution was to serve as an innocuous magnesium free analogue to the CMA. The solution was made from 8,9 kilograms of pure calcium acetate with a content of dry salt of about 90 per cent, and 24,4 kilograms of tap water.

According to a chemical table, a saturated solution of calcium acetate in water at 0°C contains 2.36 mol of calcium acetate per 1000 gram of water. As one mol of calcium acetate dissociates into three ions, the ionic molality of this solution should be equal to 7,1 mol per 1000 gram of water. The salt should be expected to dissolve ice better than CMA but not so well as sodium chloride.

The solution was colourless, and its viscosity did not appear very much higher than that of pure water.

2.6 Calcium chloride

This salt was dicussed when the work had already run for several months, and no damage to the mortar prisms in the sodium chloride solution could be observed. The aim with starting a test with calcium chloride solution was to confirm that there is a difference between the two chlorides as to the attack on cement mortar.

In the literature study (1984) three works were referated, Smolczyk (1968), Chatterji and Damgaard Jensen (1975), and Nielsen and Krogh (1976). Together they showed that a medium strong solution of calcium chloride, i e 3 mol per liter, within some days or weeks induced cracks in cement mortar, and later total destruction.

For preparing the two baths of 20 liter of saturated solutions of calcium chloride, 24,1 kg of hexahydrate salt was used, which contained 12,2 kg of anhydrous salt and 11,9 kg of water. As 20 liter of saturated solution has a mass of 28,6 kg, only 4,5 kg of water needed to be added.

Over a saturated solution of calcium chloride, the relative humidity is only 40 % at +5°C, and 32 % at +20°C. Thus, it is not too wrong to describe this solution as "an unusually dry bath".

3. Model concretes

In this work, it was practical to use test specimens with moderate size, preferably 4 x 4 x 16 cm. This put a limit for the maximal size of the aggregate grains.

Mortars with the range of 0,08 to 2,0 mm for the aggregate was chosen.

An ordinary Portland Cement was used, Slite Standard Portland Cement from CEMENTA AB. The chemical composition corresponds to:

K_2O = 1,25 %

Na_2O = 0,22 %

SO_3 = 3,1 %

The clinker typically contains:

CaO = 63,9 %

SiO_2 = 21,3 %

Al_2O_3 = 4,6 %

Fe_2O_3 = 2,4 %

MgO = 4,2 %

The aggregate was composed from three fractions of sand, all of them with rounded quartz grains:

1.	Fine sand	0,08 - 0,5 mm
2.	Medium sand	0,5 - 1,0 "
3.	Coarse sand	1,0 - 2,0 "

We composed the mortar with the water cement ratio 0,45 starting from the CEMBUREAU mortar, the water cement ratio of which, however, is 0,50. The water content was reduced from 250 to 240 gram, and the cement content was correspondingly increased from 500 to 533 gram. Thus, we got the desired 0,45 mortar.

For composing the 0,60 mortar, we proceeded in the following manner:

1. The contents of water and of the Medium and Coarse sand fractions were similar to the corresponding amounts of the 0,45 mortar.

2. The cement contents was reduced from 533 to 400 gram.

3. The contents of the Fine sand was increased in order to compensate for the loss in solid volume of the cement. The density of cement is assumed to be 3,1 and the density of the sand 2,6 gram per cubic centimeter. Thus, the contents of Fine sand was adjusted from 500 to 612 gram.

The object of this special way to compensate for the reduced cement contents was mainly to get two mortars with small, and equal, tendency to separate water on the mortar surface after the casting, and not so much to give the two mortars exactly the same consistency. Thus, the specimens have a reasonable chance to keep their water cement ratio undisturbed by water separation after casting.

The batches for the two types of mortar were increased with a factor of four (Table 3.1).

Table 3.1

Water cement ratio in mortar		0,45	0,60
Water	gram	960	960
Cement	gram	2133	1600
Fine sand	gram	2000	2448
Medium sand	gram	2000	2000
Coarse sand	gram	2000	2000

Each of the two batches corresponds to a mortar volume of about 3 liter.

4. Casting of the test specimens

For each mortar, triplicates of test specimens were made for storing in four test liquids at two different temperatures. Thus, 24 specimens were cast of mortar with water cement ratio 0,45, and 24 specimens of the 0.60 mortar.

For the determination of the mass of the specimens, and also for the strength tests, 4 x 4 x 16 cm test specimens were cast. The mould was filled to somewhat more than half of its height, and the mortar was compacted with a short period of vibration on a vibrating table.

Then the residual volume of the mould was filled, and the mortar was vibrated and steel-trowelled.

The mould was stored for one or two days in a closed plastic bag, and after this time the test specimens were stripped.

It was decided that a separate series of prisms with the sizes 2 x 2 x 28 cm should be cast for measuring the change in length. For this purpose, available moulds were used, some of steel, and some of acrylic plastic. The prisms had dowel rods with plane ends, and the length was checked with a dial indicator between spherical measuring surfaces. 24 slender prisms were cast from 0,45 mortar, and 24 from 0,60 mortar.

5. Curing of the test specimens

The test specimens were stored for 7 days in tap water (It is not necessary to use lime water) of room temperature (If the stripping was made after 2 days, 6 days was sufficient).

After this, the specimens were carried over to boxes with 75 per cent relative humidity, placed in a climate room adjusted for 20°C. They were stored there for 20 days. No measurement was performed as to the degree of carbonation of the test specimens.

6. Storing of the test specimens in salt solutions at +5 and +20°C

The test specimens were immersed in the baths after 28 days of curing.

In the Chapter 2, the liquids for the storing test are described.

Each liquid batch of 29 liters was made in duplicate, one was stored in a climate room at +5°C and the other in a room at +20°.

Each plastic box contains (see the Figure 6.1):

1. One small plastic box containing three prisms 4 x 4 x 16 cm of mortar with the water cement ratio 0,45. The box is divided in one space for each prism. The box was intended for taking up material, lost from the prisms during the storing.
2. One similar small box containing three prisms of the same size of 0,60 mortar.
3. Three prisms 2 x 2 x 28 cm with dowel rods. The prisms are made of 0,45 mortar.
4. Three similar prisms of 0,60 mortar.

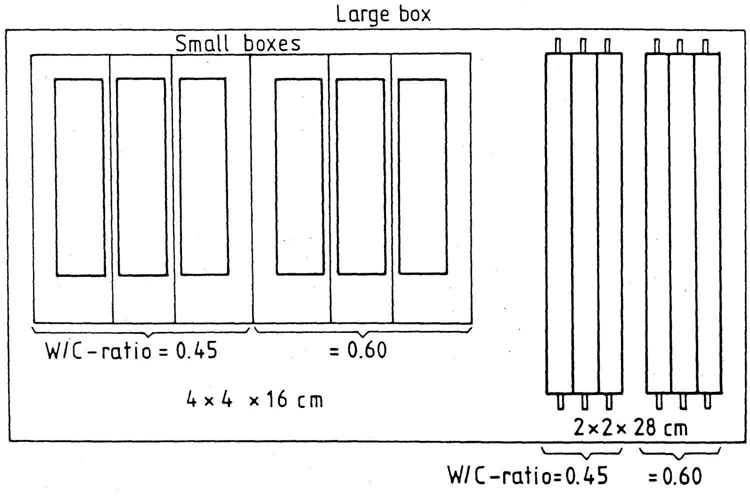


Figure 6.1: Plastic box for one solution.

7. Methods for comparison

The objective of the work was to investigate the effects of the different solutions on the mortars. Therefore, the test specimens were investigated after reasonable time intervals, normally one month.

* Length change.	The 2 x 2 x 28 cm prisms had dowel rods with plane ends, and the length was checked with a dial indicator between spherical measuring surfaces. The absolute length was checked with a calibration rod.
* Mass change.	The 4 x 4 x 16 cm prisms were wiped free from liquid with an absorbing non-wowen cloth, and the mass was determined with a balance with a precision of 0,01 gram. The mass value was compared with the value, determined just after stripping.
* pH value.	A sample was taken from each bath, and the pH value was determined at room temperature by means of a glass electrode.
* Flexural strength	At the end of the work, the 4 x 4 x 16 cm prisms were tested by means of a testing machine in accordance with CEMBUREAU. In some cases, the area of the prism had become so much reduced because of attack that a correction of the section modulus had to be applied.

* Compressive strength	After the flexural strength test, the two halves of each prism were tested in a tool, also in accordance with CEMBUREAU.

8. Length change

8.1 Method

In order to follow any length change, a separate set of prism had been made, see chapter 4. Their size was 2 x 2 x 28 cm, to be compared with 4 x 4 x 16 cm for the main series of prisms.

This choise of size of the measuring prisms was based upon two reasons:

* If chemical reactions with the bath occur, which cause a change of length, this will be indicated earlier when a slender type of prism is used.

* Experience has shown that a dowel rod with a plane end and a spherical measuring surface at the dial indicator more easily gives a reproducible reading than other types of dowel rods and measuring surfaces.

A reading was made:

1. Directly after the stripping of the prisms, two days after the casting.

2. After curing for six days in water, and for twenty days at 75 % relative humidity, i. e. at a total age of 28 days, immediately before the immersion in the solutions.

In the main series, the prisms were stored in

* water
* saturated sodium chloride solution
* strongest possible solution of calcium magnesium acetate, made in the Netherlands
* saturation calcium acetate solution

In a later complimentary series, another set of prisms were made. They were stored in a saturated solution of calcium chloride, with a solution of calcium acetate as a reference.

At suitable intervals, the lengths of the prisms were measured, and the values for the prisms just after stripping were subtracted. The length change of each prism, in mm, was divided by 0,28.

Thus, the result were given in mm/m. The arithmetic mean for the three prisms were tabulated and, together with the results of other measurements, placed in the Appendix.

8.2 Results and comments

The table of results is found as Table A.1 in the Appendix.

8.2.1 Water

All prisms did shrink about 0,4 millimeters per meter at curing, from the measurement just after stripping to the measurement just before immersion in the water bath.

The 0,45 mortar prisms showed a small net expansion (0,2 mm/m) during the first month of immersion. No further expansion toke place during the 22 months long time of immersion.

For a future work, a measurement is planned for the age of 8 days, when the period of water curing is terminated. At this state, the pore system is probably filled with liquid to a degree which is most similar to the immersed state.

The immersion of the 0,60 mortar prisms gave also an expansion, but this one was not great enough for full compensation for the curing shrinkage. Thus, the prisms after immersion in water at +5°C for one month, and also for 22 months, showed a residual shrinkage of 0,15 mm/m. The prisms, which were immersed in +20°C water, showed a residual shrinkage of 0,07 mm/m after one month of immersion, and 0,2 mm/m after 22 months.

A reasonable explanation of this late shrinkage can be a slow carbonation of the porous mortar.

8.2.2 Sodium chloride

The 0,45 mortar prisms did not expand very much more during the first month of immersion than the corresponding prisms in water.

During the immersion, they gradually expanded about 0,25 mm/m during the 22 months immersion time. This corresponds to about 0,4 - 0,5 mm/m, starting from the just stripped state.

This slow expansion could be stated only to a very small degree in the 0,60 mortar prisms.

A reasonable explanation may be the formation of the Friedel's salt:

(5) $3CaO.Al_2O_3.CaCl_2.12H_2O$

which is combined with the formation of two molecules of sodium hydroxide.

8.2.3 Calcium magnesium acetate (CMA)

Diagrams from the table in Appendix A.1 are shown in Fig. 8.1.

The 0,45 mortar prisms immersed in solution at 5°C did not expand more than those stored in water. When immersed in solution at 20°C, this was true for 4 months. After 5 months, the average expansion suddenly had increased to 0,33 mm/m, and one of the three prisms had expanded 0,43 mm/m. After 6 months, one of the prisms had broken, and also the two others were severely corroded. The test was discontinued.

The 0,60 mortar prisms immersed in solution at 5°C started to expand already during the first month of immersion. At 6 months, they had expanded 0,76 mm/m and from this time, the expansion was very slow. From 11 to 15 months, the expansion stayed at a level of 0,9 mm/m. When immersed in solution at 20°C, the expansion started already during the first month and exceeded 1 mm/m already after 5 months. The prisms were severely corroded, and one of the prisms had broken. The test was discontinued.

It is very probable that the calcium acetate component in the CMA is the cause of the expansion in those cases were an expansion was observed.

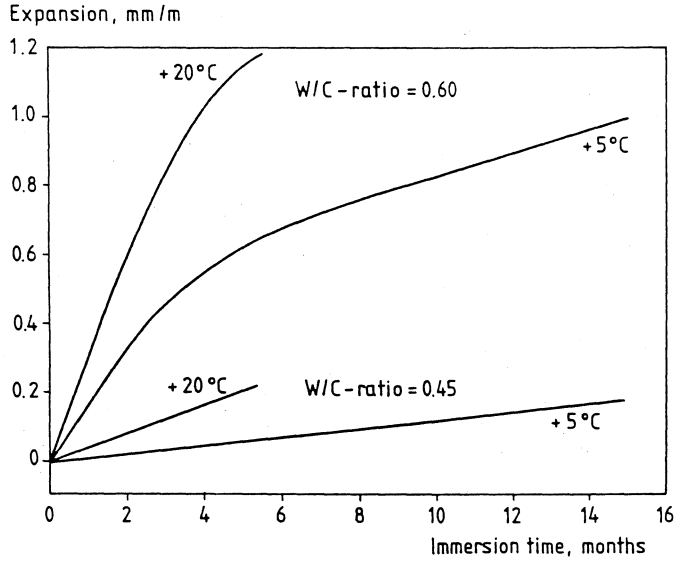


Figure 8.1: Diagram indicating length change on immersion in calcium magnesium acetate solution.

Figure 8.3: Slender prisms, distorted during immersion in calcium acetate solution.

Code	161	162	261	262
Mortar	<- w/c-ratio = 0,45 ->		<- w/c-ratio = 0,60 ->	
Temp., °C	+5	+20	+5	+20

8.2.5 Calcium chloride

The tables in the Appendix indicate that saturated calcium chloride solution allowed the prisms to keep their length after 28 days curing. No expansion occurred, not even the small one which was observed in water immersion.

Long time before it was commonly known that a calcium chloride solution could damage concrete, physical and chemical tables contained knowledge about stable phases, which form when calcium hydroxide is treated with calcium chloride solutions of various concentrations. International Critical Tables (1930); Atherton Seidell (1940).

Below the concentration limit 1,88 mol/liter, calcium chloride allows calcium hydroxide to be the stable solid phase, and in such a low concentration calcium chloride is not more deleterious to concrete than sodium chloride.

In the range 1,88 - 4,00 mol/liter, the calcium hydroxide phase will change to the basic chloride phase:

(1) $Ca_5Cl_2(OH)_8.10H_2O$

8.2.4 Calcium acetate

Diagrams from the table in Appendix A.1 are shown in Fig. 8.2.

The results show that the prisms expanded strongly and rapidly without formation of macro-cracks. The 0,45 mortar expanded more than the 0,60 mortar, and the expansion was more rapid at +20°C than at +5°C

We got the impression that the expansion was caused by some mineral with smeary consistency. See Fig. 8.3, which shows a quite visible degree of distorsion.

Some calcium hydroxy acetate is to be suspected, but we have not found any written evidence about the existence of compounds of this type.

The expanded prisms seem to carbonate in course of time, and this makes them less smeary and more disposed to break.

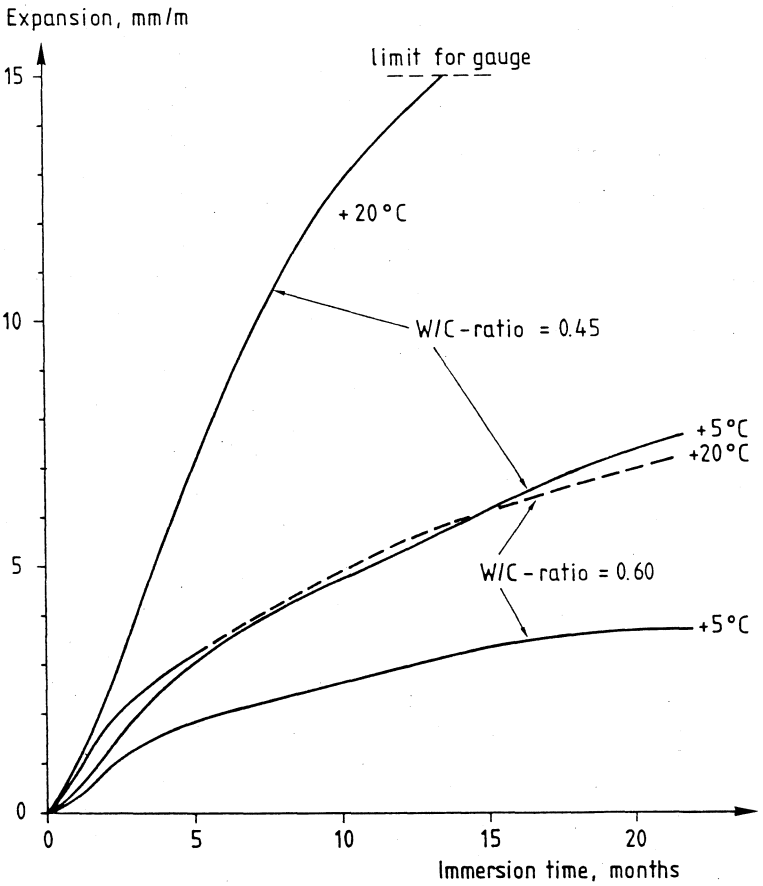


Figure 8.2: Diagram indicating length change on immersion in calcium acetate solution.

This will form the solid phase at room temperature.

A 3,0 molar solution did, within a few days, destroy the prisms. The first steps of this destruction was not accompanied by any change of the length of the prism, but the side surfaces of the prisms expanded and scaled from the core. See Fig. 8.4. Very probable, the expansion is caused by the formation of the basic chloride phase (1).

Figure 8.4: Prism stored for 20 days at 20°C in 3 molar solution of Calcium chloride

Finally, above the concentration limit 4,00 mol per liter (to saturation at room temperature) another basic chloride will form the stable phase:

(2) $Ca_2Cl_2(OH)_2.H_2O$

Our impression was that the 4,5 molar solution did not make more damage than the saturated solution. Still, the measurements of length indicated (only one prism for each mortar and temperature) that this rather concentrated solutions could make the prisms to expand slowly. After storing in saturated solution, only one figure supported this, namely 3,9 mm/m for 0,60 mortar at +20°C. When the solution was 4,5 molar, all four prisms expanded, the 0,60 mortar more than the 0,45 mortar.

It is quite possible that the phase (2) is as deleterious to the mortar as the phase (1). Very probably, it was the fact that the prisms previously were immersed in saturated solution, which saved them from damage, when they were carried over to 4,5 molar solution. The Figure 9.2 in the Paragraph 9.2.5 shows that storing in saturated calcium chloride solution made the interior of the prisms dry. Thus, they did not probably contain water enough for changing calcium hydroxide to the calcium hydroxy chloride (2).

9. Mass change

9.1 Method

Each 4 x 4 x 16 cm prism was weighed at several occasions:

1. Just after stripping, at an age of two days. This value is used as the reference value of the prism

2. At an age of 8 days, after completed wet curing

3. At an age of 28 days, after completed curing at 75 % relative humidity. After the weighing, the prism was transferred to the test bath

4. After 1 month of storing in the test bath. This procedure was repeated, normally with an interval of one month, until the test was terminated

The average of the mass values for each set of three prisms was recorded in one table for each bath composition. The table has one column for each mortar type and storing temperature, i. e. totally 4 columns.

In the tables, the mass value according to point 1. is recorded as just a mass value, on the line "2 days (=0)".

For all later mass values, the difference to this value is recorded on the line for the corresponding time, with the sign "+" if the mass is greater than the 2 days value, and "-" if the mass is less.

During the wet storing period, a small increase of the mass is noted. During the following storing in air with 75 % relative humidity, a loss of mass is noted. As expected, this loss is greater in mortar with the water cement ratio 0,6 than in 0,45 mortar.

9.2 Results and comments

The table of results is reproduced in the Appendix A.2

9.2.1 Water

The masses of the prisms have, already after one month, exceeded their mass after 8 days moist curing. During the whole storing period, until 22 months, they continued to increase slowly.

The mass gain was greater for the 0,45 mortar prisms than for the 0,60 mortar prisms, but there was hardly any difference between immersion in +5 and the +20°C. Probably, the increase in mass to a great extent is caused by continuing hydration.

9.2.2 Sodium chloride

As a rule, the mass of 0,45 mortar prisms increased less than that of corresponding prisms stored in water, and the mass of 0,60 mortar prisms increased more.

As for the prisms stored in water, the changes in mass during the storing were very small.

9.2.3 Calcium magnesium acetate (CMA)

The loss of mass is shown in Fig. 9.1. The values are taken from Appendix A.2.

After 1 month of storing, all prisms have increased their mass from 28 days curing, but unlike the water stored prisms, their values of mass never reached those of the mass at stripping.

At 20°C, the mass started to decrease after 2 months of storing. Interesting enough, until a time limit of 7 months, the 0,45 mortar prisms have lost their masses more rapidly than the 0,60 mortar prisms. After 8 months, the surfaces of the 0,60 mortar prisms start to lose material, not only by dissolution of the hardened cement with accompanying loss of aggregate. In addition, the surface layer starts to expand, and spalls from the core of the prism.

In this way the loss of mass from the 0,60 mortar prisms started to proceed much more rapidly than the loss from the 0,45 mortar prisms, and after 15 months there remained 252 gram of a prism, the stripping mass of which was 558 gram. After 17 months, there only remained a sandy mass from the 0,60 mortar prisms.

At 5°C, the speed of loss is essentially lower than at 20°C, and this may explain why, according to American experience, the CMA is claimed to be harmless as a deicing salt for concrete.

After 22 months at this temperature, it is still the 0,45 mortar prisms which lose their mass most rapidly. The total loss would correspond to about 1,2 mm. During the same time, the 0,60 mortar would lose only about 0,46 mm.

9.2.4 Calcium acetate

Like water and sodium chloride solution, the calcium acetate solution caused a slight gain in mass of the specimens. The mortar with the water cement ratio 0,60 increased a little more in mass than the 0,45 mortar.

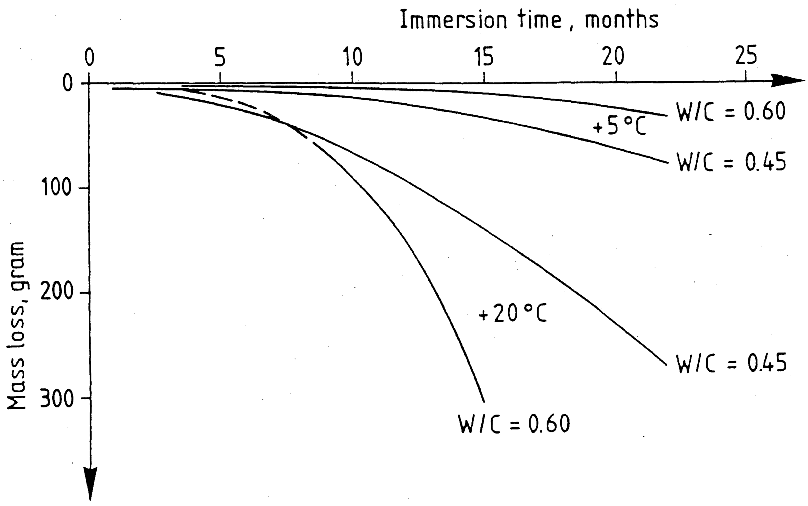


Figure 9.1: Loss of mass from prisms in CMA solutions.

9.2.5 Calcium chloride

The prisms were weighed an extra time after 5 days immersion in saturated calcium chloride solution because of our expection of rapid deterioration. At this time, the prisms showed a gain in mass, rather similar to the gain of the prisms, which were stored in calcium acetate solution.

At all later wheighings, and especially at 20°C, the 0,45 mortar prisms lost a few gram of mass during the first 7 months. The 0,60 mortar prisms did not lose any mass at all.

The explanation was obvious since the flexural test had been performed, see Figure 9.2. In spite of long storing in the salt solution, the fracture surface was dry, except for a wet mortar layer along the sides of the prisms. The photographic picture shows the wet and dry parts of the fractures of eight prisms.

The dry area has formed by evaporation of the cement paste water and diffusion of the vapour to the saturated salt solution. The vapour pressure is higher over fresh cement paste than over saturated calcium chloride solution.

The wet layer along the sides had formed by capillary suction of salt solution from the bath.

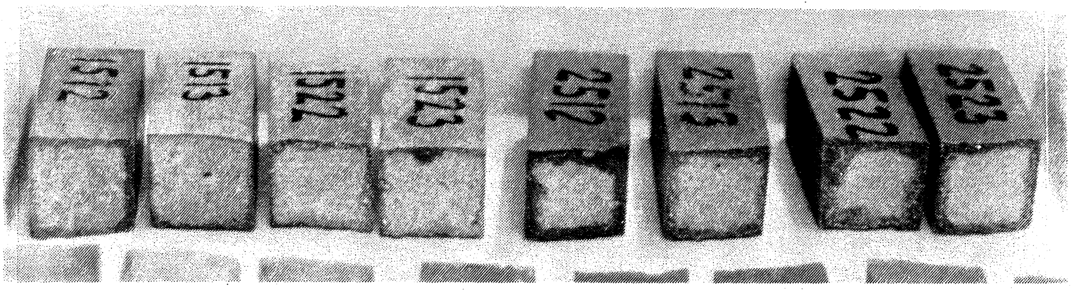


Figure 9.2 Fracture surfaces of mortar prisms, stored for 966 days in calcium chloride solutions:

Code	1512	1513	1522	1523	2512	2513	2522	2523
Mortar	<--w/c-ratio = 0,45 -->				<--w/c-ratio = 0,60 -->			
Mol/liter	4,5	Sat.	4,5	Sat.	4,5	Sat	4,5	Sat
Temp. °C	+5	+5	+20	+20	+5	+5	+20	+20

In the 0,45 mortar prisms, the layer was about 1 mm in saturated solution and about 2,9 mm in 4,5 molar solution.

In the 0,60 mortar prisms, the layer was about 4,6 mm in saturated solution and about 6 mm in 4,5 molar solution. The thicker diffusion layer certainly explains, why no loss of mass could be observed in the 0,60 mortar prisms. The mass of the penetrating salt solution was great enough to balance the mass of the evaporated water almost precicely.

There was no essential difference in diffusion depth between solutions at +5°C and +20°C.

Probably, this special behavour of a prism of dense mortar, immersed in a saturated calcium chloride solution, explains why the prisms did not suffer any damage.

All prisms which were immersed in 3 molar solution became totally deteriorated, see Figure 8.4.

It is true that calcium hydroxide in 3,0 molar calcium chloride solution changes to another phase than in 4,5 molar calcium chloride solution. Still, the results do not prove that the latter phase is harmless for the cement paste, only that the water content in most of the mortar may be too small for the equilibrium phase to form.

If the mortar is sprayed with a calcium chloride solution and than stored in air, like the concrete of a bridge deck, the relative humidity of the surrounding air will govern the concentration of the salt solution on the mortar surface.

At 40 % RH at +5°C, and 32 % at +20°C, the salt solution will become just saturated, and no damage will happen.

At 77 % RH, the solution will only become 2,8 molar, and this solution will severely damage concrete and mortar in the same way as did the 3 molar solution, by expansion.

At 91 % RH, the solution will become still more diluted, i. e. 1,4 molar, and this solution will not be more harmful to the mortar than a saturated sodium chloride solution.

The relation between the relative humidity of the air and the concentration of the calcium chloride solution is calculated according to Göran Hedenblad (1987).

10. pH-values of the storing baths

10.1 Method

Before the test specimens were transferred to the bath, the pH-value of the bath was determinated. Later, the pH-value was followed up with suitable intervals.

The pure drinking-water bath and the solutions of strong electrolytes, such as sodium chloride and calcium chloride, were not examined before the immersion of the mortar prisms. The buffer capacity of those liquids is so small that it takes a very long time for the reading to stabilize, and still this reading will not tell anything about the solution, but its content of, e. g., carbon dioxide.

An acetate is a salt of acetic acid, which is a weak acid. A concentrated solution of an acetate of a "strong" metal ion, such as calcium or magnesium, should be expected to have a pH value not very far from 9,0.

10.2 Results and comments

The results of the pH measuring was tabulated in the Appendix, Table A.3.

10.2.1 Water

The pH value of the 20°C bath reached a maximum of 11,5 after 2 months of storing. After 4 months, the value decreased gradually and after 29 months, it reached 8,9.

The rise after the immersion of the test specimens is due to the calcium hydroxide, which is liberated at the hydration of the cement, and also to alkali compounds in the cement.

The decrease after the rise is due to the carbon dioxide in the surrounding air, combined with a moderate tightness of the plastic lids.

The +5°C bath had its maximal pH value of 10,5 after 1 month, and the value decreased to 8,6 after 29 months. Probably, the plastic lid was less resilient at the lower temperature, and as a consequence the sealing was less effective.

10.2.2 Sodium chloride

The pH value of the 20°C bath reached a maximal value of 11,8 after 3 months. After 10 months, the value was 10,85 (9,7 for drinking water), and after 29 months 9,3.

The +5°C bath showed a quite different pH value development: 11,4 after 1 month, 11,7 after 5-10 months, and 11,5 after 29 months. The difference, most probably, is due to slightly slower hydration reactions at the lower temperature, combined with exceptionally good tightness of the lid.

Chemical reactions exist, which can cause a somewhat higher pH value in the sodium chloride bath. However, it is difficult to distribute the responsibility between sodium hydroxide formed by chemical reactians and possible differences in tightness of the lids.

10.2.3 Calcium magnesium acetate (CMA)

The pH value of the fresh solution, 9,25, did only increase some tenths of a unit, when the test specimens were immersed in the solution.

In spite of the small changes, powerful chemical reactions between the solution and the calcium hydroxide of the hardened cement paste has taken place.

Magnesium hydroxide has been precipitaded, and an equivalent amount of calcium hydroxide has been dissolved from the paste:

(3) $Mg^{2+} + 2Ac^{-} + Ca^{2+} + 2OH^{-} \longrightarrow$

$\longrightarrow Mg(OH)_2 + Ca^{2+} + 2Ac^{-}$

The solubility product of the magnesium hydroxide is an essential parameter, which influences the pH value of the system.

(4) $(Mg^{2+}) \times (OH^{-})^2 = 1,2 \times 10^{-11}$ (mol/liter)^3

In a strong CMA solution, a pH value of about 8,5 should be theoretically enough for precipitating solid magnesium hydroxide. Hardened cement mortar, immersed in pure water (see the Paragraph 10.2.1), gave a pH value of more than 11 to the water. Thus, if a magnesium salt like CMA is added, the conditions for precipitation of magnesium hydroxide are favourable.

When this happens, hydroxide ions will be consumed all the time from the calcium hydroxide, and also from the calcium silicate hydrates of the hardened cement paste.

In practice, a magnesium salt acts as a concentrated, but weak, acid upon concrete, and during the test, the pH value of the solution was kept in the range 9,3 - 9,5 for at least five months, or until the mixture started to carbonize.

10.2.4 Calcium acetate

The pH value of the fresh solution was 7,5. As follows from sub-chapter 10.1, this value seems low. Maybe the preparate is "corrected" with acetic acid for getting the natural basic value more neutral. However, the value did increase, as soon as the mortar specimens were immersed in the solution.

The pH value increased somewhat slower than in the drinking-water bath, or in the sodium chloride bath. However, the value also continued to rise for longer time than most of the other baths.

Though the bath eventually became carbonated, the pH value in the calcium acetate solution at 20°C continued to increase, even after 29 months. In the drinking-water bath, for comparison, the values had decreased clearly after 6 months.

The explanation may be unusually good tightness of the lid, but more probable, the same whitish slimy phase which allowed the slender prisms too expand 7 mm/m without cracking has worked as a sealing agent, delaying the carbonation of the mortar.

We have not managed to find any information about what happens to solid calcium hydroxide that is immersed for a long time in a solution of calcium acetate.

At the cleaning of the plastic boxes after the test, we found that much of hard white crusts had formed, which contained carbonate. This corresponds very well with the fact that the slender prisms, which for a long time behaved in a plastic way, eventually turned brittle. Thus, we do not know the chemical composition of the white, slimy mineral, but we know that it can become transformed into calcium carbonate.

10.2.5 Calcium chloride

The pH value of the saturated calcium chloride solution was about 7,6 during the first time of immersion. Later the value grew somewhat lower, but it always remained almost neutral during the whole test time, 22 months. As for other unbuffered solutions, the readings took a very long time to stabilize.

Theoretically, this could mean that the hydroxy chloride phase, which is stable in saturated solution,

(2) $Ca_2Cl_2(OH)_2.H_2O$

is not very soluble in saturated calcium chloride solution. This may be true, but the Paragraph 9.2.5 indicates that the more probable explanation is that most of the test specimens had lost their pore water and with that their capacity to increase the pH value of the bath.

The 3,0 molar solution of calcium chloride assumed a pH value about 10,6, which is only half a unit lower than the baths of water or sodium chloride solution.

This indicates that the hydroxy chloride phase, which is stable in 3,0 molar solution,

(1) $Ca_5Cl_2(OH)_8.10H_2O$

has a capacity to emit hydroxide ions in a 3 molar solution of calcium chloride, which is not very much less than that of the calcium hydroxide phase in cement paste, when immersed in pure water.

The 4,5 molar solution of calcium chloride assumed a pH value near 9. The Paragraph 9.2.5 indicates that one should be cautious in making any conclusions about the basicity of the hydroxychloride phase (2), because also the 4,5 molar solution did not penetrate the surfaces of the test specimens so much better than the saturated solution.

11. Strength of test specimens

11.1 Test method

When the mortar prisms, sized 4 x 4 x 16 cm, had been stored in the different solutions for the desired times, changes in appearance were noted, and the flexural strength of the prisms were determined. Normally, the two pieces of each prisms were also tested for compressive strength.

If possible, three prisms were used for each combination of water cement ratio of mortar and storing temperature.

This means that each figure for flexural strength is the arithmetic average of three values, and each figure for compressive strength is the arithmetic average of six values.

The work was performed as one main series with specimens stored in water and in solutions of sodium chloride, calcium magnesium acetate, and calcium acetate. The prisms in this series were immersed for totally 22 months, from May 1985 to March 1987.

This main series was supplemented with a second test series with specimens immersed in solutions of calcium chloride and calcium acetate during a total period of 966 days, from December 4, 1985, to July 27, 1988.

All test specimens in the calcium chloride solutions were expected to break down totally within a few days, but nothing like that did happen.

Therefore, on August 1, 1986, after 240 days of immersion, one prism out of each set of three was transferred into a 3,0 molar calcium chloride solution, and one other prism into a 4,5 molar solution. This last-mentioned concentration is not very far from that of a saturated solution.

Thus, two sets of specimens were stored in the two weaker calcium chloride solutions during 726 days, and the third set of specimens was allowed to remain in the saturated solutions.

After this time, the specimens were inspected and tested for flexural strength and compressive strength.

11.2 Results and comments

The results of the strength tests was tabulated in the Appendix, Table A.4, where the first table represents the main series and the second table the supplementary series.

The column for "Water" in this supplementary table is copied from the table of the main test, and consequently this column corresponds to a storing time of 22 months, to be compared with 966 days, or 32 months, for the other columns in the table. The change in strength on storing in water is, however, very small after so long a time, and we have neglected this possible effect.

11.2.1 Sodium chloride

The specimens looked quite unattacked, and the flexural strength had changed only insignificantly.

The compressive strength was reduced, at both temperatures, and in both types of mortar. This is in accordance with Smolczyk (1968).

In the Paragraph 8.2.2 was mentioned that slender mortar prisms with the water cement ratio 0,45 expanded about 0,25 mm/m during 22 months, the first month counted as the zero point. This indicates that some chemical reactions happens to the mortar when stored for a long time in saturated sodium chloride solution, e. g. the formation of the Friedel's salt (5). Compare the Paragraph 8.2.2.

11.2.2 Calcium magnesium acetate (CMA)

The specimens were attacked, starting from the surface, and the attack was observed first at the corners, later at the edges, and at last on the flat surfaces. So, the compressive strength could be tested only for specimens, stored at 5°C and, strange enough, only if they were made from mortar with the higher water cement ratio of 0.60.

The flexural strength of specimens, stored at 5°C, was unchanged for mortar with the water cement ratio 0.45, and significantly improved for the 0.60 mortar. The compressive strength of the latter was significantly reduced, probably because the dissolution of the cement paste had made the test surfaces highly imperfect.

The specimens stored at 20°C were all severely attacked, and the ones from mortar with the water cement ratio 0,60 were broken down to sand. The prisms from 0.45 mortar had lost about 47 % of their original mass. They could still be tested for flexural strength, but an actual value of the moment of inertia had to be calculated for each of the three specimens.

For this purpose, the cross section of each test prism at the fracture was drawn on a paper. The area was divided by vertical lines. Thus, the irregular area of the fracture was substituted by a series of vertical rectangles, which facilitated the calculation of the **moment of inertia** of the section. By dividing this quantity by the maximal height of the section over the neutral line we obtained the **section modulus**.

Calculated in this way, the flexural strength of the residual cores of the three test prisms came out to be greater than that of the test prisms stored in water. The cause for this may be that some new mineral had formed in the pore system of the mortar. Caution should be used, however, when flexural strength values for slender prisms is compared with values for normal prisms, because the slender prisms have a tendency to give too high results.

In the Paragraph 8.2.3, an expansion of 0,35 mm/m is shown after 5 months for slender prisms. This indicates that some new mineral has been formed. The consequence for the strength may first be an increase, but later cracks may be formed, and the strength will decrease, or disappear. The slender prisms, quite correctly, broke spontaneously.

11.2.3 Calcium acetate

The saturated solution of calcium acetate was chosen because it did not contain magnesium, and we looked upon this solution as a comparatively nonaggressive alternative to calcium magnesium acetate.

After storing for 22 months at 5°C, the flexural strength of the mortar specimens had changed only insignificantly from that of the corresponding specimens stored in water.

The same was true at 20°C for mortar with the water cement ratio 0,45, but the 0,60 mortar specimens had lost much of their strength, compared with the specimens stored in water.

The compressive strength was significantly lower after storing in calcium acetate solution than after storing in water. This was true for 5 and 20°C storing temperature, and for the water cement ratios 0.45 or 0.60 of the mortar.

Fine networks of cracks were observed at the surfaces of the prisms.

As a rule, the loss in compressive strength was greater after storing in calcium acetate solution than after storing in sodium chloride solution.

A saturated calcium acetate solution was used as a reference also for the calcium chloride test.
In this case, the prisms had been stored for 32 months before testing.

After this long storing, also the flexural strength had decreased, strongly at 20°C, and moderately at 5°C.

An interesting observation is the influence of the storing temperature. For 5°C, the 0,45 mortar prisms had the least depression of the flexural strength compared with water storing. At 20°C, both types of mortar had strongly reduced flexural strength, but now it is the less dense 0,60 mortar that has the highest residual strength.

Also the compressive strength had been strongly reduced after long (32 months) storing in calcium acetate solution, especially at 20°C.

11.2.4 Calcium chloride

In the two columns in Table A.4 for storing in calcium chloride solutions, no figures are given for "Deviation". The explanation is that the original sets of three test specimens in saturated solutions were split in three sets, each with only **one** specimen. One of this single specimen was stored in solutions with 3,0 mol calcium chloride per liter, another in solutions with 4,5 mol per liter, and the third specimen was stored in the original saturated calcium chloride solution.

All test specimens, stored in 3,0 mol per liter solution, were broken down into flakes within rather few days, and consequently no column is needed in the table for this solution.

As a consequence of the split, the flexural strength is determined with only one value, and the compressive strength normally with two values. No deviation is calculated, but no decimal is written when there is a difference between the two pieces of more than one unit.

Surprisingly enough, no deterioration could be observed as a consequence of storing in saturated calcium chloride solutions, even after 966 days.

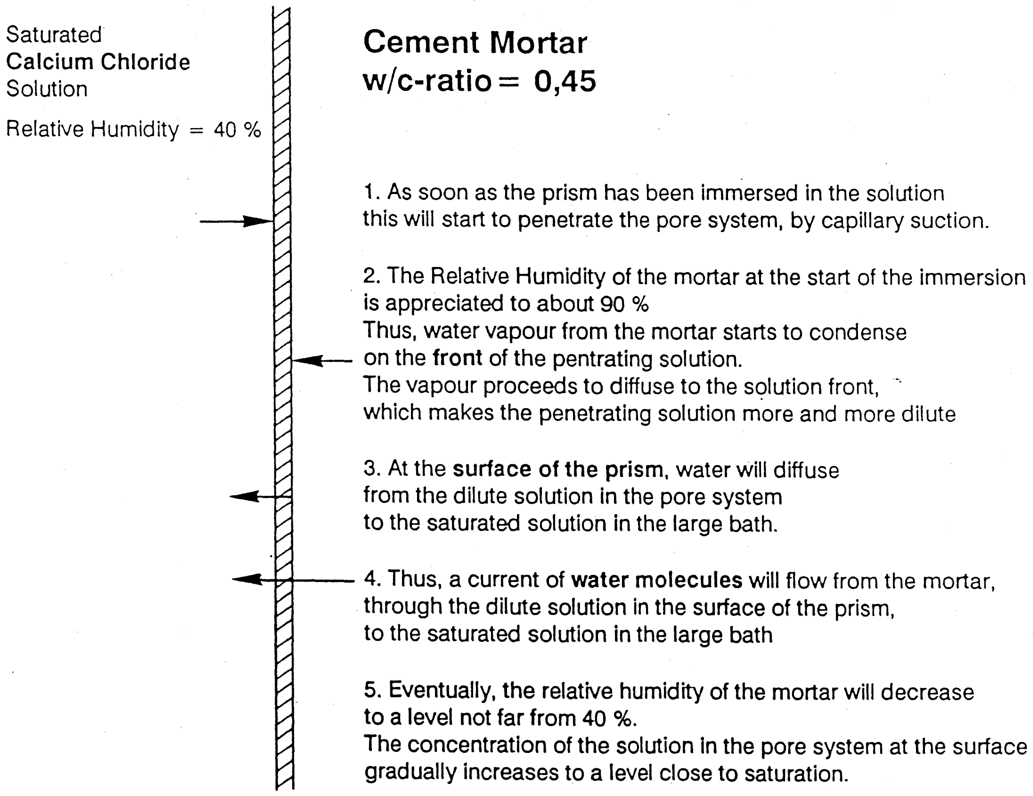
When tested at that time, the flexural strength seemed to be at least as good as that of water stored prisms, and for 0,45 mortar prisms, the flexural strength, as a rule, was **much** better. One exception is the prism stored at 20°C in 4,5 molar solution, which had the same value as water stored prisms.

The compressive strength was always **lower** than for water stored prisms.

An interesting observation on prisms after storing in saturated solution, valid for all specimens from mortar with water cement ratio 0,45, was that the main part of the fracture surface was **dry**. Only the mortar within one mm from the surface of the test specimen was wet with salt solution. Compare the Figure 9.2.

If the water cement ratio was 0,60, the salt solution penetrated deeper, to about 4,6 mm.

The dry core was probably shaped because of the low relative humidity of the saturated calcium chloride solution, about 32 % at 20°C, and 40 % at 5°C. This corresponds to a fairly dry mortar, and any excess of water will gradually diffuse to the saturated calcium chloride solution (Figure 11.1).



1. As soon as the prism has been immersed in the solution this will start to penetrate the pore system, by capillary suction.

2. The Relative Humidity of the mortar at the start of the immersion is appreciated to about 90 %
Thus, water vapour from the mortar starts to condense on the **front** of the pentrating solution.
The vapour proceeds to diffuse to the solution front, which makes the penetrating solution more and more dilute

3. At the **surface of the prism**, water will diffuse from the dilute solution in the pore system to the saturated solution in the large bath.

4. Thus, a current of **water molecules** will flow from the mortar, through the dilute solution in the surface of the prism, to the saturated solution in the large bath

5. Eventually, the relative humidity of the mortar will decrease to a level not far from 40 %.
The concentration of the solution in the pore system at the surface gradually increases to a level close to saturation.

Figure 11.1: Principal sketch of penetrating the prism with salt solution by capillary suction, and transport of water vapour out from the prism by diffusion

It is possible that the dry core is responsible for the high flexural strength of 0,45 mortar prisms and that the penetration of the surfaces with salt solution is responsible for the less good values of compressive strength.

The 3,0 molar solution of calcium chloride destroyed the mortar within a few days. Slices with a thickness of a few mm spalled from the surfaces, until the prism was totally broken down. Even after 728 days, however, the top and bottom flakes (4 x 16 cm) remained coherent so that the marking text could be read perfectly. However, it is possible that the destruction would have developped otherwise if the just cured prisms had been immersed directly in the 3,0 molar solution.

The 4,5 molar solution influenced the prisms in almost the same way as the saturated solution, but its penetration in the mortar was deeper, about 2,9 mm in 0,45 mortar prisms, and about 6 mm in 0,60 mortar prisms. It is quite possible that the 4,5 molar solution would have reacted more aggressively upon the prisms, if they, just cured, had been immersed in the solution.

12. Chemical changes on storing

12.1 Scope

Well-documented knowledge exists concerning how the calcium hydroxide in hardened cement paste is expected to react, when immersed in a solution of calcium chloride (1930, 1940).

We have not been able to find any corresponding documentation about what happens when the mortar is exposed to a solution of calcium acetate or calcium magnesium acetate. Some tests were made in connection with this work, the results of which are presented and discussed below.

The first part concerns the observation that the mechanism in breaking down the mortar in a strong solution of calcium magnesium acetate at 20°C was so much influenced by the water cement ratio of the cement mortar.

The second part concerns the question, why the mortar does expand on storing in a saturated solution of calcium acetate.

12.2 Calcium magnesium acetate (CMA)

When test specimens of cement mortar are stored in a strong solution of calcium magnesium acetate at a temperature of 20°C, the mortar prisms with a water cement ratio of 0,45 started to lose mass earlier than the 0,60 prisms. The loss of mass also proceeded more rapidly than in prisms of 0,60 mortar.

It would be reasonable to expect that the dense mortar would resist the attack better than the more porous 0,60 mortar.

At a later stage the speed of attack on the prisms of 0,60 mortar increased, and after 7 months they had, totally, lost more material than the prisms of 0,45 mortar.

It appears as though the 0,60 mortar was broken down according to a mechanism which is different to the one that is valid for the 0,45 mortar.

The 0,45 mortar prisms seem to be attacked exclusively from the surface, by dissolution of the hardened cement paste.

In the 0,60 mortar prisms, some process seems to set in, which has the effect that the surface layer starts to expand and eventually separates from the core of the prism. After a storing time of 17 months (out of a total time of 22 months) at 20°C, this process has reached through all the prisms, which this way had been almost totally transformed into a sandy slurry.

After storing during the same time in the same solution at the same temperature, the 0,45 mortar prisms certainly had proceeded to lose material from the surfaces, but their flexural strength could still be determined. The loss in section area did, however, make it a necessity to correct the results with regard to the reduced section modulus.

In the Chapter 6. was explained, how the 4 x 4 x 16 cm prisms of 0,45 mortar were stored in one small box and those of 0,60 mortar in another. Thus, it was possible to examine solid materials, originating from the two types of mortar, separately, and so was done after 26 months of storage.

First, the solid materials were separated from the calcium magnesium acetate solution by filtering, and the filtrates were returned to the storing bath. Then, the two solid materials were washed with deionized water. The washing processes were followed by measuring the electric conductivity of the used wash liquid. The procedure was continued until the conductivity had been reduced to a constant level, which was 1,5 mS/cm for slurry from 0,45 mortar, and 3,9 mS/cm for slurry from 0,60 mortar (1 milliSiemens is equal to 1 mA/V, and deionized water normally has a conductivity of 1 µS/cm).

We concluded that the higher conductivity for the washwater from the 0,60 mortar slurry was generated from a greater content of hardened cement paste (with calcium hydroxide as the main conductive component).

After this treatments, the slurries appeared to consist of a small quantity of a very fine whitish material, and a main quantity of a sandy residue. The fine whitish material from the two mortars was analyzed with a scanning electron microscope with an energy dispersive x-ray analyzator. The results are presented in Table 12.1

Table 12.1

Mortar	0,45	0,60
Element	Relative intensity	
Magnesium	1,000	1,000
Aluminium	0,101-0,107	0,079-0,112
Silicon	0,250-0,370	0,213-0,281
Calcium	0,067-0,100	0,202-0,213

Magnesium was the main element in the fine whitish material from both mortars. The reasonable source is magnesium hydroxide from the attack of the magnesium acetate component on the hardened cement paste.

The aluminium and silicon may originate from the mortar aggregate, or from the cement.

The purpose of this test was to find something, which could explain the rapid destruction of the 0,60 mortar at 20°C. The higher calcium content of this matter may be part of a component, formed during the immersion, e. g. a calcium hydroxide acetate hydrate, which caused the expansion.

There is another alternative, namely that the calcium is part of the undissolved cement paste of the 0,60 mortar, disintegrated by expansion. There is, however, a fact which speaks against this alternative, namely that the calcium was found in the finest fraction of the collected material.

12.3 Calcium acetate

The calcium acetate was chosen as one of the test baths, because this salt, unlike the calcium magnesium acetate, does not contain magnesium.

Surprisingly enough, the slender type of prisms, used for length measurements, could expand as much as 15 millimeter per meter for 0,45 mortar at 20°C. This corresponded to the range of the length gauge, and was exceeded after 15 months.

The most expanding prisms were curved, but not severely cracked. The appearance is reproduced on a photographic picture in Figure 8.3.

Typical for test specimens which had been stored in saturated calcium acetate solution was thet they were covered with a white, slimy material, which was easy to remove. The material could very well be responsible for the expansion of the prisms, and also for the fact that the prisms did not crack. See Figure 12.1.

In Paragraph 12.2 was decribed how the materials were prepared which had been collected in the small plastic boxes for the 4 x 4 x 16 cm prisms. In a similar way, the lose white slimy material from the reactions with calcium acetate solution was collected, filtered and washed.

The slimy white material was examined with an optical microscope. Its structure was, however, too fine for the resolution of the microscope, irrespective of whether the source was a 0,45 mortar or a 0,60 mortar. As comparison, pure calcium acetate solution, dried at 40°C, looked like well shaped, needle-like crystals when observed with the optical microscope.

Chemical analyses of the two preparates were performed by acidimetric titration. An appreciation of the acetate contents gave a molar fraction of 0,10 - 0,15 for the preparate from the 0,45 mortar prisms, and 0,15 - 0,20 of that from 0,60 mortar prisms.

Thus, the difference was small, if any. The accuracy of such a titration is low.

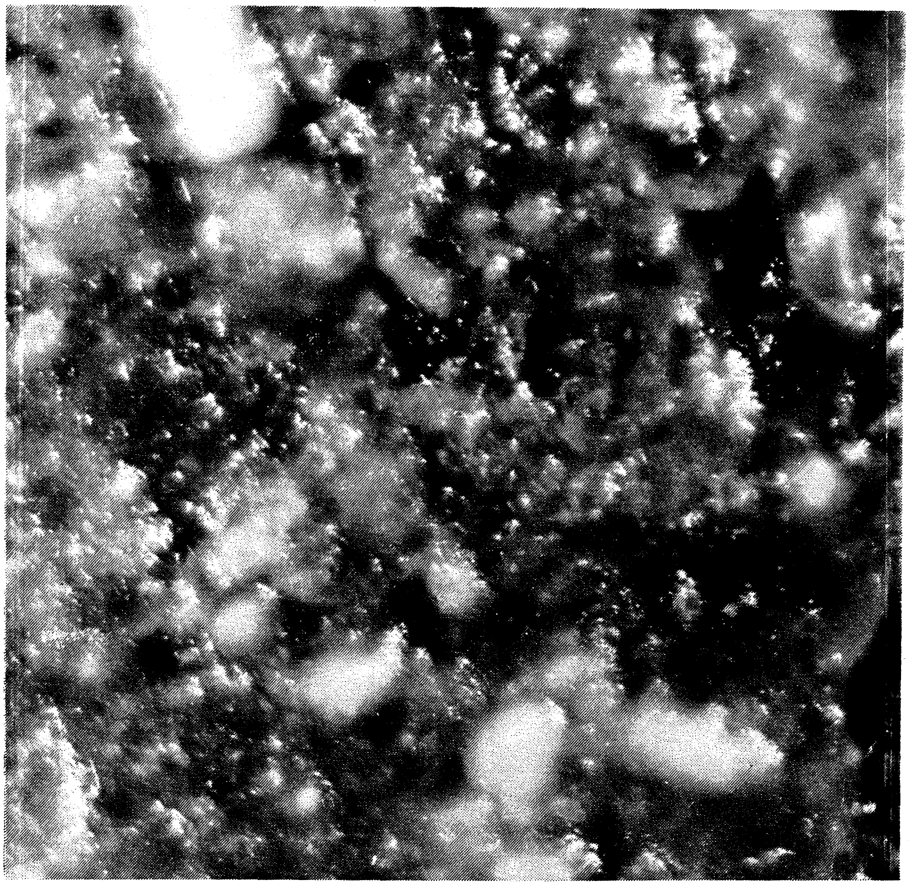


Figure 12.1 Macrophoto, 37x, of 0,60 mortar. Gel formation after immersion in saturated calcium acetate solution

Another factor that, probably, made it difficult to get good information of the chemical composition of the slimy matter, is the gradual formation of calcium carbonate in the two plastic boxes where the precipitates were collected. This process gradually sets free a corresponding quantity of acetate, which is soluble and will be lost for analysis at the washing procedure.

A support for this assumption is that, at the end of the work, the internal walls of the large plastic boxes for the calcium acetate baths were covered with a hard precipitate of calcium carbonate. No such precipitates occurred in the boxes for water or for the solutions of sodium chloride, calcium magnesium acetate, or calcium chloride.

Just in the calcium acetate solution there existed a high pH value (from the submerged mortar prisms), a high concentration of calcium ions, and carbon dioxide at the same time. Those conditions are favourable for the crystallization of a calcium carbonate phase.

We have not managed to give a complete elucidation of the chemical background of the expansion of mortar on storing in a saturated calcium acetate solution.

12.4 Calcium chloride

The chemical conditions for changes of the portlandite phase (calcium hydroxide) in hardened cement paste are well described in chemical and physical literature [Critical Tables (1930), and Seidell (1940)].

In contact with a calcium chloride solution with a concentration below 1,88 mol per liter, the portlandite (crystalline calcium hydroxide) in the hardened cement paste is stable.

On the other hand, the aluminate, and probably the ferrite, phases may be attacked already at this low concentration of calcium chloride. A type of double salts will result, called the Friedel's salt:

(5) $C_3A.CaCl_2.12H_2O$

Compare the Paragraph 8.2.2. There is a difference, because two molecules of sodium hydroxide are formed in addition, when calcium chloride is replaced by sodium chloride.

In the concentration range 1,88-4,00 mol of calcium chloride per liter, the portlandite in the hardened cement paste is not stable any more, but will change to one of the "basic chlorides":

(1) $Ca_5Cl_2(OH)_8.10H_2O$

The formation of this phase at +5 and +20°C destroys the mortar prisms very rapidly (days and weeks) due to expansion. According to Chatterji and Damgaard Jensen (1975), no damage happens at 40°C, even within 3 months.

In the highest concentration range, above 4,00 mol of calcium chloride per liter, another basic chloride turns stable:

(2) $Ca_2Cl_2(OH)_2.H_2O$

Mortar prisms which have been stored for 24 months in calcium chloride solution in this concentration range (after 7 months storing in saturated solution) have not changed. Still we cannot claim that the phase (2), if it forms, is innocious to the mortar. It is quite possible that the previous immersion in saturated calcium chloride solution gave the specimens a protection.

At the time of transfer to the 4,5 molar solution, the prisms were dry in the interior, and much of the cores were still dry after 24 months of immersion in 4,5 molar solution. (See Figure 9.2).

It is quite possible that the specimens would have cracked if they, just after curing, had been immersed in a 4,5 molar calcium chloride solution. Still, the difference in concentration between saturated solution and 4,5 molar solution is small.

In the Paragraph 10.2.5 it was demonstrated how the pH value of a calcium chloride solution depends on the concentration of the solution.

3,0 mol per liter,	pH value 10,6
4,5 mol per liter,	pH range 7,9 - 9,0
Saturated solution,	pH range 5,6 - 7,7

The results indicate that the basic chloride (1), formed from the 3,0 molar solution, is somewhat less basic than the portlandite.

The basic chloride (2) may be essentially less basic than the phase (1), but we can not claim that this is true. The dry state of the internal of the specimens may be enough for making it difficult for the strongest solutions to reach an equilibrium with the portlandite phase in the hardened cement paste.

13. Conclusions

The type of calcium magnesium acetate which was used in this work contained in the concentrated solution 0,69 mol magnesium and 0,87 mol calcium per liter of solution. At +20°C, the solution dissolves the hardened cement paste even in a dense mortar with the water cement ratio 0,45. At +5°C the dissolution proceeds essentially slower, and may sometimes be accepted.

At a temperature of +20°C, mortar with the water cement ratio 0,60 is at first attacked less than the 0,45 mortar. After 6 months, however, a new type of attack is added to the pure dissolution, and the surface of the mortar prisms started to expand, and later to spall.

This second type of attack has not been observed at +5°C, where the 0,60 mortar was less attacked than the 0,45 mortar even after 22 months of immersion.

A really surprising observation was that mortar was attacked at storing in saturated calcium acetate solution (a solution free from magnesium). The mortar did not dissolve in this solution, but slender prisms expanded rapidly. The chemistry behind this attack is still not explained.

Especially interesting is the behaviour of concrete in calcium chloride solution. Solutions with very low and very high concentration does not attack the concrete, but solutions with an intermediate concentration may destroy the concrete by strong expansion within very few days. However, it is to be remembered that a calcium chloride solution on a concrete surface will, all the time, adapt its concentration to the relative humidity of the air.

The attack of the CMA product according to our sample was so severe that this product should not be used for deicing purpose of bridges and concrete roads. An essential condition for this attack is, however, that the temperature of the solution has the opportunity to rise rather much above the ice temperature.

There existed a cirumstance in the curing of the test specimens, namely in the second step. The prisms were stored in boxes with air, and the relative humidity was kept at 75 per cent with wet sodium chloride. Certainly, the carbonation of the test specimens was somewhat less profound than the carbonation of concrete cured for the same time in open air. Still, the pH measurements indicated that the diffusion of hydroxide ions to the surrounding solutions was essentially less than would be the case if the specimens were quite uncarbonated.

According to Mr Kent Gustafsson of the Swedish Road and Traffic Research Institute, another quality of calcium magnesium acetate has gone into production at BP CHEMICALS, Hull, England. The new product is claimed to be a real double salt with the molar quotient calcium to magnesium of 1/1, to be more convenient to handle, to give off less dust, and it is also claimed to attack concrete in a less severe manner than the quality of CMA, used in the present test.

Mr Kent Gustafsson recommends that another test with this new type of calcium magnesium acetate should be performed, and that two different concentrations should be used. No other reference solutions than water and sodium chloride solution needs to be used, and the same two temperatures as in the present study, 5 and 20°C, are recommended also for the new test.

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Appendix

Results in tables

Table A.1 Length changes, mm/m

Water cement ratio		0,45		0,60	
Storing temperature, degrees Celcius		5	20	5	20
Bath	Storing time				
	Date of casting	85-04-09	85-04-10	85-04-15	85-04-17
	2 days	0	0	0	0
	28 days	-0,41	-0,36	-0,53	-0,45
Water	1 month	+0,15	+0.21	-0,15	-0,07
	2 m.	+0,12	+0,21	-0,21	-0,07
	3 m.	+0,14	+0,21	-0,20	-0,09
	4 m.	+0,18	+0,21	-0,18	-0,07
	5 m.	+0,17	+0,20	-0,17	-0,05
	6 m.	+0,10	+0,20	-0,2	-0,10
	7 m.	+0,13	+0,17	-0,2	-0,11
	8 m.	+0,09	+0,14	-0,2	-0,07
	9 m.	+0,08	+0,15	-0,2	-0,09
	10 m.	+0,11	+0,15	-0,20	-0,10
	11 m.	+0,11	+0,15	-0,17	-0,09
	12 m.	+0,11	+0,13	-0,18	-0,08
	15 m.	+0,07	+0,08	-0,19	-0,16
	22 m.	+0,12	+0,09	-0,15	-0,2
	Date of casting	85-04-09	85-04-10	85-04-15	85-04-17
	2 days	0	0	0	0
	28 days	-0,30	-0,35	-0,50	-0,45
	1 month	+0,17	+0,27	-0,09	-0,02
NaCl	2 m.	+0,11	+0,33	-0,12	0,00
	3 m.	+0,19	+0,33	-0,05	+0,05
	4 m.	+0,21	+0,33	-0,05	+0,06
	5 m.	+0,21	+0,36	-0,02	+0,09
	6 m.	+0,22	+0,36	-0,07	+0,07
	7 m.	+0,24	+0,37	-0,05	+0,07
	8 m.	+0,31	+0,38	+0,01	+0,1
	9 m.	+0,28	+0,38	-0,04	+0,07
	10 m.	+0,29	+0,32	-0,01	+0,14
	11 m.	+0,43	+0,44	+0,13	+0,05
	12 m.	+0,32	+0,37	-0,01	-0,10
	15 m.	+0,34	+0,36	-0,01	0,0
	22 m.	+0,43	+0,50	+0,07	+0,07

NaCl Saturated solution of sodium chloride.

Table A.1. continued (Length changes, mm/m)

Water cement ratio		0,45		0,60	
Storing temperature, degrees Celcius		5	20	5	20
Bath	Storing time				
	Date of casting	85-04-09	85-04-10	85-04-15	85-04-17
	2 days	0	0	0	0
	28 days	-0,37	-0,48	-0,40	-0,38
CMA	1 month	-0,02	-0,02	+0,15	+0,31
	2 m.	-0,04	+0,10	+0,33	+0,7
	3 m.	+0,01	+0,08	+0,50	+1,9
	4 m.	+0,03	+0,13	+0,54	+0,9
	5 m.	+0,05	+0,33	+0,66	+1,15
	6 m.	+0,07	One prism was broken. The test was discontinued	+0,76	One prism was broken. The test was discontinued
	7 m.	+0,04		+0,67	
	8 m.	+0,10		+0,74	
	9 m.	+0,02		+0,76	
	10 m.	+0,01		+0,82	
	11 m.	+0,21		+0,93	
	12 m.	+0,21		+0,88	
	14 m.	+0,03		+0,98	
	15 m.	+0,08		+0,95	
	22 m.	-		-	

CMA Maximally concentrated solution of calcium magnesium acetate

Table A.1. continued (Length changes, mm/m)

Water cement ratio		0,45		0,60	
Storing temperature, degrees Celcius		5	20	5	20
Bath	Storing time				
	Date of casting	85-04-09	85-04-10	85-04-15	85-04-17
	2 days	0	0	0	0
	28 days	-0,30	-0,39	-0,45	-0,55
$CaAc_2$ (1)	1 month	+0,46	+1,0	+0,38	+0,79
	2 m.	+1,17	+2,5	+0,90	+1.88
	3 m.	+1,92	+4,1	+1,33	+2,34
	4 m.	+2,59	+5,6	+1,60	+2,88
	5 m.	+3,15	+7,2	+1,84	+3,42
	6 m.	+3,43	+8,1	+2,04	+3,6
	7 m.	+3,86	+9,3	+2,18	+3,95
	8 m.	+4,14	+11	+2,34	+4,3
	9 m.	+4,43	+12	+2,47	+4,6
	10 m.	+4,65	+12,6	+2,61	+4,9
	11 m.	+5,06	+13,5	+2,9	+5,2
	12 m.	+5,40	+14,2	+3,05	+5,6
	15 m.	+6,17	>+15	+3,2	+6,15
	22 m.	+7,70	>+15	+3,74	+7,3
	Date of casting	85-11-06	85-11-06	85-11-06	85-11-06
	2 days	0	0	0	0
	28 days	-0,5	-0,32	-0,48	-0,42
$CaAc_2$ (2)	1 month	+0,23	+ 0,8	+0,60	+1,55
	2 m.	+0,59	+1,9	+1,05	+2,26
	.3 m.	+1,1	+3,3	+1,45	+2,77
	4 m.	+1,4	+5,0	+1,7	+3,2
	8 m.	+2,9	+10	+2,6	+6
	31 m.	+6,6	>+17	+3,7	+5,6

$CaAc_2$	Saturated solution of calcium acetate
(1)	Main series, simultaneous with water, sodium chloride, and calcium magnesium acetate.
(2)	Second series, simultaneous with calcium chloride.

Table A.1. continued (Length changes, mm/m)

Water cement ratio		0,45		0,60	
Storing temperature, degrees Celcius		5	20	5	20
Bath	Storing time				
	Date of casting	85-11-06	85-11-06	85-11-06	85-11-06
	2 days	0	0	0	0
	28 days	-0,6	-0,31	-0,45	-0,46
$CaCl_2$ sat.	1 month	-0,58	-0,48	-0,44	-0,32
	2 m.	-0,6	-0,51	-0,45	-0,24
	3 m.	-0,6	-0,49	-0,42	-0,20
	4 m.	-0,57	-0,51	-0,38	-0,17
	7 m.	-0,62	-0,55	-0,35	-0,11
	8 m. (1)	-0,57	-0,36	-0,46	-0,07
	31 m. (1)	-0,43	-0,42	0	+3,93
	Date of concentration change	86-08-01	86-08-01	86-08-01	86-08-01
$CaCl_2$ 3,0 mol/lit.	18 days (1)	-0,36	destr.	destr.	destr.
	31 months (totally) (1)	destr.	destr.	destr.	destr.
	Date of concentration change	86-08-01	86-08-01	86-08-01	86-08-01
$CaCl_2$ 4,5 mol/lit.	18 days (1)	-0,71	-0,50	-0,29	-0,11
	31 months (totally) (1)	-0,11	+0,57	+1,43	+1,07

$CaCl_2$	Solution of calcium chloride in water.
sat.	The test was started with saturated solution.
3,0 mol/lit. 4,5 mol/lit.	On August 1st, 1986, one 3,0 mol/liter solution, and one 4,5 mol/liter solution were prepared.
(1)	Before that day, the prisms were stored in triplicate. Then, **one prism** of all groups of three was carried over from the saturated solution to the 3,0 mol/liter solution, and **a second one** was carried over from the saturated solution to the 4,5 mol/liter solution.

Table A.2. <u>Mass changes</u>, gram

Water cement ratio		0,45		0,60	
Storing temperature, degrees Celcius		5	20	5	20
Bath	Storing time				
	Date of casting	85-04-09	85-04-10	85-04-15	85-04-17
	2 days (=0)	575	579	559	566
	8 days	+2,1	+2,3	+1,6	+1,5
	28 days	-10,5	-9,0	-15,7	-15,1
Water	1 month	+3,1	+3,8	+2,4	+2,7
	2 m.	+4,1	+5,1	+2,9	+3,2
	3 m.	+4,7	+6,1	+3,3	+3,7
	4 m.	+5,2	+6,6	+3,6	+3,8
	5 m.	+5,5	+7,3	+3,8	+4,3
	6 m.	+6,1	+7,95	+3,8	+4,4
	7 m.	+6,6	+8,2	+4,4	+4,6
	8 m.	+6,8	+8,5	+4,6	+4,7
	9 m.	+7,0	+9,1	+5,1	+5,4
	10 m.	+7,1	+9,2	+5,0	+5,5
	11 m.	+7,4	+9,5	+4,6	+5,9
	12 m.	+7,7	+9,3	+5,2	+5,5
	15 m.	+8,2	+9,7	+5,6	+6,2
	22 m.	+9,0	+10,4	+6,2	+7,0

Table A.2. continued (Mass changes, gram)

Water cement ratio		0,45		0,60	
Storing temperature, degrees Celcius		5	20	5	20
Bath	Storing time				
	Date of casting	85-04-09	85-04-10	85-04-15	85-04-17
	2 days (=0)	582	573	567	565
	8 days	+2,3	+2,6	+1,4	+1,2
	28 days	-10,0	-9,1	-15,7	-15,3
NaCl	1 month	+2,8	+1,8	+6,1	+4,2
	2 m.	+3,2	+1,8	+7,0	+4,1
	3 m.	+3,4	+2,3	+7,3	+4,6
	4 m.	+3,5	+2,4	+7,2	+4,9
	5 m.	+3,6	+2,8	+7,3	+5,5
	6 m.	+4,0	+3,6	+7,7	+6,35
	7 m.	+4,1	+3,7	+7,9	+6,6
	8 m.	+4,2	+3,6	+8,1	+6,95
	9 m.	+4,1	+4,0	+8,4	+7,1
	10 m,	+4.8	+4,7	+8,65	+7,6
	11 m.	+4,6	+4,7	+8,0	+7,5
	12 m.	+4,8	+5,1	+8,7	+8,2
	15 m.	+5,1	+6,4	+8,5	+8,1
	22 m.	+6,0	+11,6	+9,0	+9,9

NaCl Saturated solution of sodium chloride

(=0) Average mass of 3 stripped prisms 4 x 4 x 16 cm
(=ref. mass)

Table A.2. continued (Mass changes, gram)

Water cement ratio		0,45		0,60	
Storing temperature, degrees Celcius		5	20	5	20
Bath	Storing time				
	Date of casting	85-04-09	85-04-10	85-04-15	85-04-17
	Mass at stripping 2 days (=0)	575	579	566	558
	8 days	+2,2	+2,5	+1,7	+1,3
	28 days	-10,5	-8,8	-15,2	-15,5
CMA	1 month	-4,4	-4,1	-6,3	-4,2
	2 m.	-4,0	-5,4	-5,8	-4,5
	3 m.	-4,5	-8,1	-5,7	-5,5
	4 m.	-5,0	-12,5	-5,5	-7,8
	5 m.	-6,1	-19	-5,3	-13
	6 m.	-7,7	-27	-5,3	-22
	7 m.	-9,4	-35	-5,2	-32
	8 m.	-11	-43	-5,2	-46
	9 m.	-12	-54	-5,1	-66
	10 m.	-14,5	-65	-4,9	-91
	11 m.	-18	-79	-5,1	-120
	12 m.	-20,6	-89	-5,9	-150
	15 m.	-37	-144	-10	-306
	17 m.	-47		-14	
	22 m.	-76	-269	-29	

CMA	Maximally concentrated solution of calcium magnesium acetate
(=0)	Average mass of 3 stripped prisms 4 x 4 x 16 cm (=ref. mass)

Table A.2. continued (Mass changes, gram)

Water cement ratio		0,45		0,60	
Storing temperature, degrees Celcius		5	20	5	20
Bath	Storing time				
	Date of casting	85-04-09	85-04-10	85-04-15	85-04-17
	2 days (=0)	573	583	569	564
	8 days	+2,3	+2,4	+1,7	+1,5
	28 days of curing	-9,6	-8,8	-15,6	-15,2
$CaAc_2$ (1)	1 month	+0,5	-0,1	+5,0	+5,5
	2 m.	+1,5	+0,9	+6,0	+6,3
	3 m.	+1,6	+1,5	+6,6	+6,7
	4 m.	+2,1	+2,2	+7,1	+7,2
	5 m.	+2,5	+2,8	+7,7	+7,8
	6 m.	+2,45	+2,9	+7,9	+8,1
	7 m.	+2,7	+3,3	+8,5	+8,6
	8 m.	+3,0	+3,5	+8,4	+8,9
	9 m.	+2,9	+3,9	+8,6	+9,35
	10 m.	+3,0	+4,4	+8,8	+9,8
	11 m.	+3,0	+4,7	+9,4	+10,1
	12 m.	+2,9	+4,7	+9,3	+10,7
	15 m.	+3,1	+5,7	+9,6	+12,3
	22 m.	+4,2	+9,7	+11,2	+15,9
	Date of casting	85-11-06	85-11-06	85-11-06	85-11-06
	2 days (=0) (stripping)	569	575	555	562
	28 days of curing	-20	-20	-19	-27
$CaAc_2$ (2)	5 days	-9	-8	+4	-3
	1 month	-6	-6	+6	-1
	2 m.	-5	-4	+7	0
	3 m.	-5	-4	+7	+1
	4 m.	-5	-4	+8	+2
	8 m.	-4	-2	+9	+3
	31 m. 88-07-27	+1	+11	+14	+8

$CaAc_2$ Saturated solution of calcium acetate

(1) Main series, simultaneous with water, sodium chloride, and calcium magnesium acetate

(2) Second series, simultaneous with calcium chloride

(=0) Average mass of 3 stripped prisms 4 x 4 x 16 cm (=ref. mass)

Table A.2. continued (Mass changes, gram)

Water cement ratio		0,45		0,60	
Storing temperature, degrees Celcius		5	20	5	20
Bath	Storing time				
	Date of casting	85-11-06	85-11-06	85-11-06	85-11-06
	Mass at stripping 2 days (=0)	569	579	568	561
	28 days of curing	-17	-27	-29	-28
CaCl$_2$ sat.	5 days	-11	-21	-17	-16
	1 month	-12	-24	-18	-17
	2 m.	-12	-26	-18	-17
	3 m.	-14	-27	-19	-17
	4 m.	-14	-28	-19	-17
	7 m.86-07-24	-14	-29	-18	-17
	Two baths diluted 86-08-01:				
sat.	8 m.	-13	-19	-14	-16
	31 m.	-15	-21	-13	-16
3,0 mol per lit.	18 days	-13	+20	-19	+43
	31 m. (tot.)	destr.	destr.	destr.	destr.
4,5 mol per lit.	18 days	-18	-36	-20	-21
	31 m. (tot.)	-18	-36	-14	-18

CaCl$_2$ sat.	Solution of calcium chloride, which was from start saturated. As nothing happened to the test specimens, two more dilute solutions were prepared.
3,0 mol per lit.	The most dilute solution was 3,0 mol per liter, and this solution destroyed the mortar prisms within few days.
4,5 mol per lit.	The 4,5 mol per liter solution did not change the mass or the appearance of the prisms much more than the saturated solution did.
destr.	The prism was destroyed because of surface expansion.

Table A.3 Results of pH readings for the baths

		pH value	
Storing temperature, degrees Celcius		5	20
Bath	Storing time		
Water	Date for start of storing	1985-05-13	1985-05-13
	0	-	-
	1 month	10,5	11,3
	2 m.	10,1	11,5
	3 m.	10,1	11,5
	4 m.	9,3	11,3
	5 m.	9,4	11,3
	6 m.	9,0	10,9
	10 m.	8,8	9,7
	29 m.	8,6	8,9
		1987-10-01	1987-10-01
NaCl	Date for start of storing	1985-05-13	1985-05-13
	0	-	-
	1 month	11,4	11,5
	2 m.	11,5	11,7
	3 m.	11,6	11,8
	4 m.	11,6	11,7
	5 m.	11,7	11,7
	6 m.	11,7	11,6
	10 m.	11,7	10,85
	29 m.	11,5	9,3
		1987-10-01	1987-10-01
CMA	Date for start of storing	1985-05-13	1985-05-13
	0	9,25	9,25
	1 month	9,3	9,3
	2 m.	9,5	9,3
	3 m.	9,4	9,4
	4 m.	9,3	9,3
	5 m.	9,3	9,3
	6 m.	9,3	9,25
	10 m.	9,2	9,2
	29 m.	8,5	8,0
		1987-10-01	1987-10-01

Table A.3. continued (pH readings for the baths)

		pH value	
Storing temperature, degrees Celcius		5	20
$CaAc_2$ (1)	Date for start of storing	1985-05-13	1985-05-13
	0	7,5	7,5
	1 month	10,15	10,4
	2 m.	10,5	10,9
	3 m.	10,65	11,0
	4 m.	10,7	11,1
	5 m.	10,9	11,2
	6 m.	11,0	11,3
	10 m.	11,2	11,4
	29 m.	10,6	11,6
		1987-10-01	1987-10-01
$CaAc_2$ (2)	Date for start of storing	1985-12-04	1985-12-04
	0	(7,5)	(7,5)
	1 month	10,6	10,75
	3 m.	10,7	11,0
$CaCl_2$ sat	Date for start of storing	1985-12-04	1985-12-04
	1 month	7,7	7,6
	3 m.	7,1	7,5
	22 m.	5,6	6,6
		1987-10-01	1987-10-01
3,0 m	Date for tranfer	1986-08-01	1986-08-01
	14 months	10,55	10,7
4,5 m	Date for transfer	1986-08-01	1986-08-01
	14 months	7,9	9,0
		1987-10-01	1987-10-01

NaCl	Saturated solution of sodium chloride
CMA	Strong " " calcium magnesium acetate
$CaAc_2$	Saturated " " calcium acetate
(1)	Main work, simultaneous with water and solutions of sodium chloride and calcium magnesium acetate
(2)	As comparison for the calcium chloride work
$CaCl_2$	Calcium chloride solution:
sat	saturated
3,0 m	3,0 mol per liter
4,5 m	4,5 mol per liter

Table A.4 Measurements of the strength of specimens, stored for 22 months in baths of water and of solutions of sodium chloride, calcium magnesium acetate, and calcium acetate
Main series

Water cement ratio	Storing temp. deg. C	Test mode	Tested after storing in			
			Water MPa	NaCl sat MPa	CMA sat MPa	CA_2 sat MPa
0,45	5	Flex	8,3	9,1	8,1	9,15
		dev.	0,3	0,4	0,35	0,10
		Compr	67,4	60,2	-	55,9
		dev.	2	2	-	2
		Ratio Cp/Fl	8,3	6,6	-	6,1
0,60	5	Flex	6,4	6,0	7,9	5,4
		dev.	0,3	0,35	0,3	0,45
		Compr	47,4	42	39,4	30,1
		dev.	1,0	1	3	2
		Ratio Cp/Fl	7,4	7,0	5,0	5,6
0,45	20	Flex	8,7	8,0	12	9,4
		dev.	0,3	0,2	2	0,8
		Compr	73,7	60,7	-	53,4
		dev.	3	2	-	3,5
		Ratio Cp/Fl	8,5	7,5	-	5,7
0,60	20	Flex	6,6	6,3	-	3,6
		dev.	0,3	0,5	-	0,2
		Compr	53,6	43,3	-	26,9
		dev.	0,8	2	-	1
		Ratio Cp/Fl	8,3	6,9	-	7,5

Table A.4 Measurements of the strength of specimens, stored for 31 months in solutions of $CaCl_2$ and $CaAc_2$

Water cement ratio	Storing temp. Degr. C	Test mode	Water MPa	$CaCl_2$		CA_2
				4,5 mol/lit MPa	sat MPa	sat MPa
0,45	5	Flex	8,3	11,4	11,0	6,4
		Dev.	0,3			1,2
		Compr	67,4	56,4	57	40
		Dev.	2			3
		Ratio Cp/Fl	8,3	4,9	5,2	6,3
0,60	5	Flex	6,4	8,3	8,2	4,3
		Dev.	0,3			0,2
		Compr	47,4	32	36,9	21,5
		Dev.	1,0			2,0
		Ratio Cp/Fl	7,4	3,9	4,5	5,0
0,45	20	Flex	8,7	8,8	11,2	2,32
		Dev.	0,3			0,15
		Compr	73,7	51	52	21,8
		Dev.	3			1,0
		Ratio Cp/Fl	8,5	5,8	4,6	9,4
0,60	20	Flex	6,6	7,8	8,0	3,1
		Dev.	0,3			0,1
		Compr	53,6	30,5	32	18,6
		Dev.	0,8			1,3
		Ratio Cp/Fl	8,3	3,9	4,0	6,0