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DELAYED EFFECTS OF SOLUTIONS OF CALCIUM MAGNESIUM ACETATE AND SODIUM CHLORIDE ON CEMENT MORTAR

AN APPENDIX TO TVBM-3049

Olof Peterson

REPORT TVBM-3050

LUND SWEDEN

Preface

This appendix deals with the the change of the test prisms during the period 6 - 22 months. The study is limited to those prisms, which were stored at $+5^{\circ}$ C. At $+20^{\circ}$ C, the strong solution of calcium magnesium acetate dissolved much of the hardened cement paste already after 4 - 6 months.

The change in mass was determined for all specimens, except for those who were stored in pure water.

The flexural strength was determined for all prisms. For those which were stored in a strong solution of calcium magnesium acetate, the section modulus had to be re-calculated because of the loss in fracture area.

The two pieces, which resulted from each prism after the flexural strenth test, were subjected to the compressive test. This could not be done with the pieces from the prisms, which were stored in the strong solution of calcium magnesium acetate, because the test surfaces of theese pieces had lost too much in planeness for making a correct test result possible.

The primary results are collected in an appendix. In the following chapters, the arithmetic means are discussed and, when necessary, the standard deviations.

Lund, March, 1993.

Contents

2

Page

â

Sum	mary
1.	Flexural strength
1.1	Sodium chloride solutions and flexural strength 4
1,2	Calcium magnesium acetate solutions and flexural strength 4
2.	Compressive strength 5
2.1	Sodium chloride solutions and compressive strength 6
2.2	Calcium magnesium acetate solutions and compressive strength 6
3.	Changes of mass
3.1	Sodium chlorid solutions and changes of mass 7
3.2	Calcium magnesium acetate solutions and changes of mass 7
4.	Covariance between change of mass and change of strength 7
4.1	Covariance in sodium chloride solutions
4.2	Covariance in calcium magnesium acetate solutions 8
5.	Conclusions
Appe	endix: Primary results for mortar prisms stored in
	water A-1
	sodium chloride solution (3 g/97 g water) A-2
	saturated sodium chloride solution A-3
	calcium magnesium acetate $(6,5 \text{ g}/100 \text{ g water})$ A-4
	calcium magnesium acetate (38,35 g/100 g water) A-5

Summary

The previous report TVBM-3049 represents a storing time of 6 months. This report (TVBM-3050) deals with the prisms stored at $+5^{\circ}C$ for 22 months.

Flexural strength

Sodium chloride solutions: the same results as water except mortar with water cement ratio 0,45 in saturated solution, which yielded +13 per cent, compared to water.

Calcium magnesium acetate, 6,5 g in 100 g water: 0,45 mortar 0,60 mortar -30 per cent

Calcium magnesium acetate, 38,35 g in 100 g water: Section modulus reduced with about 30 per cent 0,45 mortar +16 per cent 0,60 mortar +18 per cent

Compressive strength

Sodium chloride solu	itions
0,45 mortar	-12 per cent
0,60 mortar	- 8 per cent
Calcium magnesium	acetate, 6,5 g in 100 g water:
0,45 mortar	-45 per cent
0,60 mortar	-60 per cent

For sodium chloride solutions, as for the dilute solution of calcium magnesium acetate, the effect on the *compressive* strength was more unfavourable than the effect on the *flexural* strength.

1. Flexural strength

The test prisms, $4 \ge 4 \ge 16$ cm, have a section modulus of 10,67 cm³. After prolonged storage in calcium magnesium acetate solution with a concentration of 38,35 g for 100 g water, the section area of the prisms was much diminished, and it was necessary to measure the section area and calculate an actual section modulus for each prism. In the Appendix, the results of these calculations are noted in the table for this strong CMA solution (the last table).

The results of the flexural tests, in MPa, are collected in the table below:

Mortar, wcr	0,45		0,60)
Liquid	Flex. strength	Std. dev.	Flex.strength	Std. dev.
Water	9,5	0,2	7,2	0,4
3 g sodium chloride in 97 g water	9,2	0,35	7,0	0,1
Saturated solution	10,7	0,3	7,65	0,5
6,5 g calcium magnesium acetate in 100 g water	7,9	0,2	5,0	0,3
38,35 g calcium magnesium acetate in 100 g water	11,0	0,7	8,5	1,2

The results are commented in the subchapters below.

1.1 Sodium chloride solutions and flexural strength

Storage in the two sodium chloride solutions did not change the flexural strength of the test prisms, with one exception: The prisms of 0,45 mortar, stored in saturated sodium chloride, got their strength increased with 13 per cent, compared to those stored in water.

1.2 Calcium magnesium acetate solutions and flexural strength

The two solutions with different concentrations influenced the test prisms in a highly different way.

4

The *low concentration solution* was intented to have a freezing point depression equal to a sodium chloride solution, 3 per cent by weight. However, storing in this solution reduced the flexural strength in comparison to storing in water, and the reduction was 17 per cent for 0,45 mortar, and 30 per cent for 0,60 mortar.

The strong solution had a dissolving action to the prisms, which was rapid at $+20^{\circ}$ C, but slow at $+5^{\circ}$ C. Because of this dissolution, the section modulus was reduced with 27 per cent for the 0,45 mortar, and with 30 per cent for the 0,60 mortar. After this correction, the strength of the 0,45 mortar in the residual core had *increased* with 16 per cent.

The tests of the prisms of 0,60 mortar showed that also the remaining "parts of this mortar had gained in strength, and the gain was 18 per cent. However, the standard deviation of the flexural strength was rather great, which reduced the sigificance considerably.

2. Compressive strength

The tests were performed with the pieces from those prisms, which were stored in water, in the two sodium chloride solutions, and in the dilute solution of calcium magnesium acetate, but not from those, which were stored in the strong calcium magnesium acetate solution.

For all these tests, the two pieces from each flexural test prism were used.

Mortar, wcr	0,45		0,60	
Liquid	Compr, strength	Std. dev.	Compr. strength	Std. dev.
Water	69	2	45	1
3 g sodium chloride in 97 g water	61	1,4	42	2
Saturated solution	60,5	1,2	41	1,4
6,5 g calcium magnesium acetate in100 g water	37,6	0,7	19,8	0,6

The results, in MPa, are collected in the table below:

The results are commented in the subchapters on the next page.

2.1 Sodium chloride solutions and compressive strength

Irrespective of which of the two concentrations was used, the strength always decreased after storage in a sodium chloride solution. The reduction was 12 per cent for 0,45 mortar, and 8 per cent for 0,60 mortar.

2.2 Calcium magnesium acetate solution and compressive strength

The strong solution caused such a dissolution effect that the planeness of the test surfaces grew too uneven for a standard test for compressive strength.

The fairly good flexural strength values indicate that, very likely, also the compressive strength of the mortar in the core of the prisms is good.

The low concentration solution, 6,5 g/100 g water, which was intended to be equivalent to a 3 per cent sodium chloride solution, by mass, reduced the compressive strength with 45 per cent for 0,45 mortar, and with 56 per cent for 0,60 mortar.

3. Changes of mass

The mass of the test specimens, which were stored in water, was not determined. Thus, only absolute values can be accounted for.

Mortar	W/c-ratio	Change of	f mass
Liquid		kg/m²	per cent
Sodium chloride	0,45	+0,352	
3 g/97 g water	0,60	+0,310	
Sodium chloride	0,45	+0,145	
saturated	0,60	+0,268	
Calcium magnesium acetate	0,45	+0,54	
6,5 g/100 g water	0,60	+0,425	
Calcium magnesium acetate	0,45		-17,0
38,35 g/100 g water	0,60		-22

The results are commented in the subchapters below.

3.1 Sodium chloride solutions and changes of mass

During the period from 6 to 22 months, the 0,45 mortar prisms had got their increase of mass changed from 0,2 to 0,35 kg/m² in a solution with 3 g sodium chloride in 97 g water. The corresponding increase for the 0,60 mortar prisms was from 0,12 to 0,31 kg/m².

In saturated salt solution, the corresponding increase for 0,45 mortar prisms was from 0,09 to 0,145 kg/m², and for 0,60 mortar prisms from 0,2 to 0,27 kg/m². Thus, the changes during the period 6 to 22 months were essentially smaller than in the dilute solution.

3.2 Calcium magnesium acetate solutions and changes of mass

There was a great difference between the action of the two concentrations on the test prisms. The low concentration solution with 6,5 g of the salt in 100 g water increased the mass of 0,45 mortar prisms from 0,38 to 0,54 kg/m² during the period 6 months to 22 months. The 0,60 mortar prisms got their mass increased from 0,4 to 0,425 during the same period.

The high concentration solution with 38,35 g of the salt in 100 g water got the 0,45 mortar prisms to increase 0,075 kg/m² after 6 month (a very small increase, indeed), but got them to lose 17 per cent in mass after 22 months. The 0,60 mortar prisms increased 0,07 kg/m² after 6 months and lost 22 per cent of their mass after 22 months.

The loss of mass is not to be compared with the losses observed at $+20^{\circ}$ after one to six months, because these losses were spontaneous. The loss after 22 months at $+5^{\circ}$ was intensified by rubbing with a brush. The purpose of this treatment was to get the most exact value of the section modulus of the prisms.

4. Covariance between change of mass and change of strength

4.1 Covariance in sodium chloride solutions

The change of mass was relatively great for the dilute concentration, but small for the saturated solution.

In both cases, the change of strength was small, irrespective of which type of strength is determined.

4.2 Covariance in calcium magnesium acetate solutions

8

It is quite possible that the rather strong decrease of strength after storing in the dilute solution had taken place already after 6 months. The loss of compressive strength was essentially greater than the loss of flexural strength.

These two subchapters indicate that it does *not* exist a covariance between strength and increase of mass. Very probably, the *characters* of the matter, which form in the surface of a mortar prism makes more influence on the strength than the *amount* of matter.

It is reasonable that the chemical substance which increases the mass of mortar in a dilute solution of calcium magnesium acetate is a double salt of calcium ions with acetate ions and hydroxide ions. This double salt forms, when a mortar prism is stored in a solution of calcium acetate. The solution brings the mortar prism to expand, and so much as 15 mm/m was observed in REPORT TVBM-3045. Still no cracks formed, probably because the substance which formed in the mortar prisms had a smeary consistency, which allowed the transformed cement past to expand without cracking.

Later, when the mortar had carbonated, calcium carbonate replaced the smeary acetate double salt. Thus the prisms turned brittle, increasing the tendency to crack formation. Still, this transformation probably would increase the compressive strength of the prism.

In the later work, reported in TVBM-3049, all salts were tested in a concentrated solution as in the previous report, but also as dilute solution with a freezing point depression similar to that of a 3 per cent sodium chloride solution. In this low concentration, calcium magnesium acetate rapidly loses its concentration of magnesium ions, because of precipitation of magnesium hydroxide, which is very difficult to dissolve. Thus the part of solution, penetrating the pore system, transforms to calcium acetate to a large extent. This effect was great enough to be shown in the table in Subchapter 11.2 in (3049), as a change in the magnesium concentration in the surrounding bath.

The report showed that the 0,45 mortar expanded essentially more than the 0,60 mortar in this dilute solution. Both types of mortar increased their mass during storing in that solution more than in other solutions, used in the work.

The compressive strength decreased more than the flexural strength after storage in the dilute solution of calcium magnesium acetate.

A reasonable explanation could be that the layer of, probably, calcium hydroxy acetate in the surface of the prism impaired the results of the compressive strength determination because of its smeary consistency.

5. Conclusions

The observations are discussed in this chapter, solution after solution.

Sodium chloride, 3 g/97 g water

Mass change, kg/m ²	Until 6 months	Until 22 months
0,45 mortar (water)	+0,21 +0,19	+0,35
0,60 mortar (water)	+0,125 +0,16	+0,31

The mass increase seems to be in the same order of magnitude as in water.

Flexural Strength, MPa	After 22 months	(Water)
0,45 mortar	$9,2 \pm 0,35$	$9,5 \pm 0,2$
0,60 mortar	$7.0 \pm 0,1$	$7,2 \pm 0,4$

The flexural strength was practically the same as after storing in water.

Compressive strength, MPa	After 22 months	(Water)	
0,45 mortar	$61 \pm 1,4$	69 ± 2	
0,60 mortar	42 ± 2	45 ± 1	

The compressive strength was about 10 per cent less than after storing in water.

Sodium chloride, saturated solution

Mass change, kg/m ²	Until 6 months	Until 22 months
0,45 mortar (water)	+0,09 +0,19	+0,145 -
0,60 mortar (water)	+0,21 +0,16	+0,27

The 0,45 mortar did not increase in mass so much as during storing in water.

45

A reasonable explanation is that the relative humidity above the solution at $+5^{\circ}$ C is 75,65 per cent, compared with the relative humidity above 0,45 mortar, being 95 per cent. Thus, only the surface of the prism takes up salt solution, whereas the core loses water by evaporation.

The 0,60 mortar increased somewhat more than during storing in water. Reasonably, the explanation is that the permeability of the pore system is greater than in the 0,45 mortar, and that the density of the salt solution is greater than the density of pure water.

Flexural strength, MPa	After 22 months	(Water)	
0,45 mortar	$10,7 \pm 0,3$	$9,5 \pm 0,2$	
0,60 mortar	$7,65 \pm 0,5$	$7,2 \pm 0,4$	

The 0,45 mortar prism yielded an about 10 per cent greater flexural strength after storage in saturated sodium chloride solution than after storing in pure water. Probably, this is an effect of the reduced moisture content in the core of the prisms in the salt solution. The change was in accordance with the one, recorded in the previous report TVBM-3045.

Compressive strength, MPa	After 22 months	(Water)
0,45 mortar	$60.5 \pm 1,2$	69 ± 2
0,60 mortar	$41 \pm 1,4$	45 ± 1

The compressive strength was about 10 per cent less than after storing in water. Possibly, this change is explained by formation of reaction products in the surface layer of the mortar. The change was in accordance with the one, recorded in the previous report TVBM-3045.

Calcium magnesium acetate, 6,5 g in 100 g water.

Until 6 months	Until 22 months
+0,375 +0,19	+0,54 -
+0,39	+0,425
	Until 6 months +0,375 +0,19 +0,39 +0.16

This dilute solution of calcium magnesium acetate caused the greatest mass gain in 0,45 mortar of all liquids tested in this investigation. The 0,60 mortar gained still more mass during the first 6 months, but the gain did not succeed on further storage. It is reasonable that the 0,60 mortar is much more permeable for the salt solution than the 0,45 mortar.

Flexural strength, MPaAfter 22 months(Water)0,45 mortar $7,9 \pm 0,2$ $9,5 \pm 0,2$ 0,60 mortar $5,0 \pm 0,3$ $7,2 \pm 0,4$

The dilute solution of calcium magnesium acetate caused the greatest loss of flexural strength of all liquids tested. The 0,45 mortar lost 17 per cent and the 0,60 mortar 30 per cent, both compared to test specimens stored in pure water.

Compressive strength, MPa	After 22 months	(Water)
0,45 mortar	$37,6 \pm 0,7$	69 ± 2
0,60 mortar	$19,8 \pm 0,6$	45 ± 1

The solution also caused the greatest loss of compressive strength of all liquids tested. The 0,45 mortar lost 45 per cent and the 0,60 mortar about 56 per cent, compared to test specimens stored in pure water. It is reasonable that these great losses were caused by formation of a smeary product in the surface layer of the mortar, probably a calcium hydroxide acetate double salt.

Calcium magnesium acetate, 38,35 g per 100 g water

Mass	change	Until 6 months, kg/m ²	Until 22 months, %
	0,45 mortar (water)	+0,075 +0,19	-17,0 -
	0,60 mortar (water)	+0,063 +0,16	-22

This concentrated solution of calcium magnesium acetate caused at the actual low temperature a very slight gain in mass within 6 months. However, after longer time the same solution caused a softening in the surface of the mortar. The strong mass loss after 22 months was determined after an energic treatment with a brush, in order to detach softened mortar, so that the fracture area could be measured accurately enough for calculating the section modulus of the broken prisms.

Flexural strength, MPa	After 22 months	(Water)
0,45 mortar	$11,0 \pm 0,7$	$9,5 \pm 0,2$
0,60 mortar	$8,5 \pm 1,2$	$7,2 \pm 0,4$

The concentrated solution of calcium magnesium acetate caused after 22 months a reduction of the section modulus of the prisms of about 30 per cent. Still, the flexural strength of the residual cores increased with about 16 per cent for 0,45 mortar and with about 18 per cent for 0,60 mortar. In the previous investigation, report TVBM-3045, the gain in 0,60 mortar was still greater, but no gain in the 0,45 mortar did occur. However, the chemical composition of the calcium magnesium acetate was different in this investigation: the molar ratio Ca/Mg was 1,26, to be compared with 0,91 in the actual investigation.

Compressive strength: no determination was performed because of the great loss of material in the test surfaces. In the previous investigation, the 0,60 mortar prisms could be tested, and a loss of 17 per cent was found, compared to test prisms stored in water.

Liquid	Mortar	Flexural	strength	Compr. s	strength			
	w/c-ratio		MPa	MPa	MPa			
Water	0,45			70,9	70,9			
			(13,2)	71,4	71,4			
				66,4	66,4			
			9,34	67,7	67,7			
				62,25	(Five values only)			
			9,59	68,0	68,0			
		Arithm. med.	9,5	68	69			
		Std deviation	0,2	3	2			
	0,60		7,26	45,1				
				45,7				
			6,86	44,75				
				43,25				
			7,57	46,4				
				45,4				
		Arithm. med.	7,2	45				
		Std deviation	0,4	1				

Primary results for mortar prisms stored in Water:

Flexural strength, Compressive strength

Primary results for mortar prisms stored in	sodium	chloride	solution	(3 g/97 g water):	Mass
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· ·	
	Flexural strength
	Compressive strength

Liquid	W/C-ratio	Mass of pr	Mass of prism (in g)		of mass	Flex. strength	Flex. strength Compr	
		After wet curing	Before flex. test	in g	kg/m²	MPa	MPa	MPa
3 g sodium chloride	0,45	571,2	581,28	+10,1		8,76	62,0	62,0
in 97 g water							62,4	62,4
		569,5	579,82	+10,3		9,34	51,7	(Five values only)
							58,8	58,8
		574,6	584,58	+10,0		9,40	61,3	61,3
							60,9	60,9
			Arithm. med.	+10,1	+0,352	9,17	59,5	61
			Std. dev.	0,15	0,005	0,35	4	1,4
	0,60	559,0	567,77	+8,8		7,06	42,75	
							42,1	
		558,5	567,54	+9,0		6,81	40,8	
							40,25	
		555,5	564,49	+9,0		7,04	43,75	:
							44,1	
			Arithm. med.	+8,9	+0,310	7,00	42	
			Std. dev.	0,11	0,004	0,1	2	

A-3

Primary results for mortar prisms stored in saturated sodium chloride solution:

Mass Flexural strength Compressive strength

Liquid	W/C-ratio	Mass of pr	ism (in g)	Change of mass		Flex. strength	Compressive strength	
		After wet curing	Before flex. test	in g	kg/m²	MPa	MPa	MPa
Saturated sodium chloride solution	0,45	568,0	572,22	+4,2	+0,146	10,42	55,4	(Five values only)
							62,5	62,5
		566,6	570,76	+4,2	+0,146	10,69	59,9	59,9
							59,8	59,8
		577,9	582,09	+4,2	+0,146	11,04	59,5	59,5
							60,8	60,8
			Arithm. med	+4,2	+0,146	10,7	60	60,5
			Std. dev.	0,0	0,000	0,3	2	1,2
	0,60	562,5	569,95	+7,5	+0,260	8,21	42,1	42,1
							42,4	42,4
		557,4	565,18	+7,8	+0,271	7,30	40,1	40,1
							39,2	39,2
		557,9	565,83	+7,9	+0,274	7,45	40,1	40,1
							38,0	(Five values only)
			Arithm, med.	+7,73	+0,268	7,65	40	41
			Std. dev.	0,21	0,007	0,5	2	1,4

A-2

Primary results for mortar prisms stored in calcium magnesium acetate (6,5 g/100 g water):

Mass Flexural strength Compressive strength

Liquid	W/C-ratio	Mass of pr	rism (in g)	Change	of mass	Flex. strength Compressive :		pressive strength
		After wet curing	Before flex. test	in g	kg/m²	МРа	MPa	MPa
6,5 g calcium magnesium acetate	0,45	570,6	586,54	+15,9	+0,552	8,08	38,7	38,7
in 100 g water							39,9	(Five values only)
		571,1	586,72	+15,6	+0,542	7,65	37,4	37,4
							37,1	37,1
		578,0	593,22	+15,2	+0,528	7,91	37,1	37,1
							37,6	37,6
			Arithm. med	+15,6	+0,54	7,9	38	- 37 , 6
			Std. dev.	0,35	0,01	0,2	1	0,7
N 0	0,60	559,0	570,66	+11,7	+0,406	5,32	20,8	20,8
							19,9	19,9
		548,4	561,08	+12,7	+0,441	4,89	19,4	19,4
							17,0	(Five values only)
		559,7	572,13	+12,4	+0,431	4,86	19,25	19,25
							19,6	19,6
			Arithm. med.	+12,3	+0,425	5,0	19	19,8
			Std. dev.	0,5	0,02	0,3	1,3	0,6

Primary results for mortar prisms stored in Calcium magnesium acetate (38,35 g/100 g water);

Mass Flexural strength

Liquid	W/C-ratio	Mass of prism (in g) Change of mass		Section modulus	Flexural strength		
		Cured for 28 days	Prism after flex. test (washed)	in g	in per cent	cm ³	MPa
38,35 g calcium magnesium acetate	0,45	569,85	469,32	-100,53	-17,64	7,91	11,21
in 100 g water		569,44	471,08	-98,36	-17,27	7,48	11,57
		572,52	481,25	-91,27	-15,94	8,03	10,29
				Arithm. med.	-17,0	Arithm. med.	11,0
				Std dev.	0,9	Std. dev.	0,7
	0,60	558,52	448,37	-110,15	-19,72	8,12	8,15
		556,38	432,52	-123,86	-22,26	8,18	7,55
		559,72	423,97	-135,75	-24,25	6,61	9,83
				Arithm. med.	-22	Arithm. med.	8,5
				Std. dev.	2,3	Std. dev.	1,2

A-5